

RARE EARTH DOPED CRYSTALS FOR CLASSICAL AND
QUANTUM INFORMATION

by

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ABSTRACT

High-quality rare-earth-ion (REI) doped materials are a prerequisite for many applications such as quantum memories, ultra-high-resolution photonic signal processing, and quantum-limited sensing. Realization of practical solid-state photonic technologies critically depends on finding materials that offer necessary combinations of optical and spin-state coherence, spectral multiplexing capacity, transition wavelengths, and many other key properties. To realize these advances, we continue to improve the fundamental understanding and control of physical processes that govern ion-ion, ion-spin, and ion-lattice interactions. Furthermore, exploring the role of material chemistry and fabrication in determining the observed properties is crucial.

With these motivations, we study a range of rare-earth-doped optical materials using powders and single crystals to understand and optimize the properties relevant to quantum memory, quantum transduction, photonic signal processing, and optical cooling applications. In addition to producing, measuring, and analysing spectroscopic and coherence properties of promising material systems, we highlight the engineering of lattice defects to manipulate both static and dynamic disorder. This work spans nine different REI doped materials: four single crystals, $\text{Tm}^{3+}:\text{Y}_3\text{Ga}_5\text{O}_{12}$, $\text{Yb}^{3+}:\text{YVO}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, and $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, and five crystalline powders, $\text{Er}^{3+}:\text{LiNbO}_3$, $\text{Tm}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Yb}^{3+}:\text{YAG}$, and $\text{Eu}^{3+}:\text{CaCO}_3$. These choices are based on material properties unique to each system, need for investigation, or potential for systematic comparison of fabrication methods and stoichiometry.

Spectral hole burning (SHB), optical and spin coherence measurement techniques are sensitive quantitative characterization tools, complementing traditional optical, chemical, and structural analysis. We find that coherence and spin lifetimes are especially sensitive to low levels of strain and defects in the crystal, undetected by other methods. Properties of REI doped materials are found to vary by orders of magnitude depending on the source, synthesis, and implementation of the materials. Even mild mechanical processing producing large variations in spin lifetimes and SHB properties. These variations are attributed to low levels of glass-like dynamics in the crystalline lattice introduced by inhomogeneous strain and chemical defects, which can be reduced or eliminated by annealing or improved fabrication. Overall, these studies reveal that SHB or coherence measurements are needed to identify material dynamics and guide the fabrication process to reach the true fundamental capabilities of REI materials.

CHAPTER 1

INTRODUCTION TO RARE EARTH IONS

Background of Rare Earth Ions in Solid State Materials

Rare earth ions doped into solid-state crystalline materials are used for fundamental research and commercial technologies because they have the most complex and useful spectra of all the known elements [1-3]. The rare earth ion's visible and infrared spectra are due to the fourteen possible electrons in the $4f^N$ shell and the energy transitions within the $4f^N$ shell. Using the resonant wavelengths of these intra-configuration transitions, the rare-earth-ion (REI) doped materials can be used for new optical technologies [4-9]. Some of these optical systems include laser frequency narrowing and stabilization [10-15], high-bandwidth optical signal processing [16-19], optical filtering for medical imaging technology [20-22], and optical memory systems [6,9,10,23-25]. The REIs can transfer and store quanta of information while preserving the frequency and phase coherently; thus, they are ideal for proof of concept and scaling quantum architectures such as quantum transducers and quantum memories [11,23-33].

Commercial applications built using REI doped materials are important in a wide range of industries. These include neodymium and ytterbium high powered lasers for manufacturing and machining, erbium optical amplifiers for global broadband communications, as well as europium and thulium phosphors used in an ever-growing number of visible optical applications.

The focus of this work is developing new and current REI doped materials for optical applications. Understanding how the materials are produced, their fundamental physical and

optical properties, and the needs of the applications, we can utilize the entire process of growing crystals and the optical technologies using them from the ground up.

The $4f^N$ Electrons of Rare Earth Ions

The lanthanide elements doped into insulators are generally trivalent ions, giving up two electrons from the outermost electron orbital shell and one from the $4f^N$ orbital shell. The radial orbit extent of the remaining 5s, 5p, and 6s electrons extend beyond the 4f orbital shell. These outer electrons of the REIs participate in the chemical bonding with the surrounding crystal ions or ligands. Unlike the $3d^N$, $4d^N$, $5d^N$ orbitals of transition metals, the $4f^N$ electron shell is effectively shielded from the host's materials bonding forces, minimizing significant changes to the $4f^N$ shell.

The central field radial contribution of the Hamiltonian, which can be modeled as spherically symmetric, separates the electron configurations but does not remove the degeneracy of the $4f^N$ configuration. The major contributions to the $4f^N$ electronic energy level structure are the inter-electronic repulsion and the spin-orbit coupling. The inter-electronic repulsion separates levels by 10^4 cm^{-1} , and the spin-orbit coupling has energy levels on the order of 10^3 cm^{-1} . An effective Hamiltonian term describing the crystal environment, the “crystal field,” makes the smallest nominal contribution, typically around 10^2 cm^{-1} . The hierarchy of these contributions is shown in Figure 1.1.

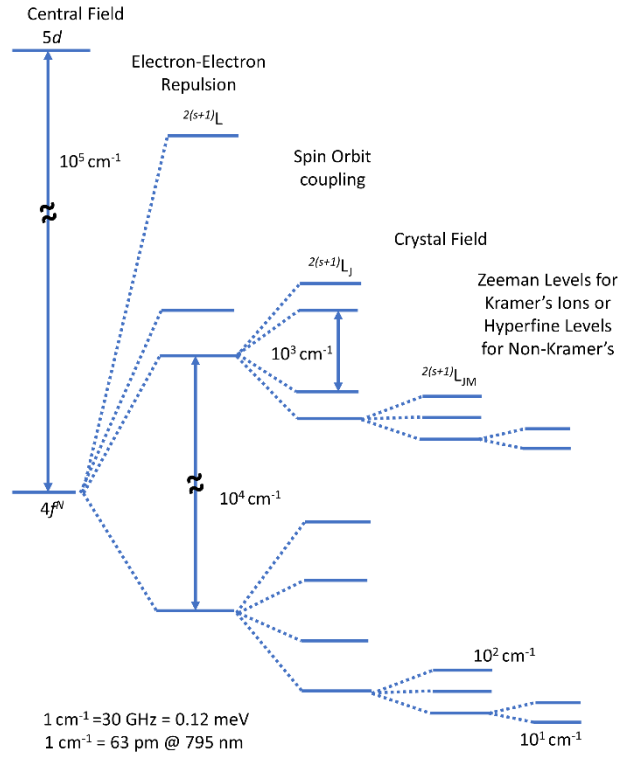


Figure 1.1. Illustration of the interactions affecting the energy levels of $4f^N$ configurations in lanthanide ions.

The partially filled $4f^N$ electron orbitals of the rare earth ions provide unique optical properties. The REI's optical transitions are between the $4f^N$ - $4f^N$ states, which are nominally forbidden quantum transitions. However, these transitions are weakly allowed due to the crystal field breaking the symmetry by adding small admixtures of opposite parity electron configurations. This “forced” electric-dipole character of the transition makes the transition probability low, and thus the oscillator strengths are weak, allowing long excited state lifetimes.

Since the $4f^N$ electrons are shielded inside the bonding electrons, unlike transition metals, the rare earth ion $4f^N$ - $4f^N$ transitions have weaker electron-phonon coupling. The REIs can have very narrow linewidths at liquid helium temperatures, which can provide large peak absorption coefficients despite the weak oscillator strength.

Narrow optical transitions occur throughout the spectrum from the infrared to the ultraviolet. Since the larger scale energy structure of the f - f transitions primarily arises from the ion's internal electronic structure and is weakly dependent on the material, the transitions in the crystal are similar in all host materials. This property allows photonic components to be designed around a particular REI transition. While many different host materials are available the details of the transitions must be measured.

A universal diagram thus can be made for REI energy levels independent of host materials. Known as the Dieke diagram, in honor of Wilhelm Dieke who directed extensive measurements of the optical transitions for each trivalent rare earth ion [1]. When choosing and identifying rare earth transitions in new materials the nominal labeling of the major $^{2S+1}L_J$ manifolds is used as seen in Figure 1.2, where S is the total spin angular momentum, L is the total orbital angular momentum, and J is the total angular momentum. The REI's require intermediate coupling, so the L and S in the REI term symbols are not good quantum numbers. The total angular momentum J is a good quantum number, and the number of crystal field levels is equal to $2J + 1$. Where the odd electron ions with half integer spin will have double degenerate crystal field levels which can be split by a magnetic field.

The lowest energy transitions between J -multiplets are of the greatest interest for spectral hole burning applications. The energy gap between the lowest level of the J -multiplet or the next lowest energy manifold needs to be large compared to the phonon energies. That ensured that the excited ions primarily relax by optical radiative emission to the lower states. The higher energy states of each J -manifold are more homogeneously broadened due to rapid non-radiative relaxation to lower states.

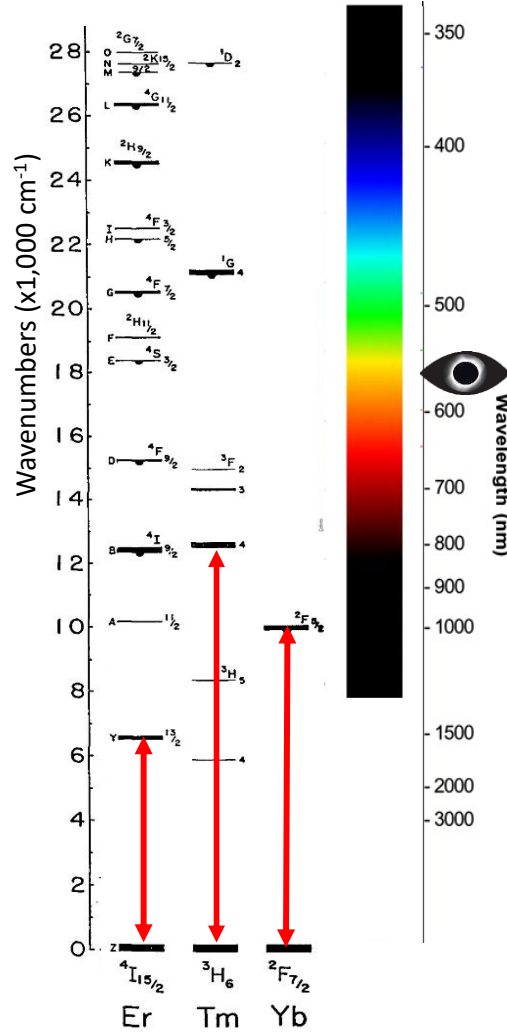


Figure 1.2. Dieke Diagram showing energy levels of the trivalent rare earth ions erbium, thulium and ytterbium. The red arrows signal the transitions in use in this thesis. The diagram is scaled in wavenumbers and wavelength and the visible spectrum, which is marked in color.

Resonant Linewidths of REI in Crystals

At room temperature, phonons are the largest contribution to the linewidth, producing homogeneously broadened spectral lines. Cooling the crystal below 10 K will suppress the dynamics phonon perturbations, and the homogeneous lines can become extremely narrow. Therefore, optical and spin properties of rare earth ions are studied at cryogenic temperatures.

The crystalline environment of a resonant ion varies from site to site within a single crystal; thus, the ions experience different local transitions due to strain, caused by crystal imperfections, impurities, or defects. The static strain variation at each site slightly shifts the center of the transition frequency, and at low temperature, the spectral lines of rare earth activated materials are inhomogeneously broadened [10]. The REI can have millions of homogeneous lines under the inhomogeneous absorption packet, where each line is an ensemble of ions, in different spatial locations, which are excited at the same frequency. The ensembles can be used to store wavelength and amplitude information as well as phase and temporal information.

The homogeneous linewidth, Γ_h , is nominally the same full width at half max energy width for each resonant ion in the material and ideally has a Lorentzian line shape. The dynamic perturbations to the transition frequency or phase due to various mechanisms, combine to broaden the homogeneous linewidth and disrupt the transition's coherence. These mechanisms include phonon scattering, electronic or nuclear spin flips, dynamic disorder, or other low energy mechanisms allowing the REI to fluctuate between similar energy states [4]. The linewidth and shape can be used as a direct measure of the static and dynamic disorder in the material, providing information on the defects responsible for the broadening [34].

The inhomogeneous linewidth, Γ_{inh} , of REI activated single crystal materials can vary in scale. For example, $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ has an $\Gamma_{inh} = 500$ MHz while $\text{Tm}:\text{YGG}$ has an $\Gamma_{inh} = 56$ GHz. Thus, there can be as many as 10^8 homogeneous lines within the inhomogeneous line for single crystal materials [24].

All these properties combine to make rare earth activated materials very useful in photonic technologies. However, choosing and finding the ideal crystal for an application is not always straightforward. Knowledge of the fundamental properties helps inform which material should be pursued next.

Outline of Dissertation

A range of rare earth ion doped materials are used to understand how the optical and quantum properties change between REIs and host materials. This study focuses on characterizing and fabricating optical materials for fundamental science and innovative technologies.

In Chapter 2, an overview of the fabrication is given for the materials used. The motivation for each material is described, with an insight into why the REI and host combination was chosen. Chapter 3 reviews the characterization and equipment for each spectroscopy method used and summarizes other characterization techniques used for both the powders and single crystals. The orientation of an anisotropic sample such as the biaxial Y_2SiO_5 is especially important. Therefore, the crystallographic orientation of birefringent materials is simple, quick, and effective using crossed polarizers in Chapter 4. Then each chapter focuses on a specific material studied. In Chapter 5, the electron spin coherence of $\text{Er}:\text{Y}_2\text{SiO}_5$ is used to demonstrate microwave to optical quantum transduction [33]. In Chapter 6, the $\text{Tm}:\text{Y}_3\text{Ga}_5\text{O}_{12}$ system g-tensor is characterized with a full rotational analysis in a magnetic field to study how linewidths and coherence properties are affected. In Chapter 7, the $\text{Yb}:\text{YVO}_4$ crystal is characterized for quantum applications and found to be an ideal candidate for the 980 nm ytterbium transition with narrow inhomogeneous and homogenous linewidths ideal for new quantum applications [35]. In

Chapter 8, the $\text{Er:Y}_3\text{Al}_5\text{O}_{12}$ crystal is characterized for photonic applications, measuring the linear and quadratic Zeeman shifts and orientation dependence, and the coherence time are measured as a function of magnetic field and temperature to study the decoherence mechanisms of the 1527 nm erbium transition. REI doped crystal powders are pursued in Chapters 9, 10, 11, and 12 to determine if powders can be used in place of a single crystal for optical technologies. The REI powders were fabricated and characterized to find how different processing influenced the material's optical and coherence properties. In Chapter 9, the $\text{Tm:Y}_3\text{Al}_5\text{O}_{12}$ spin relaxation properties were used to characterize the powder fabrication process [36]. In Chapter 10, The mechanical processing and annealing of Er:LiNbO_3 powder is studied [37]. In Chapter 11, the relaxation dynamics of Tb:YAG are altered through different fabrication techniques [38]. Chapter 12 explores optically levitated particles and solid-state laser cooling for quantum limited optical sensors. Finally, a closing perspective on the materials used in this thesis and concluding remarks are given in Chapter 13.

CHAPTER 2

RARE EARTH ION DOPED MATERIAL PROPERTIES AND SYNTHESIS

Survey of Materials Studied

The Cone/Thiel group has a long history of studying materials for quantum and classical information processing. Many materials are characterized in the quest to find the ideal material.

Ideally, the spectral properties of every crystal that can incorporate a rare earth ion would be characterized. At least 500 single crystals have been identified to be useful as a laser material and there are many more that may be useful for new technologies [39,40]. Therefore, a few selected high-quality single crystal materials and powders produced and compared to the bulk crystal are studied in detail.

All the crystal materials used are insulating dielectric inorganic oxides doped with REIs at suitable concentrations. The materials include $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Ga}_5\text{O}_{12}$, Y_2SiO_5 , YVO_4 and LiNbO_3 . Obtaining high-quality single crystal samples of these materials can be difficult, so it has been to our advantage that the Cone/Thiel group has collaborated with Scientific Materials since they started growing crystal in Bozeman in 1989. The quality of the crystal can significantly influence the properties of the material, which are especially pronounced when the optical and electron spin coherence of the REI material are measured.

The chemical properties, dopant levels, symmetry, orientation, and other physical properties along with material production, should all be considered. The materials chosen all have the essential crystal properties needed for laboratory and industrial use. The requirements include several factors such as, chemical inertness and stability at standard temperatures and

atmospheres, hardness, and fabrication considerations such as toxicity, melting point, the feasibility of growth, cleavage planes, availability of material and an operational transparency range around the REI transition of interest [42]. Low defect and inclusion density is wanted to minimize scattering for high clarity. Choosing host materials with low or zero nuclear spin atoms can reduce decoherence mechanisms in the REI [41,43].

Single crystals are more easily grown into large boules if they have uniform thermal properties; specifically, higher thermal conductivity and lower thermal expansion coefficients are desirable and are especially beneficial for high-power laser materials. Hardness, chemical, and atmosphere stability allow more uniform, longer lasting polished optical surfaces.

Powders of crystalline material are of interest because many devices are miniaturized, and the powders can give insight into how a REI material will perform when scaled down. Materials properties such as size and shape that could not be investigated as single crystals can also be characterized. Powders also open the possibility to survey a larger number of material iterations without the cost of growing single crystal boules.

There are hundreds of REI transitions across the series; therefore, the best transitions will depend on the research or application of interest. The REI will have long lifetimes and long coherence times; thus, the transition will not have energy levels close enough together that the ion can relax through phonons or non-radiative transitions. A transition that is resonant with commercially available laser technology is also a great advantage in technology. Each REI material has distinct differences and advantages, therefore, the motivation and the details of the transition for the REI used in each study are discussed.

Rare Earth Doped Single Crystals

The single crystals studied here are $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ (Er:YSO), $\text{Tm}^{3+}:\text{Y}_3\text{Ga}_5\text{O}_{12}$ (Tm:YGG), and $\text{Yb}^{3+}:\text{YVO}_4$ (Yb:YVO), along with the single crystals compared to the powders, $\text{Er}^{3+}:\text{LiNbO}_3$ (Er:LN), $\text{Tm}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (Tm:YAG), and $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (Tb:YAG).

Both single crystals and powders were studied to find materials for quantum information systems. However, often it was found that the single crystals have superior optical and coherent properties compared to the powders. Thus, they are generally preferred over powders and often needed to compare against for high resolution spectroscopy research. All single crystals were grown using the Czochralski growth technique, which has advantages over powders, include longer absorption paths; they can be oriented, faceted, and polished. However they are more expensive to synthesize and fabricate.

$\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$

The motivation to use erbium doped yttrium orthosilicate, $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, (Er:YSO), started with a collaboration between the Cone Lab and Scientific Materials when the first photon echoes were observed in Er:YSO [45,46]. Erbium doped into the YSO crystal is attractive because the $^4\text{I}_{15/2} \leftrightarrow ^4\text{I}_{13/2}$ transition has a radiative excited state lifetime of 10 ms. A series of Er:YSO growths enabled the crystal's quantum properties to be engineered to produce the narrowest optical linewidth of any solid state material, 75 Hz. These groundbreaking studies have influenced research groups worldwide to study many REIs in the YSO crystal [107,118].

The study here began with an international collaboration between the Cone/Thiel group and the Goldner group in Paris, France. The goal was to develop an understanding of how the spin coherence properties of YSO could be influenced by introducing disorder to the crystal.

New YSO growths with a range of REI and other dopants including calcium were produced by the Goldner group and brought to Bozeman by Sacha Wilinski to study. This collaboration demonstrated that Er:YSO is an ideal material for transferring quantum information between microwave frequencies and optical frequencies.

The crystal chosen for the experiments was 0.005% Er:YSO (#6-429) grown by Scientific Materials. This particular crystal was used because only 50 ppm of the natural abundance of erbium isotopes erbium was doped into the crystal allowing the Er^{167} zero nuclear spin isotope's electron spin transitions to be measured with little interference. Y_2SiO_5 is also a low nuclear spin host, which significantly decreases the decoherence of the erbium ions. Where yttrium only has spin of $\frac{1}{2}$ in the single stable isotope, and the major natural abundance of silicon and oxygen have 0 spin. . The YSO unit cell's space group is C_2/c , No. 15, with 64 atoms, consisting of 8 formula units [47]. The rare earths substitute into the two spatially and symmetrically different Y^{3+} sites. Both sites have the lowest C_1 symmetry but are surrounded by a different number of oxygen ions. There are two magnetically inequivalent subgroups for each site [48].

We built custom RF waveguide holders to measure the electron spin lifetimes and the spin coherence as seen in the supplementary material in Chapter 5. A magnetic field can split the optical transitions of erbium to be in resonance with a microwave signal. As a result, the quantum efficiency in transferring photons from microwave to optical is nearly 100%. Furthermore, the optically excited-state electron spin coherence properties were found to be ideal since the excited state population can be controlled and the decoherence of the spin flip flops are minimized [33].

Tm³⁺:Y₃Ga₅O₁₂

The thulium doped yttrium gallium garnet, Tm³⁺Y₃Ga₅O₁₂ (Tm:YGG), is a material being used in emerging photonic technologies such as signal processing and quantum memories in quantum information applications. Ensembles of Tm³⁺ ions in YGG are ideal for high-bandwidth quantum memories because the material has long coherence times up to hundreds of μ s and the narrowest homogeneous linewidths of any thulium doped material known today [25-27,49].

The Tm³⁺ ion has three J-multiplets absorbing in the near infrared. The ground state is the ³H₆. The absorption around 1750 nm is to the ³F₄, that at 1200 nm is to ³H₅, and that at 795 nm is to ³H₄. The ³H₆↔³H₄ transition in Tm:YGG is centered at 795.325 nm (vacuum) with a 56 GHz inhomogeneous linewidth and an absorption coefficient of 0.4 cm⁻¹ for a 1% Tm concentration [49]. The index of refraction of YGG is 1.95 at 795 nm [179]. The absorption coefficient is relatively weak [25] with an oscillator strength of about 18 x 10⁻⁹, smaller than other Tm³⁺ doped materials [24].

The yttrium gallium garnet, YGG, is a direct analog to the yttrium aluminum garnet, YAG, substituting gallium for aluminum. They are chemically resistant and non-hygroscopic, have a high optical damage threshold, and incorporate rare earth ions into the yttrium sites. Both YGG and YAG crystals can be produced using the Czochralski technique for high quality optical oxide materials. Gallium garnets have a body centered cubic structure, space group Ia3D (O¹⁰_H, # 230), with formula units A₃B₂C₃O₁₂, where the A is the dodecahedral site, B is the octahedral site, and C is the tetrahedral site, all trivalent cations. The O is the O²⁻ divalent oxygen anion in an octahedral site. A unit cell of the yttrium gallium garnet contains; 24 yttrium, 40 gallium, and 96 oxygen atoms, consisting of eight Y₃Ga₅O₁₂ formula units, totaling 160 atoms in a cell [174].

The cubic symmetry requires the dielectric constants to be isotropic. Therefore, there is no optical axis or piezo properties that can be used to find the orientation. Laue X-ray photographs are most commonly used to determine the crystal axes.

The increased static strain due to the gallium substituted for the aluminum makes Tm:YGG's inhomogeneous linewidth more than three times as wide as Tm:YAG. Making Tm:YGG ideal for extreme bandwidth RF spectrum analyzers or wide bandwidth photonic memories. Scientific Materials/FLIR has produced over ten separate crystal growths of Tm:YGG to be investigated as the core component of a photonic signal processing systems in a collaboration between the Cone/Thiel group and S2 Corporation [17-20].

A collaboration with the quantum information group at the Delft University of Technology also produced a study on Tm:YGG. Jake Davidson spent a few months at MSU mapping out the thulium ion spin-Hamiltonian in YGG using a combination of spectral hole burning, absorption spectroscopy, and optically detected nuclear magnetic resonance techniques. Chapter 9 shows different orientations of the Tm:YGG crystal in an external magnetic field that can extend the optical coherence times and or narrow spin inhomogeneous linewidths or improve optical pumping by mixing spin states.

Yb³⁺:YVO₄

The Yb³⁺ ion is an attractive choice when surveying REI materials for new technologies because the single $4f^N$ excited state manifold of the trivalent ytterbium ion is at 980 nm, where many optical components are commercially available, including single-mode laser diodes. The Yb³⁺ doped yttrium vanadate (Yb:YVO₄) crystal itself has an extremely high oscillator strength making it very interesting for quantum information [50, 51]. In addition, the YVO₄ material is a

relatively low nuclear spin host allowing for less decoherence in a paramagnetic ion, such as Yb^{3+} or Er^{3+} , with an odd number of electrons, also known as a Kramers ion. These properties and the fact that fabrication techniques for nanoscale devices were recently developed for quantum resonators using YVO_4 as a host [52] make $\text{Yb}^{3+}:\text{YVO}_4$ a promising material for next-generation technologies.

The $\text{Yb}:\text{YVO}_4$ was surveyed for the energy level structure, the oscillator strengths, and the coherence of the optical and spin transitions using high resolution spectroscopy. The high absorption coefficient was measured using a crystal polished down to 90 μm to ensure the material was not over absorbed. An external cavity diode laser was used to excite and scan across the optical absorptions revealing the underlying hyperfine transitions.

YVO_4 has excellent thermal, chemical, mechanical, and optical properties for the growth of high quality materials. The pure material is widely used in fiber isolators, circulators, beam displacers and other polarizing devices in the optical communication industry. The crystal is a tetragonal uniaxial birefringent material with the space group D_{4h} [53]. The Yb^{3+} ions substitute for Y^{3+} ions in sites of D_{2d} point symmetry. The crystals were produced by Gamdan Optics using the Czochralski growth method at a melting point is 1825 C.

$\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$

Current telecommunications infrastructure could be used in a quantum information processing technology based on the 1.5 micron transition of an erbium doped material. Erbium doped yttrium aluminum garnet, $\text{Er}:\text{YAG}$, is a well known commercial product in the laser industry. The YAG crystal is cubic and has the same symmetry as the YGG crystal and the Czochralski techniques to grow high quality samples are optimized and multiple different

concentrations can be produced. This makes Er:YAG an ideal candidate to perform a full high resolution spectroscopic characterization under various conditions to determine the fundamental physics allowing applications to develop around the material.

High resolution absorption measurements of the electronic structure of the excited state crystal field levels of $^4I_{13/2}$ at the 1.5 micron wavelengths were made. Then fluorescence measurements were made to determine the ground state crystal field levels $^4I_{15/2}$, time resolved fluorescence and hole decays to measure the excited state lifetimes. The lowest to lowest transition was measured on a 1% and 0.1% doped crystal, showing very little broadening of the 8 GHz inhomogeneous line. However, a 0.05% Er:Y_{1.5}Lu_{1.5}Al₅O₁₂ was found to have a 250 GHz inhomogeneous linewidth, which could be quite interesting for wide bandwidth applications. The inhomogeneous line was also measured in the 1% Er:YAG as a function of temperature; a frequency shift was also observed.

The linear and quadratic Zeeman effects were mapped as a function of magnetic field strength, up to 7 tesla magnetic field, and orientation using hole burning spectra to determine each of the six erbium sites. The coherence lifetimes were also measured as a function of field, orientation and temperature, and the spectral diffusion. Overall, the coherence lifetime was only weakly dependent on orientation.

Rare Earth Doped Powders

The powder materials used here are Tm³⁺: Y₃Al₅O₁₂ (Tm:YAG), Tb³⁺:Y₃Al₅O₁₂: (Tb:YAG), and Er³⁺:LiNbO₃ (Er:LN). The powders were produced and characterized to decide the practicality of using simpler and more economical growth techniques to develop materials for quantum memories and other hole burning applications.

Tm³⁺:Y₃Al₅O₁₂

Tm:YAG was chosen for study in a powder form because the YAG crystal has been used extensively to host rare earth ions and is used for a wide range of advancements in fundamental material studies and applications [17,36,54,55,]. The material is an excellent host material for the REIs with a cubic unit cell and the inversionless D₂ local symmetry of all six Y³⁺ sites. The yttrium dodecahedral site is a good fit for REI's size and charge [56]. While the higher symmetry can forbid transitions, the 793 nm transition of interest in Tm:YAG is allowed.

Tm:YAG is one of the most promising materials for new quantum or classical information technology systems. With kHz homogeneous spectral lines under a 20 GHz wide inhomogeneous absorption line, information can be stored at 100 Gbits/in² or higher [61,62]. Tm:YAG is used to process high time-bandwidth signals using coherent light interactions under a multiple patents and can be used as a laser frequency stability reference using spectral holes [63,64]. The branching ratios for a lambda system have also been mapped out enabling spectral tailoring with coherent interactions [57-60].

The lowest energy transition of the ³H₆ ↔ ³H₄ crystal field levels of Tm³⁺ in YAG is centered at 793.379 nm. This level can be programmed and characterized with commercially available lasers, such as the Titanium:Sapphire laser, GaAlAs semiconductor diode lasers, as well as frequency doubled 1590 nm lasers.

Thulium has the advantage of having an even number of electrons and only a single isotope, ¹⁶⁹Tm, which has a ½ nuclear spin. The even number of electrons implies non-degenerate electronic states. Each electronic state only has Zeeman splittings in a magnetic field due to the ½ nuclear spin of thulium giving two levels in the excited state and two in the ground state [54]. Energy levels can also be split due to superhyperfine interactions with the nuclear

spins of the host material. The ^{27}Al super-hyperfine energy level structure can also be resolved using spectral hole burning. The lifetimes of the thulium nuclear spins in Tm:YAG are shown to be strongly affected by the fabrication process. The quality of the material was characterized over a large dynamic range by measuring the hyperfine spectral hole lifetimes. Persistent population storage in the nuclear spin hyperfine state of Tm:YAG has long lifetimes, optically pumped and probed using a tunable laser on the order of hours. The resolution of the super-hyperfine levels is used as a measure of the powder material quality along with SEM and XRD.

High energy and low energy types of crushing and ball milling were used to produce the Tm:YAG powder material. Several different annealing processes were used to relieve the strain in the material after it was crushed. After annealing powders of Tm:YAG in a tube furnace, the coherence properties of the bulk crystal could be largely re-established in powders that were ground by hand. However, the amount of strain induced into a powder during the grinding is not always completely removed by the annealing process. Annealing at temperature up to 1400 C did not provide enough thermal energy to drive the mechanically induced defects back into a configuration that could regain the REI's coherence quality in the bulk crystal.

Tm:YAG powder was also produced using the co-precipitation aqueous solution fabrication technique [65]. A flux material such as Li_2CO_3 can be used to lower the melting point of the YAG powders. The flux changed the surface and shape of powders producing dodecahedral crystallites and increased the growth rate at lower temperatures. However, contamination can then become an issue and can increase the decoherence of the material. The growth of the powders does not induce strain in the material like the mechanical crushing, so if

the impurities could be removed the powder growth could be an ideal way to survey Tm:YAG and various iterations of the crystal and many different REI doped materials

Er³⁺:LiNbO₃

Er:LiNbO₃ erbium lithium niobate (Er:LN) is a desirable material for high bandwidth quantum and classical information processing with narrow homogeneous lines under a wider inhomogeneous line, with an unusually strong transition in the telecommunication C-band. The host material is also well known to many industries and can be fabricated into devices. Furthermore, the push to smaller size, weight, and power in all technology has increased the demand for nanofabrication of optical devices. However, few studies have been done on how reducing the size of the crystal material will affect the optical and coherent properties.

LN is the most produced transparent single crystal globally, with a production of over 50 tons per year. The growth of the LN crystal was developed at Bell labs [66]. It has been used for linear and nonlinear devices, in situ biological imaging, modulators, lasers, and waveguides [67]. The congruent melting point is significantly non-stoichiometric (48.6 mol% of Li₂O). Thus, most of the material is produced congruently, however stoichiometric LiNbO₃ can be grown [68] and is of great interest [69].

LN has many properties that make it particularly interesting, including the ability to dope the crystal with a wide variety of ions and all the REIs. The telecom wavelength transition of Er:LN makes it a particularly useful and interesting material for applications. Good coherence properties under a wide inhomogeneous absorption along with an unusually high oscillator strength in the transition of interest allow lower concentrations of erbium if needed, which also has the advantage of limiting the decoherence from Er³⁺-Er³⁺ interactions.

The crystal displays $3m$ point symmetry with a trigonal lattice structure described by the $R3c$ (no. 161) space group. The shifting of the lithium and niobium ions makes the material ferroelectric, with a curie temperature of 1210 C. By symmetry, lithium niobate is piezoelectric, pyroelectric and birefringent [66]. This richness of exploitable physical properties and availability has enabled widely-varied research to be performed on the crystal. There are even references to a “Lithium Niobate Valley” in the future where the crystal will surpass the use of silicon [70].

In this study, the coherence properties of Er:LN were characterized using three complementary techniques; spectral hole burning, two-pulse photon echoes, and free induction decay. The three techniques were needed due to the large dynamic range of coherence properties seen between fabrication runs.

Tb³⁺:Y₃Al₅O₁₂

The Tb³⁺ doped yttrium aluminum garnet was of interest because the energy level structure would prove that REI materials can be engineered to minimize the phonons that exist in the material. The phonons can be restricted by designing the material to be smaller than the phonon’s wavelength [38]. Most of the phonon density of states can be quenched by lowering the temperature of the material to liquid helium temperature. However, the lowest energy phonons can still be present at 3 kelvin. This is because the lowest energy phonon modes are proportional to the acoustic velocity of the material. YAG has a relatively high acoustic velocity of 6400 m/s. Thus, the shortest wavelength phonon mode can in the powders are smaller than ~100 nm. Therefore, particles under 100 nm should not support phonon vibrational modes.

The lowest crystal field energy levels of $\text{Tb}^{3+}:\text{YAG}$ in the $^5\text{D}_4$ excited state have a splitting of only 35 GHz. The small energy gap can be bridged by low energy phonons present in the material. By observing the population difference between the two crystal field energy levels the density of states of the lowest phonon energy mode could be monitored.

A Cone Lab built nitrogen laser pumped a Hänsch-type blue dye laser to excite the $^5\text{D}_4$ levels of Tb^{3+} . A double monochromator was used to resolve the 35 GHz difference between the fluorescence peaks from the two lowest $^5\text{D}_4$ crystal field levels in the excited state of the $\text{Tb}:\text{YAG}$ powders. The population difference between the two states was monitored by comparing the relative area of the two fluorescence peaks. Minimizing the density of phonons in the material by making the powders smaller could be determined when the higher energy fluorescence peak was smaller in magnitude due to less population in the energy level. The optical relaxation dynamics were correlated with other factors, including the crystal powder fabrication techniques, the crystalline structure and powder properties such as size, morphology and phase. An in-situ temperature measurement of the material was also made by monitoring the relative population of the two lowest levels in the ground state, which is separated by 85 GHz, equivalent to a temperature of about 4 kelvin.

Synthesis of Rare Earth Doped Crystals

An overview of single crystal growth is given to focus on essential parameters of the Czochralski (CZ) method normally used in growing single crystal oxide materials used here. Several different powder growth techniques were used to produce small crystallites of REI materials compared to each iteration and characterized relative to a single crystal to decide which production technique is most suitable to produce high optical quality REI materials.

Single Crystal Growth

Many different methods are used to produce large single crystals, ranging from high temperature melts to room temperature aqueous solutions. However, the single crystal oxides used in this work can only be grown using a high temperature or high pressure system. The Verneuil process is regarded as the first synthesis of high temperature single crystal gems, and the first rubies were grown using it. Verneuil presented his sealed notes at the Paris Academy of Science in 1891 but only announced his discovery ten years later in 1902. The method is still used today for crystal growth, and many other techniques have been developed since, including the Czochralski, Bridgeman, floating zone, and Kyropoulos methods.

For us, the most notable technique was developed by Jan Czochralski. While studying the crystallization of metals in 1917, he accidentally dipped his pen into a crucible of cooling molten tin and pulled the first crystal out of a melt of the molten material. He could not have imagined the technological and industrial usefulness of this crystal growing technique for our society. The After WWII, the technique was optimized at Bell Labs to grow large single crystals of germanium containing p-n junctions [44].

Czochralski Method

The Czochralski or CZ method is now the preferred method for growing high-performance single crystals we rely on today, including silicon, gallium arsenide, sapphires, and REI doped oxides, silicates, vanadates, niobates, fluorides and many others. Moreover, the general design developed by Czochralski over 100 years ago is still being used today to produce new optical technologies because large crystal boules grown and fabricated for devices.

The CZ method uses a seed crystal dipped into a melted mixture of the material to be grown. Then, the crucible is held slightly above the melting point of the material of interest; the grown material is delicately pulled while atoms or molecules transfer from the liquid melt to the solid crystal surface in atomic order.

Parameters of CZ Growth Technique

A Czochralski growth apparatus can be divided into two systems, the furnace and the pulling system. The design of the furnace has a significant effect on the thermal axial and radial gradients and the stability of the temperature. The pulling system influences the melt flow dynamics by controlling the rotation rates of the seed and the diameter of the crystal. Each type of crystal will also require different care on cool down procedures to prevent strain and cracks. The coverage of all parameters of the CZ process is beyond the scope of this work. However, some specific points have a considerable influence on the quality of the materials grown.

The interface between the solid and liquid is of particular interest for the growth of all crystals because that is where the atoms are solidified into place, and the crystal structure is formed. The solid-liquid interface in the CZ method can be concave, flat, or convex into the melt. A fluctuating interface has been shown to produce problems in many types of crystals [42], including thermal stresses, faceted interfaces, crystal cracking, impurity inhomogeneities, core segregations and changes in stoichiometry. Therefore, the interface needs to be controlled throughout the pulling of the CZ crystal growth. There are three distinct stages of the growth, the shouldering, the body, and end growth, where the rotation and pull must be monitored to ensure the interface is stable to produce high quality materials.

The parameters that give the greatest control of the interface are the rotation rate, pulling rate, and thermal gradients. The rotation and pulling rate can control the flow direction of the melt, the dynamics of the melt gradients and the shape of the interface.

The thermal gradients depend on the diameter of the crucible and crystal and the shape and depth of the interface, which can lens blackbody radiation into the crystal having significant effects depending on the absorption profile of the material. Radiative heat loss from the top of the crucible is the main mechanism for the loss of thermal energy from a CZ system and the main cause of thermal gradients outside of the crystal and melt. After-heaters can be used to control thermal gradients as necessary to prevent the crystal from cracking and breaking when cooling to room temperature.

Powder Synthesis of REI Doped Materials

Powder materials can be synthesized by two general methods, from the “bottom-up” or “top-down.” Chemical synthesis or producing powders from the bottom up, starts with separate chemical constituents that are reacted to produce the composition and phase of the powder desired, and ideally, the size and shape as well. Two different chemical methods were used to produce powders: the solgel technique and the co-precipitation technique. The advantages of these methods include low sintering temperatures, good morphology homogeneity, and distribution of particle sizes that can be made. The final stage of both methods is a solid-state reaction, where the starting reagents have small volumes and large surface areas to maximize the contact between reactants. The top-down route uses mechanical grinding or fracturing processes on a single crystal of the necessary material composition to produce a powder of the desired size and morphology.

Pechini/SolGel Chemical Synthesis of Powders

The Pechini or SolGel method is a chemical synthesis route for oxides that can be performed in a solution surrounded by a gel that allows oxides to be produced at temperatures below their melting point. For example, using an aqueous solution of metal (M) alkoxide, $M-OC_2H_5$, where the hydrolyzed precursor forms to make a polycondensation gel of $M-O-M$ that are cross-linked and uniform. The gel is aged for 24 hours and dried at 300 C to remove water and residual organics. Higher temperatures are then used to synthesize the powder into the crystal phase of interest using temperatures lower than the melting point of the specific material's phase.

Co-Precipitation

The co-precipitation method relies on a source of ions in an aqueous solution to react by adding a precipitating agent, ammonium bicarbonate, or ammonia. The precipitating agent was mixed dropwise into the solution to precipitate a precursor powder of the two constituent metals such as aluminum and yttrium in an aqueous form. Oxides of the starting material can be used as precursors but need to be dissolved in an aqueous solution such as nitric or hydrochloric acid. Tm:YAG was synthesized using the co-precipitation method by dissolving nitrates into an aqueous solution with ammonium bicarbonate. The precipitate was stirred in solution to ensure the full reaction is complete. A polar soluble polymer such as polyvinylpyrrolidone was used in the solution to keep the precipitate from agglomerating. A centrifuge was used to separate the size of particles of interest, which are then filtered and washed to eliminate residual unwanted material. The thermal processing on the precursor powders consists of drying the materials above

100 C and finally sintering the material at high temperatures between 1000 C and 1500 C, significantly lower than the 1950 C melting point of the bulk YAG materials.

Mechanical Processing of a Single Crystal into Powder

The mechanical processing of a single crystal into powder consists of crushing the crystal into smaller pieces using various processes. Larger crystal can be thermally cycled to break into smaller pieces, but more grinding or milling is needed to produce crystals powders with diameters between 500 μm and 10 nm. Smaller pieces can be crushed by hand using a mortar and pestle, a vice or press. Low and high energy ball mills were used to produce powders, and results were compared to determine if the impact energy on the millings balls would produce more strain in the powdered REI doped crystals. Although crushing and milling processes introduce significant strain into the crystal, annealing the powder materials can relieve strain, especially if the parent bulk material was not significantly strained.

Powders Post Processing

Annealing can repair the crystal powders to be the same quality as the bulk crystal in some cases. Temperatures close to the materials melting point are favorable to relieve strain in oxide materials, where lower temperatures do not supply enough energy for the defects to be significantly moved in the material. A tube furnace is used in annealing runs where the atmosphere is controlled; however, the peak temperature of our tube furnace was limited to 1400 C continuously. A high temperature box furnace was also used in later experiments, annealing materials up to 1600 C continuously.

Summary of REI Doped Material Properties

Synthesis of many REI doped materials for optical applications uses high temperature techniques. The materials studied here are rare earth doped insulating oxides of YAG, LN, YGG, and YSO in the form of single crystals and powders. The REI include thulium, erbium, and ytterbium with concentrations as low as 2 ppm up to a few atomic %. Several techniques were used to produce REI powders, which we compared to single crystals grown using the CZ growth method.

Both powders and single crystals have their advantages. Powders can be produced in multiple different methods to be surveyed quickly and are much less expensive to produce. However, they can have unexpected problems such as excessive strain, impurities, agglomeration, and surface effects. Single crystals have the advantage of being easily handled, cut, and oriented with respect to the crystal symmetry and polished to produce smooth surfaces with less optical scattering. However, single crystals are expensive to produce making it hard to iterate between growth parameters. Overall, fabricating and using both forms of the material and characterizing them with high resolution optical techniques can provide the best solution to finding new and exciting materials for the next generation of technologies.

CHAPTER 3

CHARACTERIZATION METHODS AND EQUIPMENT

Overview of Characterization

REI transitions characterized during this work range from the ultraviolet through the visible into the infrared. The REI's presented in the following chapters include terbium, thulium, erbium, and ytterbium. These measurements build on the wide variety of equipment, knowledge, and crystal materials studied over decades in the Cone/Thiel Rare Earth Spectroscopy Lab. The REIs presented here were chosen because of their respective transition wavelengths and relevance to the coherence and other optical properties needed for applications.

High resolution optical spectroscopy is the main characterization tool used when studying rare earth ions in crystals. Imaging, structural, and chemical characterization techniques are also used to draw correlations between traditional material properties and optical properties. Crystal structural tools such as x-ray diffraction techniques were used to determine the crystalline phase of new materials. Laue x-ray and optical birefringence were used to find the orientation of single crystals before performing spectroscopy. Finally, the powders' size, morphology, and facets were characterized using optical imaging and scanning electron microscopy.

Optical Spectroscopy EquipmentOptical Components

The optical experimental setups include light sources, optics, cryostats, detectors, electronics, and computers. Each REI transition requires different lasers, window coatings,

fibers, and detectors. For the highest resolution spectroscopy stable lasers are needed, and preferably a laser system that scans across a wide optical frequency range without mode hopping or large variations in output power. Often the limiting factor in measuring REIs is the laser's linewidth or the ability to tune a laser across the frequency of the REI transition.

Single-mode diode lasers are becoming more common at a few of the REI wavelengths of common use, such as 795nm Tm^{3+} , the 980nm Yb^{3+} , and the 1535nm Er^{3+} transitions. Moreover, with commercially available laser diodes, external cavity diode lasers in the Littrow or Littman-Metcalf configuration can be built or purchased for tunable spectroscopic characterization.

The measurements on the erbium ion in Chapter 5 and 10 used external cavity diode lasers (ECDL) in the Littman-Metcalf configuration. Erbium doped fiber amplifiers were also used to increase the optical power while preserving single mode narrow laser linewidth of the ECDL. In Chapter 7 the ytterbium transition was probed with a home built ECDL in the Littrow configuration. For thulium experiments, a Coherent 899-21 Titanium-Sapphire tunable bow-tie ring laser is a workhorse in the near infrared because of the tuning range, narrow spectral linewidth, and high output power. The terbium fluorescence measurements used a lab built pulsed nitrogen pumped Hänsch-type dye laser, using 6 ns pulses and Coumarin 481 dye to provide the 485 nm photons.

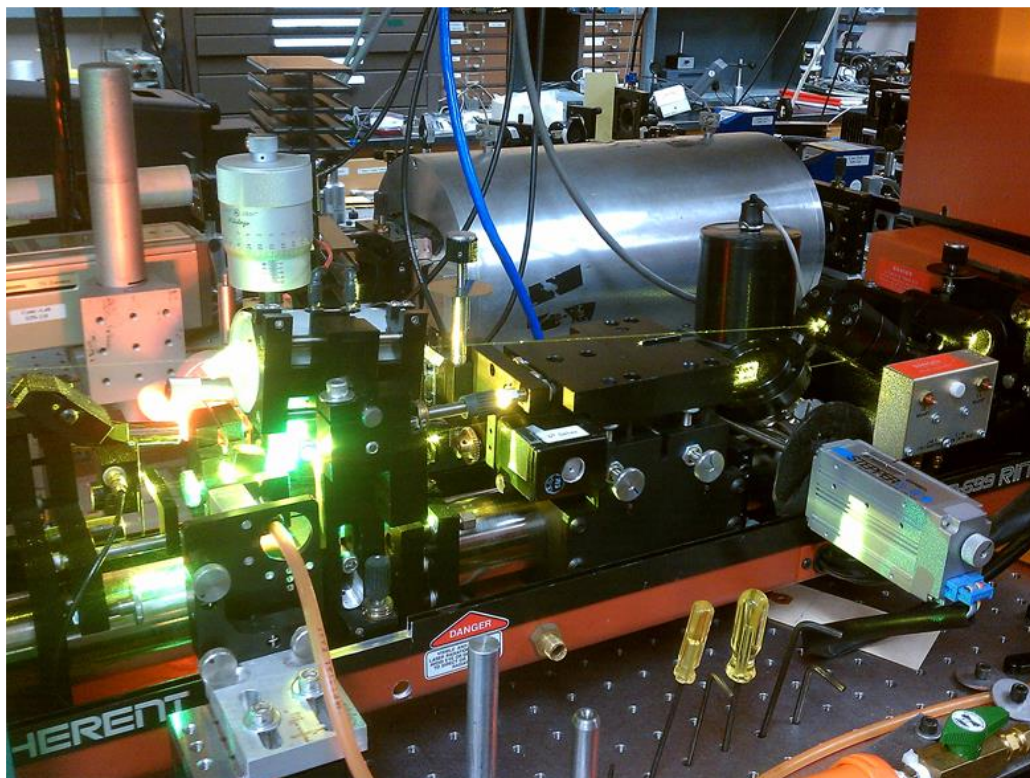


Figure 3.1. Image of a Coherent 699 Dye ring laser being pumped with a 532 nm laser.

Wavelength dependent optical components such as polarizers, mirrors, isolators, acoustic optical modulators, fibers, Fabry–Pérot interferometer, wavemeters and even lenses or windows with coatings should be optimized for the REI transition of interest. Lenses are usually borosilicates and can be coated with multiple layers of dielectric material to reduce reflections. Quartz and other single crystals can also be used in specific applications. Silver mirrors have the best reflectivity across the visible range, while aluminum is a cheaper alternative; it has a significant loss in the near IR region where gold is superior. Dielectric coated mirrors are used when the highest reflectivity is needed. Broadband light sources such as tungsten halogen lamp are used for wide spectrum absorption scans, and mercury lamps, LEDs, or the appropriate lasers are used for fluorescence excitation. The detectors in this work can be split into visible and

infrared. Photomultiplier tubes or silicon diodes are used in the visible and indium gallium arsenide diodes, or germanium detectors are used in the near-IR wavelengths.

Cryostats

The optical measurements of REI crystals are performed at liquid helium temperatures. Cryostats are common to all optical experiments, and various types of cryostats are used to achieve the needed temperature ranges, magnetic fields, RF inputs, and optical access to the crystal. The two basic helium types of cryostats are open liquid helium bath and closed cycle helium refrigerators. Bath cryostats hold liquid helium in a dewar and bathe the crystal in the liquid or near liquid helium gas. Two open helium bath cryostats were used in this work including an Oxford SpectroMag and an Oxford Optistat. The SpectroMag is equipped with a superconducting split solenoid capable of producing up to eight tesla magnetic fields, and it can be kept cold for several days after being filled. The Optistat can hold temperatures below 2 kelvin for 12-16 hours. A lab-built water-cooled Helmholtz coil is used with the Optistat to produce fields up to 250 Gauss at 45 Gauss/Amp.

The most common close cycle cryostats include pulse tubes and Gifford-McMahon types. Recently developed technologies were also used in experiments, including helium sorption fridges manufactured by PhotonSpot and a sub-2 kelvin closed cycle pumped liquid helium cryostat manufactured by Montana Instruments, as seen in Figure 3.2



Figure 3.2. Five different cryostats used in this work. Top Left: Montana Instrument's C2 closed cycle Gifford-McMahon system. Top Center: Oxford SpectrumMag helium bath cryostat. Top Right: PhotonSpot's helium sorption fridge. Bottom: Cryomech's closed cycle pulse tube in the silver cylinder and Roger Macfarlane aligning a beam through an Oxford Optistat.

Materials Characterization of Resonant Frequencies through Optical Spectroscopy

When new REI doped materials are produced, absorption and fluorescence spectroscopy are often the first optical measurements performed. Optical absorption spectroscopy is used to measure the absorption of excited state energies along with the inhomogeneous linewidths, center frequency, and absorption coefficients of the transitions. Fluorescence spectra are used to find the energy levels of the ground multiplet, and time resolved fluorescence decays allow the excited-state lifetimes to be quantified.

Once the wavelength of the transition of interest is identified, lasers are employed to further characterize the material with higher resolution techniques. The optical coherence properties of REIs are useful for applications, so they are often of the greatest interest to the REI and quantum information community. The coherence lifetimes and spectral hole burning structure can also be used as a sensitive characterization tool to determine material quality. Techniques such as photon echoes, spectral hole burning, and free induction decays can be used to measure coherence lifetimes over a large dynamic range. Nuclear-spin frequencies, lifetimes, and spin coherence can also be used to probe the properties of the REI doped materials, giving insight into the REI quantum structure as well as the host quality. Magnetic fields are often used to study the Zeeman interactions of the REI's spins. Radio frequency oscillators can also be used to drive the low energy spin transitions to study their dynamics which are of interest for microwave to optical transducers and quantum memories.

Absorption and Fluorescence

The excited state crystal field energy levels of REIs are characterized and identified using optical absorption measurements. The REI energy levels of interest are cataloged for many

common REI doped crystals by Morrison and Leavitt [2]. However, the linewidths, absorption coefficients and relative oscillator strengths of individual crystal field transitions need to be measured, since they depend on specific crystals, crystal composition and history.

A broadband lamp and a spectrometer or optical spectrum analyzer are used to detect the amount of light transmitted by the material. Filters should be used to select ranges of light when using broadband sources to reduce the heat load on the crystal and minimize the involvement of REI transitions out of the range of interest. The spectrometers used are the SPEX 14018 and the SPEX 1000; each uses dispersive gratings to filter the light have a resolution of $0.1\text{cm}^{-1} = 3\text{ GHz}$. When using a spectrometer, the slit widths should be optimized for resolution; the wavelength should be calibrated with an absolute frequency reference, such as a laser, a uranium lamp, or a mercury lamp. Multiple calibrations should be taken if measurements are made throughout the day to ensure the highest accuracy because pressure and temperature fluctuations in the room can also cause changes to the index of refraction of the air. The optical spectrum analyzers (OSA) use a dispersive grating or a Michelson interferometer. The Michelson interferometer OSA uses a He-Ne laser as a reference with a resolution of 900 MHz in the 1550 nm range and drops slightly as the wavelength decreases toward the visible.

Accurate measurements require the absorption transition to be detectable, ideally with an optical density no greater than $\alpha L \sim 1$, because over-absorbed transitions give nonlinear results and materials with low absorption can be difficult to measure. The inhomogeneous width also gives a sensitive measurement of the distribution of the rare-earth ion's local environment and the degree of order in the crystal [34]. The crystal can be cut thin to make accurate measurements if a transition is over absorbed. In some cases, very thin samples are needed where high oscillator

strengths and narrow inhomogeneous linewidths can give REIs very high absorption coefficients. For example, a Yb:YVO₄ crystal with only 10 ppm of Yb needed to be cut down to 90 μm . Materials with broader inhomogeneous lines and lower absorption coefficients require longer samples and higher concentrations to achieve an optimal optical density, as in the case of Tm:YGG, in Figure 3.3, which needs to be ~ 10 mm and a concentration of 2% to have an $\alpha L \sim 1$

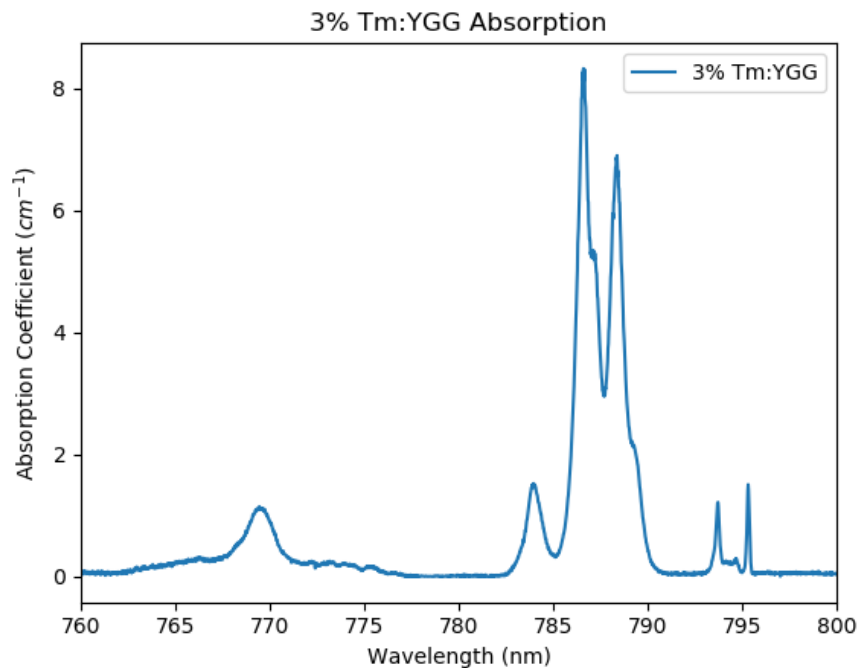


Figure 3.3. Absorption spectra of the $^3\text{H}_4$ levels of 3%Tm:YGG.

Laser absorption spectra can show high-resolution detail when the linewidth is too narrow to resolve with the spectrometers. Tunable lasers also can selectively excite specific absorption lines of rare-earth ions to identify transitions with a specific site, a capability especially useful for crystals with multiple sites or defect sites. Narrow lasers that scan rapidly, often by current or piezo tuning, are needed for precise measurements. Low laser power should

always be used to prevent optical broadening and spectral hole burning, altering the absorption coefficient and linewidths [71-73].

Fluorescence spectroscopy is used to observe the photons emitted by the material after the ions have been excited by a resonant light source to an excited energy level. The energy levels of the ground-multiplet are measured using the spectrometer to scan across the energies of the fluorescence peaks. For example, the energy level structure of ${}^4\text{I}_{15/2}$ was determined by exciting the sample with a broadband tungsten-halogen lamp and recording the fluorescence spectra using a SPEX1000M spectrometer with 3 GHz resolution and a liquid-nitrogen cooled germanium photodiode. The highest energy fluorescence peak will be at the same energy as the lowest energy absorption peak when symmetry allows the lowest-to-lowest transition to be observable. The sources used are lasers and high-powered broadband lamps such as mercury vapor or a xenon lamp. Once the wavelengths of the transitions of interest are identified, a resonant laser can be tuned for direct excitation. Time-resolved fluorescence is used with pulsed excitation sources to determine excited-state fluorescence lifetimes, relaxation mechanisms and decay pathways.

Spectral Hole Burning

Spectral hole burning (SHB) is an optical pumping process that occurs when a laser excites an ensemble of ions of an inhomogeneous absorption line into an excited state. The ions are optically burned out of the absorption profile, leaving a spectral hole. Spectral holes can only be burned into materials with inhomogeneously broadened absorption lines, usually requiring low temperatures. REI doped solids cooled to low temperatures reduce the homogeneous broadening by phonons, producing inhomogeneously broadened absorption lines.

The detected spectral hole is at least twice the intrinsic homogeneous linewidth of the transition because the laser is on the transition twice; it is burned and scanned to measure the width. Laser jitter, power broadening, and spectral diffusion also increase the linewidth.

The population lifetime and decay pathways can be determined by measuring the decay of the spectral hole through time-resolved hole burning. If the hole lifetime is limited by the excited-state or an intermediate bottleneck state, it is known as a transient spectral hole.

Longer lived persistent spectral hole population reservoirs can be Zeeman levels, hyperfine, or superhyperfine levels. Optical pumping of hyperfine and superhyperfine states in materials can produce persistent spectral holes lasting minutes, hours, and even week. In Tm:YAG and Er:LN, the nuclear spin state lifetimes are used to assess the quality different fabrication methods of the materials.

Photon Echoes

Two-pulse photon echoes use a sequence of optical pulses that effectively remove the inhomogeneous broadening to measure the coherence time, T_2 , the homogeneous linewidth, Γ_h , where $T_2 = 1/(\pi\Gamma_h)$. The ultimate limit for T_2 is set by the excited-state lifetime through the relation $T_1 \leq 2T_2$. A truly isolated ion would exhibit a natural linewidth caused by the finite lifetime of the transition; however, this is rarely the case because of heating, ion-ion coupling, and other material dynamics. In rare cases, the homogeneous linewidths can be nearly lifetime limited [13]. Since the homogeneous linewidths may be much narrower than the laser linewidth, the photon echo technique is a convenient way to measure the homogeneous linewidth because it overcomes the laser's instability.

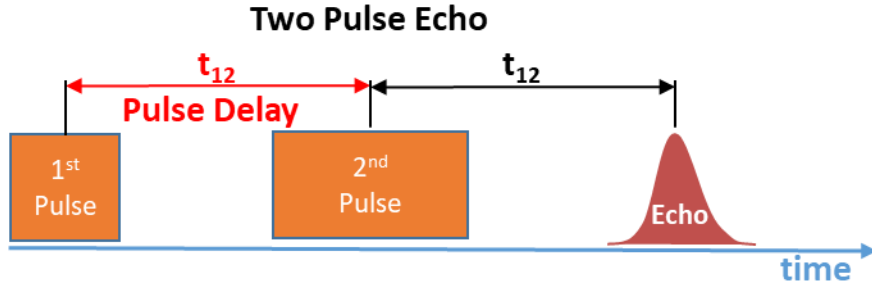


Figure 3.4. Block diagram of a two pulse photon echo experiment where the echo area is measured as a function of the t_{12} pulse delay. As the pulse delay is increased, the area of the echo is measured.

In a two-pulse echo measurement, Figure 3.4 two pulses, the first with a pulse area of $\pi/2$ and the second is nominally double the pulse area and separated in time by τ are used to probe the ions. In practice the second pulse is often slightly smaller than the twice the first pulse area. The first pulse excites an ensemble of resonant ions into a coherent superposition between the ground and excited state. After the pulse, the ions oscillate in phase while the dipole moment produces coherent emission for a short amount of time after the pulse is turned off, emitting a free induction decay. The ions will dephase from each other while they are in the superposition. The second pulse, at a time τ , flips the phases by inverting the transition moment precession, which effectively reverses the dephasing. After the same amount of time, τ , between the pulses the dipoles rephase to produce a coherent pulse of light, the photon echo.

For example in Tm:YGG, two-pulse photon echo decays were measured using a laser with a center wavelength at 795.334 nm. A slow continuous scan of 2 GHz per 25 seconds was used to prevent pumping population into the bottleneck state. The optical pulse lengths were set using a pulse generator to open and close an RF switch connected to the synthesizer amplifier, variable attenuator, and acoustic optic modulators (AOMs). The pulse lengths were set as short as possible, down to 100 ns. Two AOMs are used in series to ensure >60 dB attenuation of the

continuous laser. A collimated or slightly divergent beam was focused to about 300 μm in the crystal using a 150 mm achromatic lens. The signal was collected from the crystal with the same type of lens for f-matching and then focused through an AOM. The AOM is used as an optical switch to block the pulses and open during the echo signal, dependent on the time delay between the two pulses. Detection was made by a Newport 1801 silicon detector or Hamamatsu R928 photomultiplier tube. The homogeneous linewidths can be measured by recording the exponential decay of echo area as the t_{12} pulse delay is increased. Below in Figure 3.5 is an example of measured echo decay curves in four different crystals.

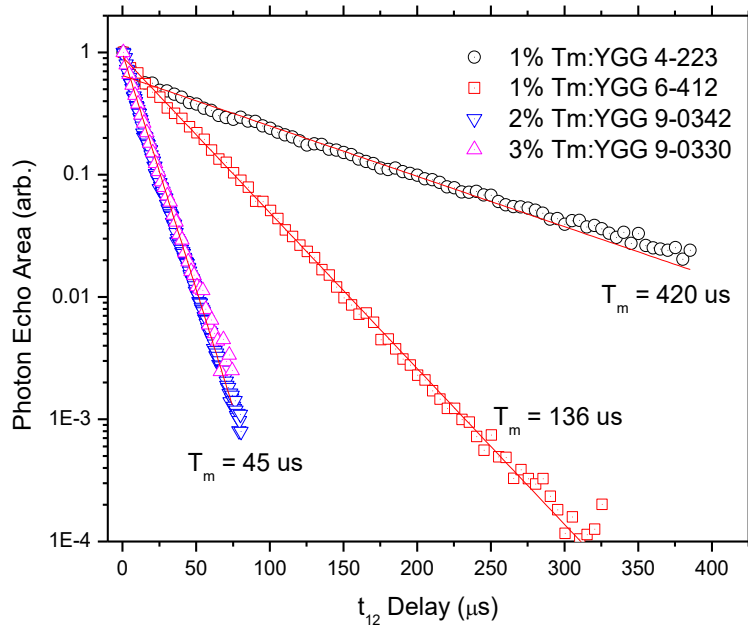


Figure 3.5 Two Pulse Photon Echo decays of four different Tm:YGG growths all taken in an Oxford liquid helium bath cryostat at 1.2K.

Electron Spin Coherence

An experimental set up to characterize the electron spins of Er:YSO was built to explore the properties of the spin lifetimes, and spin coherence. The experiment included an optical and RF system to interact with the resonant splitting of erbium in an external magnetic field.

A static magnetic B field created by an external Helmholtz coil was applied parallel to the D_1 axis of the crystal. The sample was mounted onto a lab built SMA coaxial $50\ \Omega$ impedance-matched copper strip waveguide through which the RF power passed, producing an RF excitation with an amplitude of several Gauss along the b axis of the crystal. An SMA male-male connector was milled out exposing the bare wire to act as a waveguide along the dimension of the crystal axis to enable the microwave field to interact with the erbium spins resonance tuned by the magnetic field. The RF transmission line was terminated by a $50\ \Omega$ impedance load outside of the cryostat to prevent back-reflection.

The optical detection after the sample was made by an amplified AC-coupled photodiode (New Focus model 1611-AC) with 1 GHz bandwidth. The acquired signal was sent to a spectrum analyzer to measure the Raman beat amplitude. An HP model E4411B spectrum analyzer with an integrated RF tracking generator to produce an RF signal of -10 dBm between 9 kHz and 1 GHz used for the continuous Raman heterodyne signal. The experiments were set up around an Er:YSO crystal in a helium flow Oxford Optistat cryostat. The laser and the RF field could be pulsed to perform excited state spin coherence measurements on Er:YSO to measure the effect of spin flip flops on the coherence and determined the quantum efficiency of the spin transition, which was found to be near 100%.

Powder Characterization Techniques

Material properties such as the structural composition, phase, size, and shape, are essential aspects to characterize when studying the fabrication effects on powders. The main non-resonant characterization techniques used are x-ray diffraction and scanning electron microscopy.

XRD

The compositional phase of each powder was determined using the x-ray diffraction (XRD) instrument at MSU's Imaging and Chemical Analysis Lab (ICAL). The XRD is a Scintag Inc X-1, Advanced Diffraction System. The x-ray source is run at 1.8 kW, 45kV and 40 mA, using the copper K- α line corresponding to 8.04 keV, which has an x-ray wavelength of 1.5406 Å. The slits on the source used are a divergence slit of 2 mm and a scattering slit of 4 mm. The detector slits used were 0.5 mm scattering and 0.2 mm receiving. Step sizes were set to 0.02 degrees and dwell times of 0.5 seconds at each step. Figure 3.6 shows a typical XRD spectrum with reference peaks.

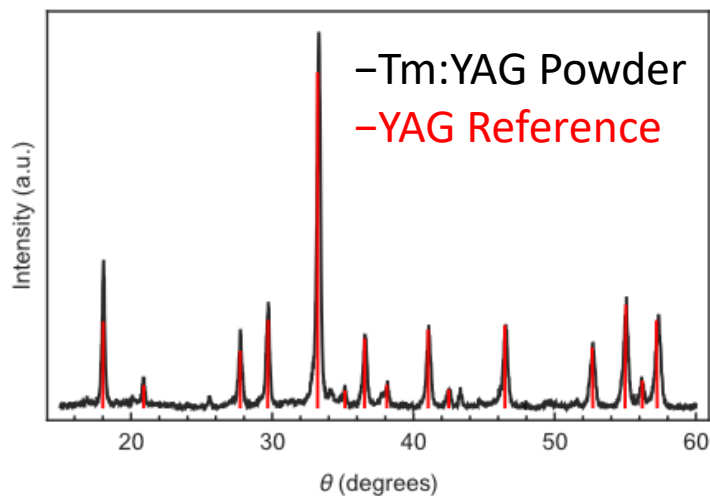


Figure 3.6. XRD spectra of Tm:YAG powder taken in ICAL. The red lines are positions of the prominent peaks of a YAG reference material.

Scanning Electron Microscope

Powders were imaged using the Zeiss SUPRA 55VP field emission scanning electron microscope at ICAL to determine their size, morphology, and distribution. In Figure 3.7, the left image illustrates the consistency of the powders, with the inset showing a typical amount of material produced from a single production run. The center image shows the well-defined

dodecahedral shapes of individual particles compared to the shape of the powders after using high-temperature treatment with metal-halide flux.

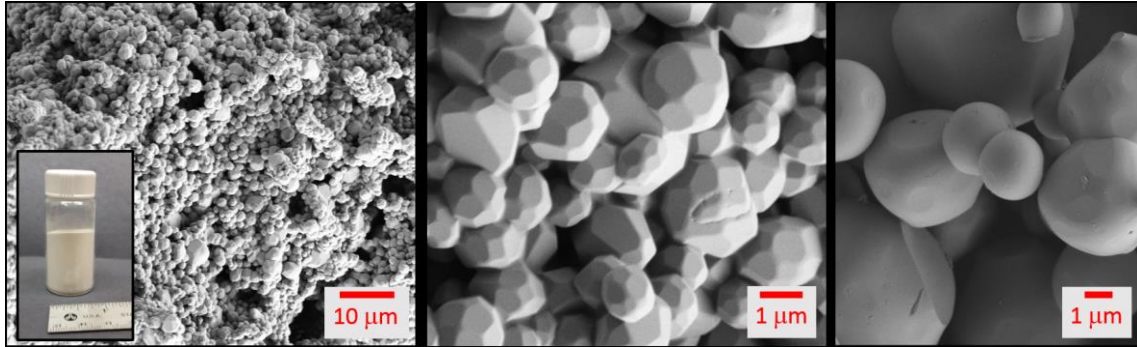


Figure 3.7. Electron microscopy images of Tm:YAG powders. Left: Images showing a larger field of view of the powders, the inset showing a typical amount of material produced from a single production run. Center: A closer view of the well-defined dodecahedral YAG crystal powders. Right: powders partially melted after being heat treated in metal-halide flux.

Single Crystal Orientation

Before optical measurements are made the orientation of the crystal should be known. Single crystals oriented with respect to the electric field polarization of the light; the external magnetic field enables fundamental physical tensors to be determined and the optical properties of the materials to be optimized in applications.

Birefringence

In the case where the crystal is anisotropic, the crystal will be optically birefringent. The birefringence can be used to orient the crystal by simply using crossed polarizers. More details on this are given in Chapter 4, specifically for the case of YSO, with an extension to other crystal symmetries as well. Since LiNbO_3 is a uniaxial birefringent crystal, the c-axis can be found by looking at the crystal between crossed polarizers as shown in Figure 3.8.

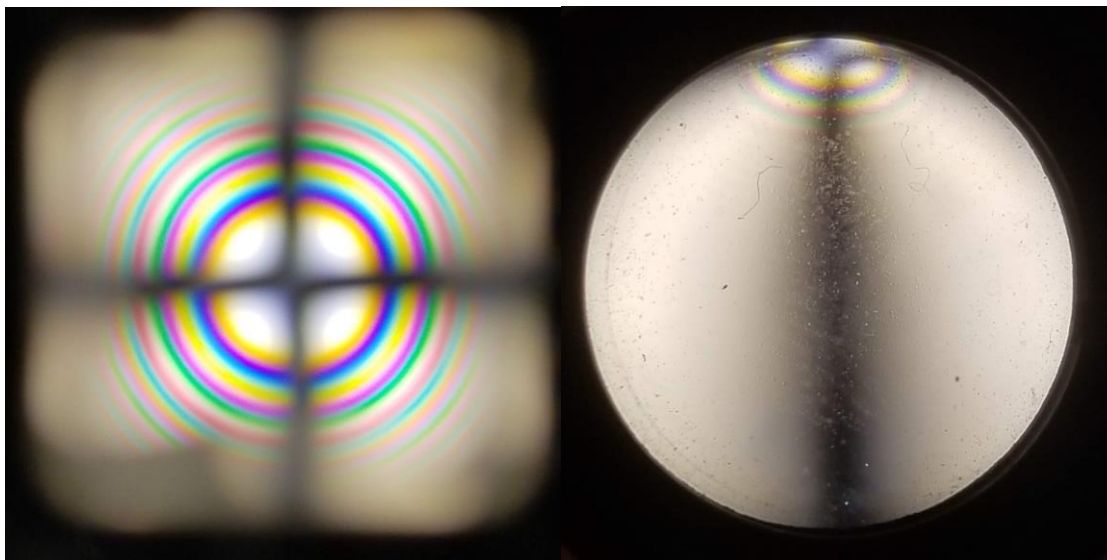


Figure 3.8. Birefringence photographs of LiNbO_3 . Left: Looking along the optical axis, the c-axis of LiNbO_3 . Right: Looking along a vertical extinction axis, the optical axis can be seen at the top of the image, showing how a crystal that is not cut along the optical axis looks between crossed polarizers.

Laue x-ray

Laue x-ray photographs are used to orient single crystals of any symmetry. The Laue system used in this work is housed at Scientific Material's/FLIR. It is a back scatter Photonic Science Laue camera, with a central hole to allow the x-rays to pass through and diffract off the face of the crystal back onto the CCD camera. The crystal is adjusted on a goniometer to find the symmetrical orientation. The program Orient Express is used to align a simulated image with the real image taken. Figure 3.9 shows a backscatter image of a YSO crystal overlaid with a simulated image on the left. On the right, the image is overlaid with the crystal axes and the dielectric axes.

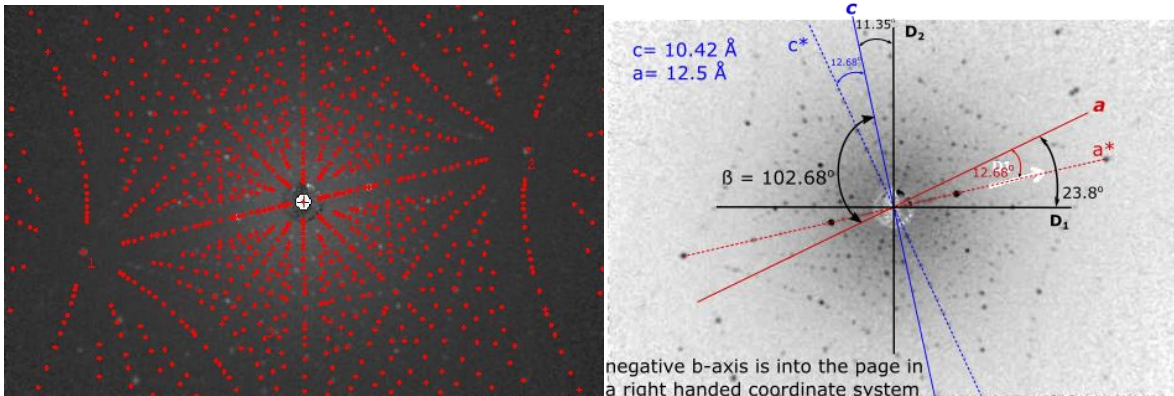


Figure 3.9. The backscatter reflection points of YSO observed with Laue X-rays. Left: The image is overlaid with the simulated points using Orient Express software to determine the orientation of the crystal. Right: The backscatter photo showing the orientation of the crystal axes with respect to the reciprocal lattice points and the dielectric axes.

Acid Etching

Chemical etching is used to find dislocation density and inclusion defects such as iridium particles arising from CZ growth or processing. In combination with optical birefringence patterns the Burgers vectors of the dislocations can be revealed. Phosphoric acid is the most common chemical etching solution for the rare-earth garnet crystal system [74]. The temperature range of 250-450°C is the preferred approach for etching the surface and “chemically polishing” the crystal to remove the higher density of shallow surface defects that are normally caused by crystal cutting and mechanical polishing. The optimal temperature for the common crystals YAG and GGG is ~435C and ~300C, respectively, suggesting a temperature near 300C should be employed for YGG, with a longer pre-etch at a lower temperature of 160C to clean the surface and enhance the uniformity of the later strong etch. Etching the {110} surface plane of the crystal shows the characteristic facets of the cubic symmetry, which can also be used as orientation markers seen in the right image in Figure 3.10.

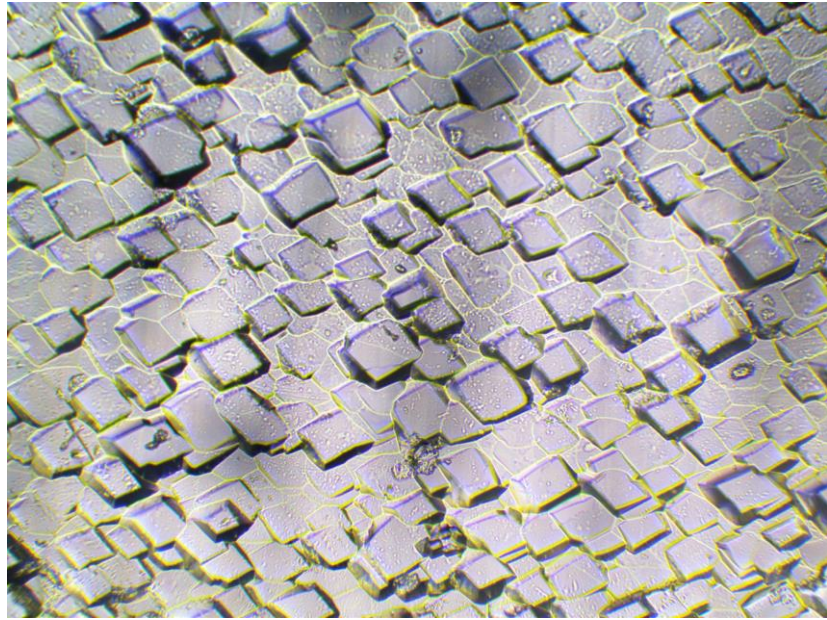


Figure 3.10. Microscope image of etched surface of a $\{110\}$ plane perpendicular to the $\langle 211 \rangle$ axis of a Tm:YGG sample. The etch was done with phosphoric acid for 1 hour at 200 C.

We have applied the acid etching approach to characterize the type and density of defects of as-grown and post-anneal crystals to quantify the effects of annealing on the large-scale lattice defects. Etch pits can also be used to help verify the orientation of single crystals.

Chemical Composition

Mass spectrometry is used to measure impurities across the periodic table that may be difficult to detect using other techniques. Several different mass spectroscopy techniques were used to measure impurities in the crystals; these include inductively coupled plasma mass spectroscopy (ICP-MS), glow discharge, and laser ablation-ICP-MS.

The time-of-flight secondary ion mass spectroscopy in ICAL was used to measure the chemical compositions as a function of depth for lithium niobate wafers with rare-earth ions diffused into the surface. Using a pulsed positive gallium ion gun to sputter material from the surface, the secondary ions are accelerated by ion optics through a series of magnetic fields and

the masses of the ions are separated by the time of flight. Depth profiles are achieved by using the ion gun to sputter an area of known spatial resolution $>10\text{ }\mu\text{m}^2$, then collecting the emitted secondary ions. The depths sputtered are measured with an atomic force microscope and sputtering rates can be determined for different crystals and orientations.

Two different methods were used to compare the concentrations of impurities in YSO. Two crystals were sent to EAG Labs to be analyzed by glow discharge and they were also analyzed by laser ablation coupled with an ICP-MS.

The concentrations of impurities in the Tm:YGG crystals show a significant amount of aluminum and silicon in all of the crystals. The original 1% Tm:YGG #04-223, which has the longest coherence, shows a larger amount of transition metals. Other impurities such as calcium and zinc are seen in the newer growths. There can be discrepancies in the absolute amount parts per million of impurities in each crystal due to contamination of the system from previous samples measured. However, the relative amounts in each crystal can be used as an indicator of the influence of the different ions on the optical coherence properties. It should also be noted that Y_2SiO_5 was analyzed in the system before the YGG and argon ($\text{AMU}=40$) is used as a carrier gas. In Figure 3.11, the full scan of impurities is given to show a wide spectrum of elements. Two scans were performed on the 1% Tm:YGG #04-223; the first was taken with a smaller number of elements to test the results. The concentrations that are significantly higher than expected are highlighted.

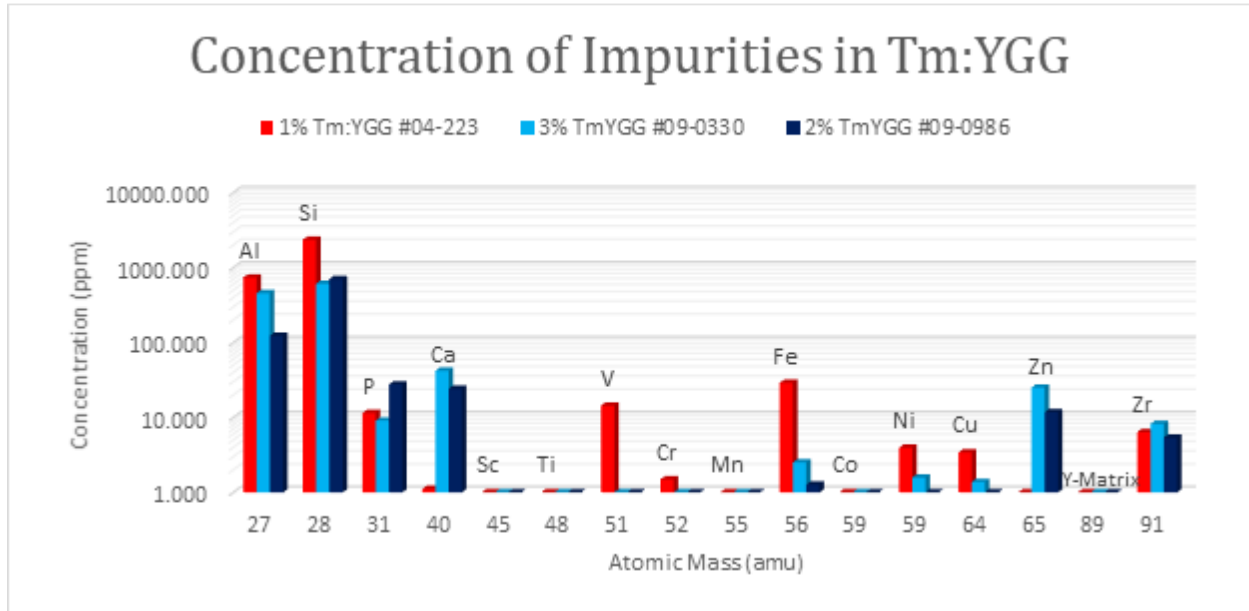


Figure 3.11. Concentration of impurities in three different Tm:YGG crystal growths using the Iridia Teledyne Photon Machines Laser Ablation Inductively Coupled Plasma Mass Spectroscopy

The Al and Si are much higher than expected, but this could be from background contamination. A few elements may have an interference peak due to ion combinations. For example, the Pd concentration is likely a yttrium ion and an oxygen ion recombining before striking the detector. The masses of yttrium and gallium are near the Gd and Tb, measured to be in excess in all the scan except the 2% Tm:YGG #03-0986, which needs to be researched further. Other concerning impurities are the Pb, which is slightly higher than expected, and Zr, which is used as an insulating material in the furnaces used in the growth of the material. The Cd is most likely an artifact of other charge/mass ratios. The Fe, V, and Ce are all higher in the original crystal #04-223, which has the longest coherence suggesting the ions either help lower decoherence or have a minimal effect. The impurities of most concern in the newer crystal, #09-0330 and #03-0986, are the Ca, Zn, and to a lesser extent, the Lu.

			1% Tm:YGG #4-223	1% Tm:YGG #04-223	3% TmYGG #09-0330	2% TmYGG #03-0986
			Tm:Y3Ga5O12			
			05-Nov-20	12-Nov-20		
	Element	Atomic Mass	Concentration [ppm]			
	Al	26.98		737.60	455.30	123.00
	Si	28.09		2354.00	608.30	704.40
	P	30.97		11.48	9.09	27.65
	Ca	40.08		1.11	41.95	24.17
	Sc	44.96		0.37	<LOD**	<LOD**
	Ti	47.87		0.27	0.04	0.02
	V	50.94		14.37	0.02	<LOD**
	Cr	52.00	1.48	1.49	0.76	0.80
	Mn	54.94		0.01	0.20	0.09
	Fe	55.85	28.69	29.06	2.51	1.27
	Co	58.93		0.02	0.01	0.02
	Ni	58.69		3.95	1.58	0.45
	Cu	63.55	3.44	3.42	1.38	0.19
	Zn	65.38		0.18	25.03	11.75
	Y	88.91		Matrix	Matrix	Matrix
	Zr	91.22		6.38	8.22	5.38
	Nb	92.91		0.43	0.02	0.00
	Mo	95.96		<LOD**	0.05	0.00
	Rh	102.91		0.06	0.04	0.04
Y+O	Pd	106.42		1043.00	994.10	1024.00
	Ag	107.87		0.82	0.81	0.81
	Cd	112.41		8.45	8.04	8.27
	La	138.91	0.01	0.01	0.01	0.01
	Ce	140.12	1.73	1.69	0.00	0.00
	Pr	140.91	0.01	0.01	0.01	<LOD**
	Nd	144.24	0.11	0.11	0.04	0.01
	Sm	150.36	0.10	0.10	0.35	0.01
	Eu	151.96	0.09	0.08	0.10	0.11
Y+Ga	Gd	157.25	12.36	12.29	0.25	0.01
Y+Ga	Tb	158.93	0.01	0.01	18.14	0.29
	Dy	162.50	0.07	0.07	0.07	0.03
	Ho	164.93	0.50	0.50	0.23	0.19
	Er	167.26	0.12	0.12	0.43	0.36
	Tm	168.93	17970.00	17910.00	52480.00	35020.00
	Yb	173.05	0.76	0.75	0.74	0.36
	Lu	174.97	0.08	0.09	0.31	1.69
	Hf	178.49		0.03	0.09	0.00
	Ta	180.95		0.00	0.01	0.00
	W	183.84		0.00	0.01	0.01
Tm+O	Re	186.21		2.08	6.41	4.25
	Ir	192.22	<LOD**	<LOD**	<LOD**	<LOD**
	Pt	195.08		0.72	0.00	<LOD**
	Au	196.97		<LOD**	0.00	0.00
	Pb	207.20	0.66	0.64	1.23	0.43
	Th	232.04	0.01	0.00	0.00	0.00
	U	238.03	0.00	0.00	0.01	<LOD**

Table 3.1. Full Impurity scan of Tm:YGG crystals using LA-ICP-MS using the Teledyne Photon Machines Iridia system.

Summary

The characterization of REI doped materials is explored using high resolution spectroscopy at liquid helium temperatures. The coherent interactions of the materials are used to determine the quality of the fabrication method and the usefulness of the material in applications over a broad range of frequencies. These spectroscopic tools provide insight over a wide dynamic range of material quality and exceptionally sensitive to material quality and purity. The materials were also characterized using more traditional techniques complimenting the spectroscopy.

CHAPTER 4

USING BIREFRINGENCE TO ORIENT CRYSTALS FOR CLASSICAL AND QUANTUM INFORMATION APPLICATIONS

Contribution of Authors and Co-Authors

Manuscript in Chapter 4

Author: Philip J. T. Woodburn

Contributions: Prepared material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

Co-Author: Aaron D. Marsh

Contributions: Prepared material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

Co-Author: Rufus L. Cone

Contributions: Analyzed and interpreted results, edited the manuscript, discussed results and implications.

Co-Author: Charles W. Thiel

Contributions: Designed and set up experimental apparatus, performed measurements to acquire data, analyzed and interpreted results, generated figures, edited the manuscript

Manuscript Information

Philip J. T. Woodburn, Aaron D. Marsh, Rufus L. Cone, and Charles W. Thiel

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- ☐ Accepted by a peer-reviewed journal
- ☐ Published in a peer-reviewed journal

Abstract

Birefringence is used to completely orient the crystal axes of YSO, yttrium orthosilicate, based on the rotation of the optical axes. The procedure is quick and accurate within the detection limits of the wavelength of light. The three dielectric axes of YSO can be found and identified visually, allowing the user to know the crystal axes including the direction of the non-symmetric b-axis. The application of optical orientation to other crystal symmetries are reviewed.

Introduction

Anisotropic crystals are used in wide range of research and nonlinear applications such as quantum photonics, optical clocks, nanophotonic light-matter interfaces, and signal processing [5-7,11-13,17-22, 75]. These materials will have significantly different interactions to applied fields depending on the orientation. Often materials are cut and oriented by the grower, but ideally the user can check the orientation of the crystal before it is used in an experiment or an application. Crossed polarizers can be used to see the orientation of most crystals due to the optical birefringence properties. Hexagonal, trigonal, and tetragonal are uniaxial birefringent, orthorhombic, monoclinic and triclinic are biaxial birefringent. Only the cubic symmetry has three equal isotropic dielectric axes, displaying no crystal symmetry birefringence.

In this letter we will focus on the monoclinic yttrium orthosilicate, YSO, a biaxial birefringent crystal because of the increased interest in its use as a quantum applications material and it can be precisely and quickly oriented using crossed polarizers. The crystal structure and dielectric axes are well known and many techniques that have been used to characterize YSO's

crystal axes and vibration axes [76-78], however a simple relationship between the optical extinction axes and the crystal axes have not been unambiguously defined. The dielectric axes are visually distinguished allowing the **b**, D_1 and D_2 axes as defined by Li et al. to be completely oriented to the YSO crystal axes using a simple optical apparatus. The direction of the b-axis of YSO [79,80], the axis normal to the mirror plane, is also defined with respect to the optical birefringence.

YSO's Dielectric and Crystal Axes

YSO has a monoclinic crystal structure with 2/m symmetry providing biaxial birefringence in the visible spectrum. The 2/m axis consists of a 2-fold symmetric axis with an orthogonal mirror plane [81,82]. Conventionally the 2-fold symmetry axis is the $\langle 010 \rangle$ axis which is also a dielectric axis labeled as the **b-axis**. The **a** and **c** crystal axes lie at an obtuse 102 degree angle to each other and orthogonal to the **b-axis** [47,48,83-85].

The three principal dielectric axes are always orthogonal to each other and make-up the index ellipsoid or optical indicatrix. Designated here as **b**, D_1 , and D_2 corresponding to X, Y, and Z axes labeled by Beach et al. The D_2 axis has the highest index of refraction, the b axis has the lowest index and the D_1 axis is the intermediate principal index.

YSO a positive biaxial crystal because the intermediate index, D_1 , is closer in magnitude to the largest index axis, the D_2 axis. Therefore, the optical axes are closest to the D_2 axis in the optical plane. The $2V$ angle, the acute angle between the optical axes, is ~ 40 degrees and the D_2 axis bisects this acute angle, making it the acute bisectrix. The **b** axis is the obtuse bisectrix, and the D_1 is the optical normal. The geometrical arrangement of these features is shown in Figure 4.1.

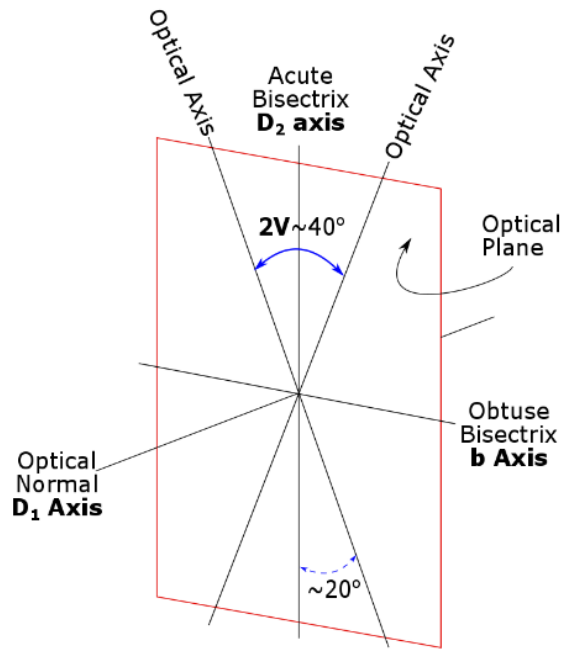


Figure 4.1. The optical plane and axes of YSO, showing a positive biaxial crystal with a $2V$ angle of ~ 40 degrees.

Laue X-Rays backscatter images were also taken to confirm the relationship between the crystal axes and the D_1 and D_2 axes. The a crystal axes of YSO is ~ 23 degrees from D_1 , dielectric axis and the crystallographic c -axis is ~ 11 degrees to the D_2 dielectric axis at a wavelength of 650 nm [86]. The direction of the b -axis is ambiguous in other references so here we use a right-handed coordinate system and define the positive direction of the b axis is out of the page in Figure 4.2.

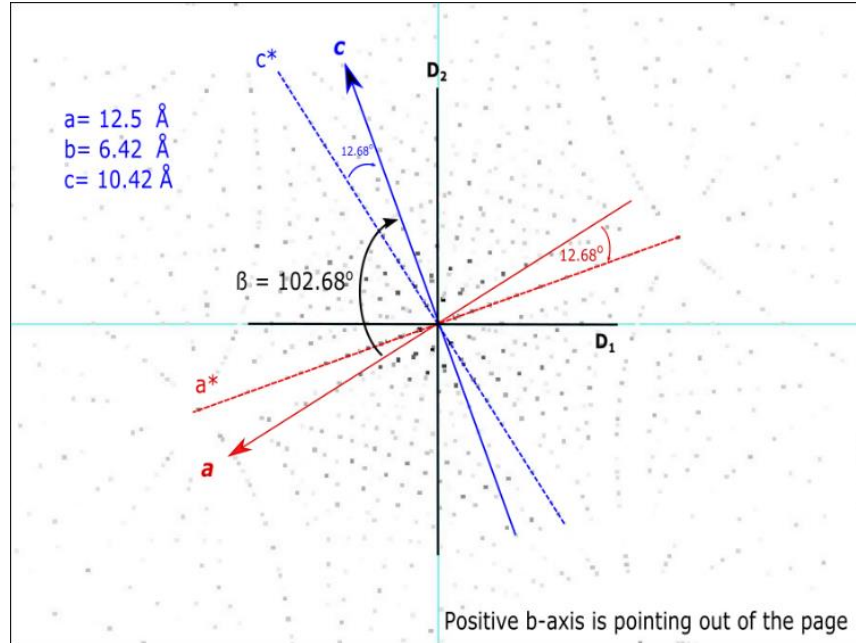


Figure 4.2. The crystal axes (solid colored lines), and the dielectric axes (black lines, horizontal and vertical) overlaid with the Laue x-ray points of YSO. The reciprocal lattice vectors (dotted colored lines) observed using Laue x-rays reflection photographs show D_1 is about 23 degrees from the crystallographic a -axis, and D_2 is about 11 degrees from the c -axis at a wavelength of 650 nm. The positive direction of the b axis is defined to be pointing out of the page.

Location and Identification of the Extinction Axes

Crossed polarizers or a polariscope can be used to find the principal axes of the optical indicatrix via extinction [86-88]. The polariscope consists of a pair of crossed polarizers and a diffuse light source, seen in Figure 4.3. When the crystal's dielectric axes are aligned with one of the polarizer's axes, the transmitted light will be nulled indicating an extinction axis. Each of the three extinction axes can be easily seen using a polariscope and a crystal that has been polished sufficiently to not scatter the polarized light. An index matching fluid such as acetone can also be used on unpolished crystal surfaces.

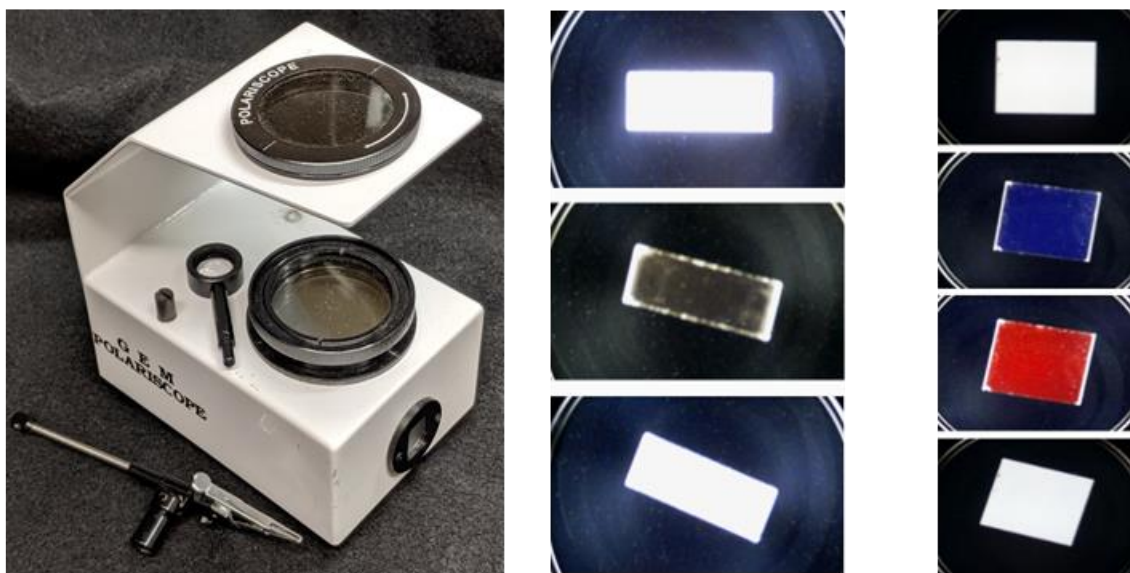


Figure 4.3. (Left) Commercial gemological polariscope. Example of YSO's extinction axes observed using a polariscope, Fig (Center) viewing the crystal along the D_1 or D_2 axis. (Right) viewing the crystal along the b -axis shows the change in transmission because of the rotation of the dielectric axes.

The optical indicatrix rotates about 2 degrees in the visible wavelength range [90,91] about the b -axis as the wavelength is varied. The rotation is enough to see the change in the transmitted color of light. This can be used as a convenient way to distinguish the b -axis from the D_1 and D_2 axes of crystal. When the polariscope and crystal transmits blue light, the extinction axes corresponding to red wavelengths are aligned with the polarizers, as seen in Figure 4.3. The rotation of the dielectric frame is not seen when looking along D_1 or D_2 axis in the polariscope, because the b -axis does not change with wavelength since it is fixed to a crystallographic axis. It should be noted that if the D_1 or D_2 -axis is not exactly normal to the polarizers, components of the index ellipsoid can cause slight color changes.

Direction of the b -axis

The positive and negative direction of the b -axis must be found for the complete orientation of YSO. There is not a standard defined for the direction of the $2/m$ symmetry, thus

the convention of Beach et al and a right-hand coordinate system of the crystal axes is used to define the direction of the **b** axis. Thus, in Figure 4.2 the **b** axis is out of the page. To find the direction of the **b** axis optically the rotation of the index ellipsoid about **b** axis with wavelength can be used. If the transmitted colors of a YSO crystal in a polariscope appear from red to blue when the crystal is turned in a clockwise rotation the positive **b** axis points towards the viewer. Conversely, when the color of the light transmitted through the extinction axes and crystal changes from blue to red in a clockwise rotation, the positive **b** axis is pointing away from the observer, as depicted in Figure 4.4.

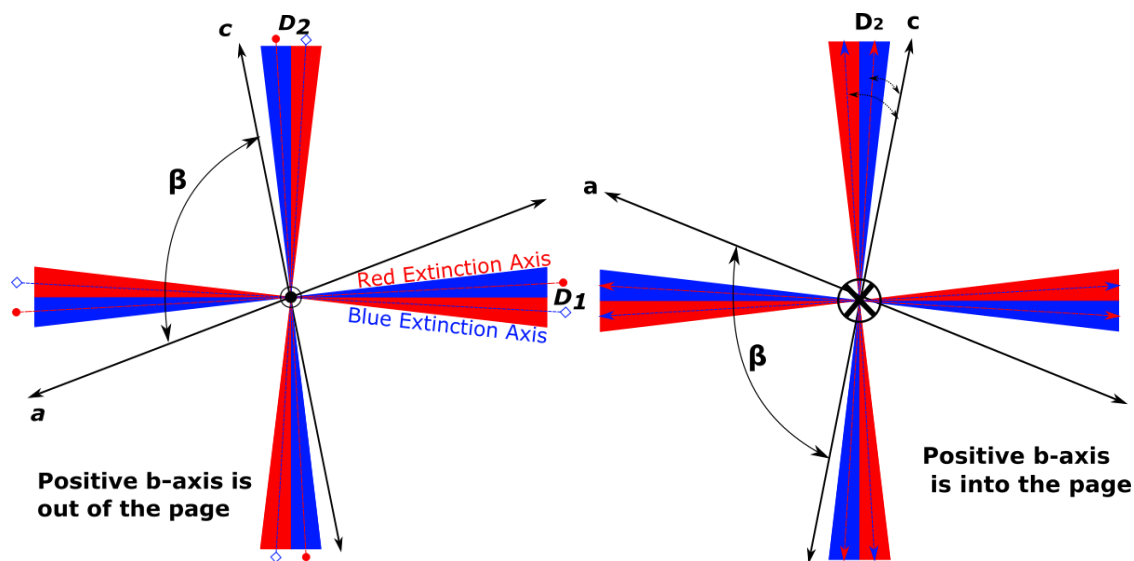


Figure 4.4. Diagrams showing the extremes of the transmitted color seen visually with the rotation of the crystal between crossed polarizers. The dielectric axes change as a function of wavelength relative to the crystal axes indicating the direction of the **b** axis.

Using a Conoscope to Locate and Identify the Axes

A conoscope is a high numerical aperture lens used with the polariscope, which can be used to locate and identify the dielectric axes. The conoscope converges the white light in the polariscope allowing the observer to see a range of optical paths through the crystal in one view.

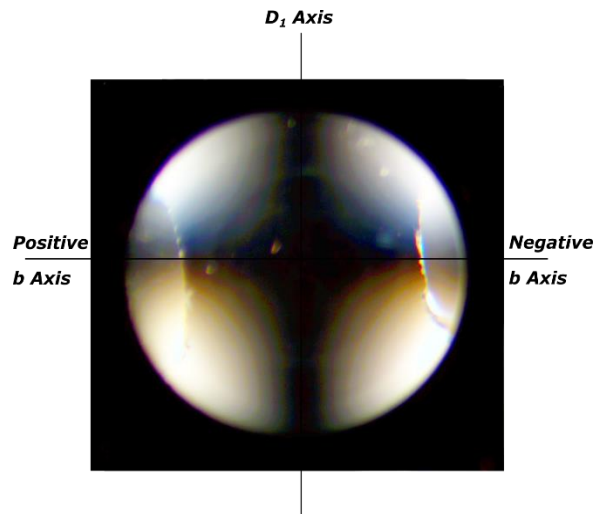


Figure 4.5 A photograph of YSO's birefringent pattern looking along the D_2 -axis using crossed polarizers and a conoscope. The horizontal b -axis and vertical D_1 -axis are aligned with the crossed polarizer axes. The blue and red fringes, parallel to and straddling the b -axis, show the rotation of the optical axis and plane. Note the sample shown has the crystal facets cut approximately 5 degrees off from the b and D_1 axes.

The extinction axes viewed with convergent light are known as isogyres. The isogyres are easiest to see when viewed along the D_2 axis, the acute bisectrix due to the proximity to the optical axes. When the crystal is rotated and viewed along the D_2 axis, curved extinction axes are seen until the b and D_1 axes are aligned with the crossed polarizer axes. The crossed isogyres indicate the alignment of all three dielectric axes relative to the sample faces, as in Figure 4.5. The red and blue light along the b -axis is known as horizontal dispersion and can be used to determine the direction of the b -axis. From this perspective, when blue is observed above the extinction axis and red light is lower on the axis, the positive b -axis points to the left. With a conoscope or polarizing microscope, all three extinction axes can be aligned and defined when the YSO sample is viewed along D_2 axis between crossed polarizers. Deviations in alignment of the crystal facets to the dielectric axes can also be determined easily using a conoscope. The

direction of the ***b***-axis is also unambiguously determined using the horizontal dispersion as a guide.

Biaxial Crystals: Monoclinic, Triclinic, and Orthorhombic Systems

The techniques shown in the case of YSO can immediately be applied to other monoclinic crystals, though some points need to be considered. If the symmetry axis is the acute bisectrix or the optical normal, the dispersion will respectively be crossed or inclined around the axis. The crystal's symmetry axes are easier to visually see if the rotation of the dielectric frame is strong. If the angle of rotation is small a polarizing microscope can be helpful, or a Malus measurement can be setup.

The principles of aligning monoclinic crystals can also be applied to other optically biaxial crystals. Each extinction axis is found by nulling the transmitted light in a polariscope or crossing isogyres. If the crystal is positive or negative biaxial, then the extinction axes may then be assigned to the crystal axes based on the relative magnitudes of their respective refractive indices by way of the acute and obtuse bisectrices.

In the triclinic crystal systems, each crystal axis will have a direction, as no crystal axis is orthogonal to the others. As a result, the optical indicatrix may freely scale in size, yaw, pitch, and roll as the frequency of light is varied. If the rotation of the dielectric frame of each axis can be observed a sense can be assigned to each axis by relating the rotation of color to the crystal's corresponding Laue pattern. Using the one direction of dielectric axis all the dielectric axes can be related to the crystal axes. The color pattern may be difficult to view or interpret in some cases as the rotation of the optical plane is unconstrained.

Orthorhombic systems have orthogonal crystal axes. Therefore, each dielectric axis is always collinear with a crystal axes, simplifying the relationships between the crystal structure and the optical indicatrix. In orthorhombic materials the optical indicatrix is fixed in place and does not pivot about any axis.

Uniaxial Crystals: Tetragonal, Trigonal, and Hexagonal Systems

The points covered in the case of biaxial materials also have relevance to the higher symmetry tetragonal, trigonal, and hexagonal crystal systems, which are optically uniaxial. Because there is only one unique refractive index the optical indicatrix will have rotational symmetry about the c -axis of uniaxial crystals. Extinction axes are visible when the c -axis is in the plane of the polarization axes of the polariscope. However, when the c -axis is perpendicular the polarizers, the material behaves isotropically. Only the alignment of the c -axis may be fully specified in a uniaxial crystal using a polariscope. The optically symmetric c -axis can have directionality, as in the case of LiNbO_3 [92], which can be distinguished using other thermal or electrical techniques [93] .

Isotropic Crystals: Cubic Systems

Cubic crystals have orthogonal and equal dielectric axes, therefore optically isotropic and do not possess extinction axes. However, some cubic systems and certain other point groups can show optical activity along specific crystal directions, which may be useful in determining directions in cubic crystals. For more information, the reader is referred elsewhere [93-97].

Conclusion

A simple optical technique using crossed polarizers is described to visually determine the optical orientation of birefringent crystals using the material's wavelength-dependent dielectric frame to quickly and accurately located the materials axes. YSO's crystal axes are related to optical dielectric indicatrix using Laue backscatter images to define the direction of the b-axis with respect to the $\mathbf{D}_1$ and $\mathbf{D}_2$ axes. With the relative orientation known between the optical indicatrix and the crystal axes, birefringent crystals can be completely oriented using crossed polarizers.

CHAPTER 5

ELECTRON SPIN COHERENCE IN OPTICALLY EXCITED STATES OF
RARE-EARTH IONS FOR MICROWAVE TO OPTICAL
QUANTUM TRANSDUCERS

Contribution of Authors and Co-Authors

Manuscript in Chapter 5

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Contributions: Prepared material samples, designed and set up experimental apparatus, performed measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

Co-Author: Philip J. T. Woodburn

Contributions: Prepared material samples, designed and set up experimental apparatus, performed measurements to acquire data, analyzed and interpreted results, generated figures, edited the manuscript.

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Contributions: Analyzed and interpreted results, wrote and edited the manuscript, discussed results and implications.

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Contributions: Prepared material samples, designed and set up experimental apparatus, performed measurements to acquire data, analyzed and interpreted results, generated figures, edited the manuscript.

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Electron Spin Coherence in Optically Excited States of Rare-Earth Ions for Microwave to Optical Quantum Transducers

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Efficient and reversible optical to microwave transducers are required for entanglement transfer between superconducting qubits and light in quantum networks. Rare-earth-doped crystals with narrow optical and spin transitions are a promising system for enabling these devices. Current resonant transduction approaches use ground-state electron spin transitions that have coherence lifetimes often limited by spin flip-flop processes and spectral diffusion, even at very low temperatures. We investigate spin coherence in an optically excited state of an $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ crystal at temperatures from 1.6 to 3.5 K for a low 8.7 mT magnetic field compatible with superconducting resonators. Spin coherence and population lifetimes of up to 1.6 μs and 1.2 ms, respectively, are measured by optically detected spin echo experiments. Analysis of decoherence processes suggest that ms coherence can be reached at lower temperatures for the excited-state spins, whereas ground-state spin coherence would be limited to a few μs due to resonant interactions with other Er^{3+} spins in the lattice and greater instantaneous spectral diffusion from the radio-frequency control pulses. We propose a quantum transducer scheme with potential for close to unity efficiency that exploits the advantages offered by spin states of the optically excited electronic energy levels.

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Rare-earth (RE)-doped crystals can exhibit long optical and spin coherence lifetimes at liquid helium temperatures that are promising for quantum technologies [1–3]. Long-lived quantum memories for light [4], entanglement storage [5], light-to-matter teleportation [6], and atomic-gas to crystal quantum state transfer [7] have all been demonstrated. These systems offer multimode storage [8,9] and high efficiency [10,11] with coherence lifetimes as long as hours [3], as well as the capability for signal processing of photonic quantum states [12]. Developments toward integrated and hybrid systems have also been reported using nanostructured materials [13,14], making RE-doped crystals a promising platform for solid-state quantum light-matter interfaces. RE ions with an odd number of electrons are particularly interesting since their strong magnetism allows efficient coupling to microwave photons. This could enable quantum-state transfer between superconducting qubits and light to build networks of quantum processors [15,16]. Strong coupling between superconducting resonators and RE ions has been demonstrated, and microwave to optical conversion has been investigated [17–20].

Using both optical and spin transitions requires strong coupling between light and microwaves. Ensembles of RE ions in crystals are generally employed to enhance the interaction with photons. While providing a number of advantages, ensembles also cause difficulties when

considering optical to spin coherence transfer and undesired effects from ion-ion interactions. The weak optical oscillator strengths also limit addressable bandwidths for π pulses to less than 100 MHz; however, optical inhomogeneous linewidths are usually ~ 1 GHz or larger [1], so that a majority of ions do not participate in the coherent excitation and are only “spectators.”

If a resonant transduction protocol, such as Ref. [16], requires coherence to be stored in a superposition of the ground-state electron spin states, two undesirable effects can occur that have not been previously considered. First, the excitation can be incoherently transferred by fast spin flip flops, or spin diffusion, to other spins in the lattice, including spectator spins, resulting in decoherence and loss of the stored quantum state [21,22]. Second, to mitigate effects of inhomogeneous broadening on the achievable coherence time, a dynamical decoupling sequence should be applied; however, this requires drive pulses with bandwidths comparable to the spin inhomogeneous linewidths, which will also excite spectator spins since there is no correlation between optical and spin frequencies within their respective inhomogeneous linewidths. Since high-bandwidth control pulses will drive a large number of spectator spins, they can cause decoherence by instantaneous spectral diffusion (ISD) from long-range spin-spin interactions [19,23,24]. This is particularly important for

paramagnetic RE ions since they exhibit significant spin-spin interactions even for concentrations as low as 10 ppm [25]. Consequently, this source of decoherence often cannot be eliminated by reducing ion concentration without also reducing optical absorption and limiting device efficiency.

We propose to circumvent these limitations of resonant transduction approaches by using spin transitions for optically excited electronic states. Because excited ions' spins are not resonant with the larger number of spectator spins, decoherence due to flip-flop processes are significantly reduced. Furthermore, only optically excited spins are resonant with the microwave fields, avoiding excitation of spectator spins by control pulses and reducing ISD to the lowest possible extent. While this scheme is limited by the excited-state population lifetime $T_{1,\text{opt}}$, this can be longer than ms for RE ions, meeting the requirements for microwave-optical transduction protocols. A particularly favorable ion is erbium with typical excited-state lifetimes of ~ 10 ms for the $^4I_{13/2}$ level [26]. This $1.5\ \mu\text{m}$ telecom wavelength transition has attracted strong interest for building fiber-based quantum networks and transducers [18,20,27]. Here, we investigate electron spin coherence in the excited state of an Er^{3+} -doped Y_2SiO_5 crystal and observe excited-state electron spin echoes for RE ions. We also present an excited-state transduction protocol that can approach unity efficiency.

The work here focuses on the effects of spin flip flops on spin coherence, spin-state lifetimes, and efficiency of resonant transduction approaches such as proposed by O'Brien *et al.* [16]. While off-resonance transduction schemes, as proposed by Williamson *et al.* [15], are not directly affected by optical or spin coherence lifetimes, they can still be affected by spin flip flops if spectral diffusion becomes comparable to the spin inhomogeneous broadening or if spin-state lifetimes become comparable to the microwave or optical cavity lifetimes. The existing theory for the off-resonant approach assumes that spin states and transition frequencies are fixed for all ions in the ensemble during the timescale of the transduction process to obtain analytical solutions for the transduction efficiency [15]. Hence, the effect of spin flip flops cannot be analyzed within the existing theory beyond a general observation that fluctuating spin states and frequencies will act to reduce transduction efficiency. It is not possible to say whether the effects are significant for practical conditions without expanding the theory to include spin dynamics.

Coherent Raman heterodyne scattering (RHS) [28] experiments were performed for the three-level schemes shown in Fig. 1. This method employs a radio-frequency (rf) field resonant with Zeeman transition $|1\rangle \leftrightarrow |2\rangle$ or $|3\rangle \leftrightarrow |4\rangle$ to create a ground- or excited-state electron spin coherence [Fig. 1(a)]. A resonant laser beam drives the optical transition $|1\rangle \leftrightarrow |3\rangle$ or $|1\rangle \leftrightarrow |4\rangle$. The combined optical and rf coherences then induce coherence on the

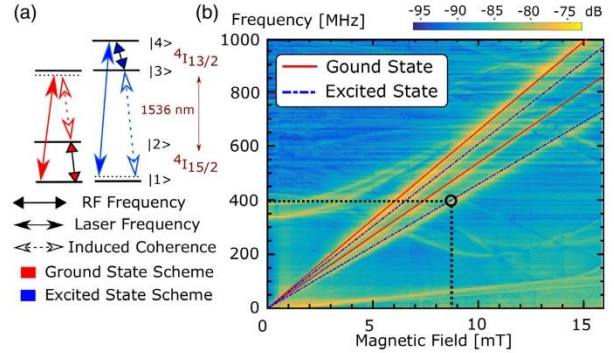


FIG. 1. (a) Energy levels of Er^{3+} and RHS schemes for ground- and excited-state spin coherence studies ($|1\rangle \leftrightarrow |2\rangle$ and $|3\rangle \leftrightarrow |4\rangle$ are electron spin transitions). (b) The RHS measurements at 3 K on Er^{3+} at site 1 of Y_2SiO_5 . Lines: fitted Zeeman transition frequencies for zero-nuclear-spin Er^{3+} isotopes. Black circle and dashed lines: spin echo experimental condition.

other optical transition $|2\rangle \leftrightarrow |3\rangle$ or $|1\rangle \leftrightarrow |3\rangle$ that then interferes with the laser field, producing a beat note at the $|1\rangle \leftrightarrow |2\rangle$ or $|3\rangle \leftrightarrow |4\rangle$ frequencies that is detected using a photodiode.

A 50 ppm Er^{3+} -doped Y_2SiO_5 sample grown by Scientific Materials Corp. was cut along the three dielectric axes: b , D_1 , D_2 [29] and mounted in an Oxford Optistat helium cryostat with a magnetic field applied along D_1 using a Helmholtz coil. Er^{3+} can substitute for Y^{3+} at two inequivalent crystallographic sites (denoted 1 and 2). An external-cavity diode laser was set at 1536.49 nm (vacuum) in resonance with the transition between the lowest levels of the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets for ions at site 1 [26]. The laser was amplified and then focused into the crystal with propagation along the b axis and polarization along the D_2 axis. The laser produced nearly equal populations in the ground and excited states over ~ 1 MHz bandwidth. Optical pumping also induced population differences within the ground- and excited-state Zeeman sublevels necessary to detect spin coherence with RHS. Transmitted light was detected by a 1 GHz ac-coupled photoreceiver. The rf pulses with magnetic field amplitudes of several Gauss were applied along b through an rf strip waveguide next to the crystal surface.

Figure 1(b) shows RHS spectra for frequencies up to 1 GHz as a function of magnetic field strength. In these experiments, an rf spectrum analyzer generated the rf excitation and analyzed the photoreceiver signal (see the Supplemental Material [30]). The four lines observed in Fig. 1(b) correspond to electron-spin transitions for the ground and excited states of Er^{3+} isotopes with zero nuclear spin, deduced from the magnetic field direction and known $\mathbf{g}$ tensors [37,38]. Two transitions are observed for each state since the magnetic field was not exactly parallel to D_1 , resulting in two inequivalent subgroups for each site. The corresponding effective ground-state

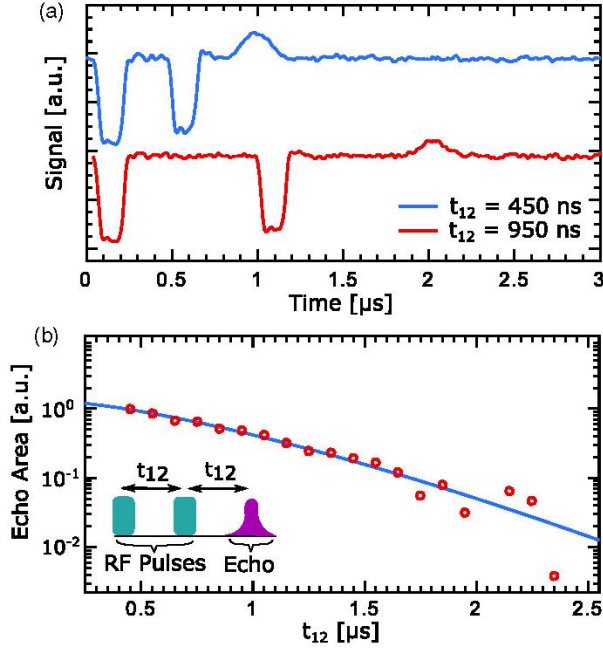


FIG. 2. (a) Optically detected electron spin echoes in the $^4I_{13/2}$ excited state for different pulse delays with $T = 1.9$ K and $B = 8.7$ mT. (b) Measurement (circles) and fit (line) of echo decay at 1.9 K, giving $T_2 = 1.6 \pm 0.2$ μ s and $x = 1.4 \pm 0.2$. Inset: rf pulse sequence.

values g_g are 4.75 and $3.85 (\pm 0.3)$, and the excited-state values g_e are 4.35 and $3.27 (\pm 0.3)$, depicted in Fig. 1(b). All spin transitions exhibited linewidths of ~ 10 MHz, similar to those previously reported [20,37]. The linewidths did not vary significantly with magnetic field strength, indicating that the spin-transition broadening does not arise from inhomogeneity in the $\mathbf{g}$ tensors or the field. Weaker transitions with complex field dependence are also visible in Fig. 1(b) and are attributed to hyperfine transitions of the $^{167}\text{Er}^{3+}$ isotope ($I = 7/2$, abundance 22.9%).

Excited-state spin echoes were measured using rf pulses generated by a gated source. The photoreceiver signal was amplified, filtered, and down mixed with a local oscillator (see the Supplemental Material [30]). A dc magnetic field of 8.7 mT was applied along the same orientation as in the cw experiments, and a frequency of 400 MHz was used to study the excited-state transition [Figs. 1(a) and 1(b)] for temperatures from 1.6 to 3.5 K.

The two-pulse echo signal is shown in Fig. 2(a) for two different delays between excitation pulses. Pulse lengths of 150 ns maximized the echo signal. Detected echoes had a π phase shift relative to the excitation pulses, confirming that the entire sequence was phase coherent. The cw laser excitation created a large excited-state population that produced strong echo signals. The integrated echo signal decay was measured as a function of the delay between the pulses [Fig. 2(b)] and fitted with a Mims function [39]

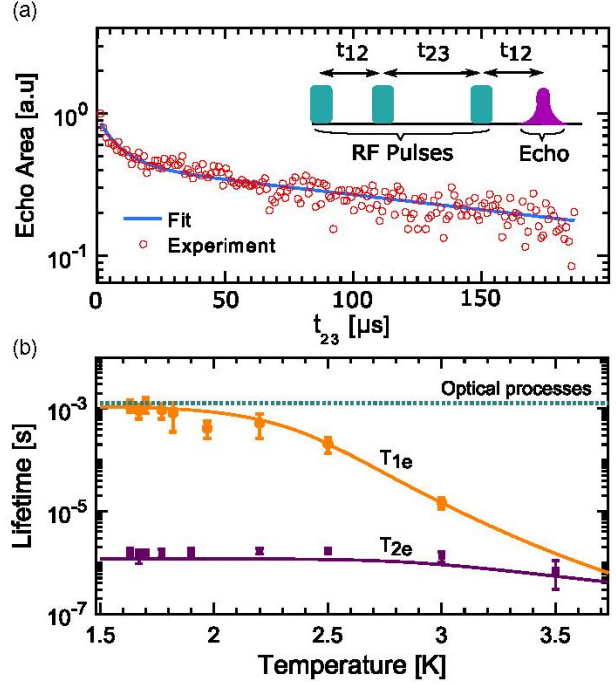


FIG. 3. (a) Excited-state stimulated spin echo decay measured at 2.5 K (circles) and fit to the spectral diffusion model (line, see text). Inset: rf pulse sequence. (b) Experimental coherence (squares) and population lifetimes (circles) as a function of temperature. Dotted line: population lifetime deduced from the sum of optical emission and excitation rates; solid lines: calculated and fitted curves (see text).

$$A(t_{12}) = A \exp[-(2t_{12}/T_{2e})^x], \quad (1)$$

where T_{2e} is the $1/e$ coherence lifetime and t_{12} is the delay between pulses. The extracted T_{2e} at 1.9 K was 1.6 ± 0.2 μ s (200 kHz homogeneous linewidth), with $x = 1.4 \pm 0.2$. The nonexponential behavior arises from spectral diffusion [39] attributed to interactions with Er^{3+} spins in the lattice. The effect of ^{89}Y nuclear spins is expected to be much weaker because of their small magnetic moment and slow flip rates [21].

To probe the decoherence mechanisms, we measured three-pulse stimulated spin echoes using the pulse sequence shown in Fig. 3(a). Stimulated echo measurements allow spin relaxation and spectral diffusion dynamics to be studied over the timescale of T_1 , whereas two-pulse echoes are limited to the much shorter T_2 timescale [21,39]. We measured three-pulse echo decays as a function of t_{23} , with t_{12} fixed at 0.3 μ s, as shown in Fig. 3(a). The initial fast decay is from spectral diffusion while the slower decay results from population relaxation.

Both two- and three-pulse echoes can be modeled by a time-dependent effective homogeneous linewidth Γ_{eff} [21] and echo amplitude

$$A(t_{12}, t_{23}) = A_0 e^{(-t_{23}/T_{1e})} e^{[-2t_{12}\pi\Gamma_{\text{eff}}(t_{12}, t_{23})]}, \quad (2)$$

where T_{1e} corresponds to the population relaxation time. Contributions to Γ_{eff} arise from ground-state Er^{3+} spins at both sites in the lattice. Because of the narrow optical excitation bandwidth, the excited-state ion concentration is $\sim 10^3$ times lower than the ground-state concentration and can be neglected. For our conditions, site 2 spins rapidly relax by mutual spin flip-flop processes (spin diffusion) due to their large ground state effective g factor of 14. A simple theoretical estimate (see the Supplemental Material [30]) shows that this causes decoherence over sub- μs timescales, resulting in a width Γ_0 that is independent of t_{23} and t_{12} . Er^{3+} spins in site 1 have a g factor of 4, and their flip-flop rate R_{ff} is roughly $(14/4)^4 = 150$ times smaller than that of site 2 spins. This slower relaxation produces a spectral diffusion of Γ_{eff} given by Ref. [21]

$$\Gamma_{\text{eff}}(t_{12}, t_{23}) = \Gamma_0 + \frac{1}{2}\Gamma_{\text{SD}}(Rt_{12} + 1 - e^{-Rt_{23}}), \quad (3)$$

where R is the site 1 spin relaxation rate and Γ_{SD} is the distribution of interaction strengths between resonant spins and other site 1 spins in the environment.

The two- and three-pulse echo decays were recorded between 1.6 and 3.5 K and fitted to Eqs. (2) and (3) using a rate R including a two-phonon Orbach term combined with the flip-flop rate R_{ff} for site 1. An example fitted curve is shown in Fig. 3(a) for $T = 2.5$ K. The fits gave values of $\Gamma_0 = 2.7 \times 10^5$ Hz, $\Gamma_{\text{SD}} = 4.3 \times 10^5$ Hz, $R_{\text{ff}} = 2.1 \times 10^4$ s $^{-1}$, which compare well with theoretical calculations (see the Supplemental Material [30]). Reasonable agreement was also found between two-pulse echo T_{2e} values fitted to experimental data using Eq. (1) and those calculated from the fit parameters [see Fig. 3(b)]. T_{1e} values were determined from the fits and were explained by the sum of optical excitation and emission rates combined with an Orbach process (see Fig. 3(b) and the Supplemental Material [30]). At the lowest temperatures, T_{1e} reached 1.2 ms, limited by optical stimulated emission due to continuous excitation by the laser. In a pulsed configuration without laser excitation during the echo sequence, T_{1e} would increase to $T_{1,\text{opt}} = 8$ ms [40].

For our conditions, T_{2e} is limited by decoherence from relaxation of ground-state spins. This decoherence would be reduced at lower temperatures since the Orbach contribution rapidly decreases as $\exp(-\Delta_g/T)$, while flip-flop rates decrease as $[\text{sech}(g_g\mu_B B/2kT)]^2$, where k is the Boltzmann factor. For example, consider a weak field of 50 mT that is compatible with superconducting resonators and where the excited-state splitting is ~ 2 GHz, in the range of typical microwave photons. At a temperature of 20 mK, decoherence only results from site 1 ground-state spin flip-flops because site 2 spins, with their large g factor, are completely polarized. The site 1 flip-flop rate R_{ff} would

be reduced by a factor of ~ 350 compared to 2 K. Together, these effects would increase the excited-state spin coherence lifetime to $T_{2e} \approx 2.9$ ms (see the Supplemental Material [30]). This is likely to approach the decoherence limit due to ^{89}Y spin flips [21]. In contrast, even at very low temperatures, site 1 ground-state excitations will experience rapid decoherence through the flip-flop process due to the large number of other resonant spins present in the lattice. In fact, spins excited into the higher energy spin state will have an increasing number of neighbors in the lower energy spin state to flip-flop with as the temperature is decreased, accelerating decoherence to as much as twice the high-temperature rate. For our system, this effect limits T_{2g} to less than 48 μs even at the lowest temperatures (see the Supplemental Material [30]). Moreover, a rephasing control pulse applied over the entire spin linewidth would cause strong ISD, further reducing T_{2g} to ~ 1 μs , independent of temperature. This effect can explain why we did not observe any ground-state spin echo for the conditions used in the excited-state measurements, as well as why long electron-spin coherence times have been difficult to achieve with ground-state spin transduction protocols. For example, our analysis is in qualitative agreement with the ground-state site 2 coherence lifetime of 5.6 μs observed at 30 mK with a different magnetic field orientation [20].

Finally, we outline an excited-state scheme for optical to microwave transduction. Previous proposals used the ground-state spin by coupling it off-resonantly [15] or resonantly [16] to a microwave cavity. One limiting factor for efficient conversion in [16] is the short coherence lifetime compared to the coupling strength.

To employ the excited state for transduction, the protocol from Ref. [16] can be modified as follows. The first step is the same as in Ref. [16]; we prepare a narrow spectral feature and then apply a magnetic field gradient to produce an inhomogeneously broadened feature. An incoming optical photon is then absorbed on the $|1\rangle \rightarrow |4\rangle$ transition. The induced inhomogeneous broadening and free evolution of the system cause dephasing of the optical coherence, preventing re-emission and ensuring that the optical photon is stored. In the next step, a series of π pulses are applied on the $|1\rangle \rightarrow |3\rangle$ transition. This is different from the original protocol, where the π pulses were applied on the $|2\rangle \rightarrow |4\rangle$ transition. The first π pulse brings the population from state $|1\rangle$ to $|3\rangle$ and subsequent free evolution further dephases the system due to the spin inhomogeneous broadening, but at a possibly different rate. After a delay, we apply a second π pulse to bring population back into $|1\rangle$, while simultaneously reversing the field gradient to begin the rephasing procedure. Since spontaneously emitted photons will have a different frequency than converted photons, inverting the population on the optical transition does not introduce photon noise at the converted frequency. Once dephasing due to inhomogeneous broadening of the excited state is compensated, we apply another π pulse, moving population

to state $|3\rangle$ to complete the rephasing. This procedure compensates for dynamical phases induced by the field gradient. To further compensate for dephasing due to intrinsic spin inhomogeneous broadening, a sequence of dynamical decoupling microwave pulses could be applied on the $|3\rangle$ – $|4\rangle$ transition. After successful rephasing, the system is in a state that strongly couples to a microwave cavity due to collective enhancement of the coupling strength, allowing for efficient transfer of the matter excitation to a microwave photon. Assuming the same spin-cavity coupling strength of $v/2\pi = 34$ MHz as in Ref. [20], which is justified since the principal values of the magnetic g tensors for the $^4I_{15/2}$ and $^4I_{13/2}$ states in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ are roughly the same [38], and using our measured spin coherence lifetime of $T_{2e} = 1.6$ μs , we can estimate the transfer efficiency of the spin excitation to a microwave photon to be $\eta \approx \exp(-\pi/2/T_{2e}v) \approx 99\%$. To obtain the overall conversion efficiency, we must combine this with the efficiency of mapping the optical photon to the spin excitation, which can be highly efficient provided a large optical depth [41] (for quantitative analysis of the effect of optical density on efficiency, see Ref. [42]); however, we note that in an actual experiment, other implementation factors, such as imperfections in optical pumping or π pulses, might cause diminishing increases in efficiency.

A further advantage of using excited-state spin transitions is that only ions in the laser beam cross section interact with the microwave cavity, making spatial hole burning, as required in the original protocol, unnecessary. Also, reversing the protocol allows conversion of a microwave photon to a propagating telecom photon. Moreover, the optical photon's bandwidth can be tuned, as in the original protocol, by controlling the strength of the field gradient.

In conclusion, we observed electron spin echoes in the optically excited state of an erbium-doped crystal. Coherence lifetimes of up to 1.6 μs were recorded for a field of 8.7 mT at 1.9 K, and analysis of the decoherence processes suggest that ms lifetimes should be reached under conditions used for superconducting qubits. We propose a scheme to exploit these long coherence lifetimes for reversible optical to microwave conversion, with our analysis predicting near unity conversion efficiency. Overall, using excited-state spin transitions opens a new and attractive way to coherently interface RE ensembles with microwave cavities and may stimulate new proposals for transducer devices.

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Note added.—A related experiment using hyperfine states of $^{167}\text{Er}^{3+}$ has been performed in parallel [43].

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- [1] C. W. Thiel, T. Böttger, and R. L. Cone, *J. Lumin.* **131**, 353 (2011).
 - [2] P. Goldner, A. Ferrier, and O. Guillot-Noël, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by J.-C. G. Bünzli and V. K. Pecharsky (Elsevier, Amsterdam, 2015), Vol. 46, pp. 1–78.
 - [3] M. Zhong, M. P. Hedges, R. L. Ahlefeldt, J. G. Bartholomew, S. E. Beavan, S. M. Wittig, J. J. Longdell, and M. J. Sellars, *Nature (London)* **517**, 177 (2015).
 - [4] C. Laplane, P. Jobez, J. Etesse, N. Gisin, and M. Afzelius, *Phys. Rev. Lett.* **118**, 210501 (2017).
 - [5] C. Clausen, I. Usmani, F. Bussi eres, N. Sangouard, M. Afzelius, H. de Riedmatten, and N. Gisin, *Nature (London)* **469**, 508 (2011).
 - [6] F. Bussi eres, C. Clausen, A. Tiranov, B. Korzh, V. B. Verma, S. W. Nam, F. Marsili, A. Ferrier, P. Goldner, H. Herrmann, C. Silberhorn, W. Sohler, M. Afzelius, and N. Gisin, *Nat. Photonics* **8**, 775 (2014).
 - [7] N. Maring, P. Farrera, K. Kutluer, M. Mazzer, G. Heinze, and H. de Riedmatten, *Nature (London)* **551**, 485 (2017).
 - [8] M. Bonarota, J.-L. Le Gou et, and T. Chaneli ere, *New J. Phys.* **13**, 013013 (2011).
 - [9] N. Sinclair, E. Saglamyurek, H. Mallahzadeh, J. A. Slater, M. George, R. Ricken, M. P. Hedges, D. Oblak, C. Simon, W. Sohler, and W. Tittel, *Phys. Rev. Lett.* **113**, 053603 (2014).
 - [10] M. P. Hedges, J. J. Longdell, Y. Li, and M. J. Sellars, *Nature (London)* **465**, 1052 (2010).
 - [11] M. Sabooni, Q. Li, S. Kr oll, and L. Rippe, *Phys. Rev. Lett.* **110**, 133604 (2013).
 - [12] E. Saglamyurek, N. Sinclair, J. A. Slater, K. Heshami, D. Oblak, and W. Tittel, *New J. Phys.* **16**, 065019 (2014).
 - [13] J. G. Bartholomew, K. de Oliveira Lima, A. Ferrier, and P. Goldner, *Nano Lett.* **17**, 778 (2017).
 - [14] T. Zhong, J. M. Kindem, J. G. Bartholomew, J. Rochman, I. Craiciu, E. Miyazono, M. Bettinelli, E. Cavalli, V. Verma, S. W. Nam, F. Marsili, M. D. Shaw, A. D. Beyer, and A. Faraon, *Science* **357**, 1392 (2017).
 - [15] L. A. Williamson, Y. H. Chen, and J. J. Longdell, *Phys. Rev. Lett.* **113**, 203601 (2014).
 - [16] C. O'Brien, N. Lauk, S. Blum, G. Morigi, and M. Fleischhauer, *Phys. Rev. Lett.* **113**, 063603 (2014).
 - [17] X. Fernandez-Gonzalvo, Y. H. Chen, C. Yin, S. Rogge, and J. J. Longdell, *Phys. Rev. A* **92**, 062313 (2015).
 - [18] Y. H. Chen, X. Fernandez-Gonzalvo, and J. J. Longdell, *Phys. Rev. B* **94**, 075117 (2016).
 - [19] S. Probst, H. Rotzinger, A. V. Ustinov, and P. A. Bushev, *Phys. Rev. B* **92**, 014421 (2015).
 - [20] S. Probst, H. Rotzinger, S. W unsch, P. Jung, M. Jerger, M. Siegel, A. V. Ustinov, and P. A. Bushev, *Phys. Rev. Lett.* **110**, 157001 (2013).

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- [21] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, *Phys. Rev. B* **73**, 075101 (2006).
 - [22] E. Z. Cruzeiro, A. Tiranov, I. Usmani, C. Laplane, J. Lavoie, A. Ferrier, P. Goldner, N. Gisin, and M. Afzelius, *Phys. Rev. B* **95**, 205119 (2017).
 - [23] B. Herzog and E. L. Hahn, *Phys. Rev.* **103**, 148 (1956).
 - [24] C. W. Thiel, R. M. Macfarlane, Y. Sun, T. Böttger, N. Sinclair, W. Tittel, and R. L. Cone, *Laser Phys.* **24**, 106002 (2014).
 - [25] E. Zambrini Cruzeiro, A. Tiranov, J. Lavoie, A. Ferrier, P. Goldner, N. Gisin, and M. Afzelius, *New J. Phys.* **20**, 053013 (2018).
 - [26] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, *Phys. Rev. B* **74**, 075107 (2006).
 - [27] E. Saglamyurek, T. Lutz, L. Veissier, M. P. Hedges, C. W. Thiel, R. L. Cone, and W. Tittel, *Nat. Photonics* **9**, 83 (2015).
 - [28] J. Mlynek, N. C. Wong, R. G. DeVoe, E. S. Kintzer, and R. G. Brewer, *Phys. Rev. Lett.* **50**, 993 (1983).
 - [29] C. Li, C. Wyon, and R. Moncorgé, *IEEE J. Quantum Electron.* **28**, 1209 (1992).
 - [30] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.122.247401> for further details on experimental conditions and apparatus, additional spin echo data and theoretical models, which also includes Refs. [31–36].
 - [31] R. C. Hilborn, *Am. J. Phys.* **50**, 982 (1982).
 - [32] B. A. Young and H. J. Stapleton, *Phys. Lett.* **21**, 498 (1966).
 - [33] G. Wolfowicz, H. Maier-Flaig, R. Marino, A. Ferrier, H. Vezin, J. J. L. Morton, and P. Goldner, *Phys. Rev. Lett.* **114**, 170503 (2015).
 - [34] T. Böttger, C. W. Thiel, R. L. Cone, Y. Sun, and A. Faraon, *Phys. Rev. B* **94**, 045134 (2016).
 - [35] H.-J. Lim, S. Welinski, A. Ferrier, P. Goldner, and J. J. L. Morton, *Phys. Rev. B* **97**, 064409 (2018).
 - [36] R. M. Macfarlane, R. Wannemacher, D. Boye, Y. P. Wang, and R. S. Meltzer, *J. Lumin.* **48–49**, 313 (1991).
 - [37] O. Guillot-Noël, P. Goldner, Y. L. Du, E. Baldit, P. Monnier, and K. Bencheikh, *Phys. Rev. B* **74**, 214409 (2006).
 - [38] Y. Sun, T. Böttger, C. W. Thiel, and R. L. Cone, *Phys. Rev. B* **77**, 085124 (2008).
 - [39] W. Mims, *Phys. Rev.* **168**, 370 (1968).
 - [40] C. W. Thiel, W. R. Babbitt, and R. L. Cone, *Phys. Rev. B* **85**, 174302 (2012).
 - [41] B. Kraus, W. Tittel, N. Gisin, M. Nilsson, S. Kröll, and J. I. Cirac, *Phys. Rev. A* **73**, 020302(R) (2006).
 - [42] N. Sangouard, C. Simon, M. Afzelius, and N. Gisin, *Phys. Rev. A* **75**, 032327 (2007).
 - [43] J. V. Rakonjac, Y.-H. Chen, S. P. Horvath, and J. J. Longdell, *arXiv:1802.03862*.

**Electron Spin Coherence in Optically Excited States of
Rare-Earth Ions for Microwave to Optical Quantum Transducers
Supplementary Material**

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EXPERIMENTAL METHODS

The experimental arrangement for our RHS measurements is depicted in Fig. 1A. A New Focus Velocity external-cavity diode laser set at a vacuum wavelength of $\lambda = 1536.49$ nm and amplified with an ILX Lightwave LDC-3724B erbium-doped fiber amplifier was sent through the crystal's b axis (3.9 mm length) with $\mathbf{E}$ parallel to D_2 . The laser linewidth was estimated to be $\Delta\nu = 1$ MHz over ms timescales. The crystal was a 0.005 atomic percent (50 ppm) $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ (YSO) crystal (No. 6-429) grown by Scientific Material Corp. / FLIR (Bozeman, MT) with an optical inhomogeneous linewidth of $\Gamma_{inh,opt} = 390$ MHz and peak absorption of $\alpha_0 = 8.1 \text{ cm}^{-1}$ for $E \parallel D_2$ [1]. The sample was mounted in an Oxford Optistat helium bath cryostat and cooled down to 3 K. The laser beam was focused with a 150 mm focal length lens into the sample to a waist of $\omega_0 = 90 \text{ }\mu\text{m}$ with a power of $P = 15$ mW at the sample. Another lens of the same focal length was placed 150 mm after the sample to re-collimate the beam. A static magnetic field $\mathbf{B}$ created by an external Helmholtz coil was applied parallel to the D_1 axis of the crystal. The sample was mounted onto a $50 \text{ }\Omega$ impedance-matched copper strip waveguide through which the RF power passed, producing an RF excitation with an amplitude of several Gauss along the b axis of the crystal (see Fig. 1C and 1D). The RF transmission line was terminated by a $50 \text{ }\Omega$ impedance load outside of the cryostat to prevent back-reflection. The optical detection after the sample was made by an amplified AC-coupled photodiode (New Focus model 1611-AC) with 1 GHz bandwidth and the acquired signal was sent to a spectrum analyzer to measure the Raman beat amplitude. An HP model E4411B spectrum analyzer with integrated RF tracking generator produced an RF signal of -10 dBm between 9 kHz - 1.0 GHz that was used for the CW RHS, as seen in Fig. 1A. The corresponding effective g of the four straight lines visible on Fig. 1B (4.75 and 3.85 ± 0.3 corresponding to the ground state, and 4.35 and 3.27 ± 0.3 to the excited state) allow us to determine the exact direction of the magnetic field with respect to the b, D_1, D_2 crystal frame: $\theta = 86.91 \pm 0.01^\circ$ and $\phi = 7.0 \pm 0.2^\circ$ (using the Euler angle convention define in [2]).

The experimental set-up for the RHS spin echo measurement (Fig. 1B) used the same sample holder and optical set-up as the CW RHS measurements. The sample was held in a superfluid liquid He bath for temperatures below 2.1 K and in a constant flow of He exchange gas for higher temperatures. The RF signal was generated by a high-stability

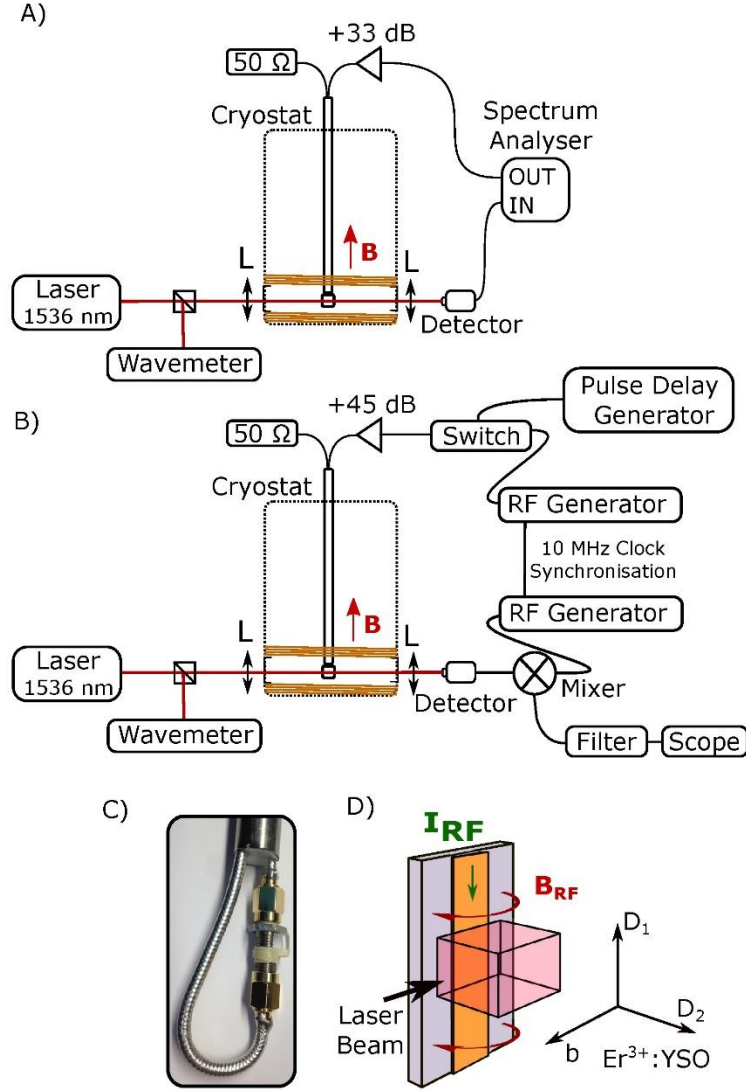


FIG. 1. Experimental set-up of A) the CW RHS and B) RHS spin echo measurements. C) Picture and D) diagram of the sample holder in the cryostat.

frequency synthesizer (Precision Test Sources PTS-500). To generate pulses, an RF TTL switch (Mini-circuits ZASWA-2-50-DR+) was used and triggered by a pulse delay generator (Stanford Research Systems DG-645) that was phase locked to the 10 MHz clock of the frequency synthesizer. We used a +45 dB amplifier (Mini-circuits ZHL-5W-1) to increase the RF power before sending it into the cryostat. The signal detected by the photodiode was band-pass filtered (using Mini-circuits SHP-400 and SLP-450) and then down mixed (using a Mini-circuits ZLW-2) with a local oscillator (LO) from a second synthesizer (PTS-500) that was phase locked to the 10 MHz clock of the first one. The LO signal was passed through a variable RF phase shifter (Merrimac PSM-3-500B) before the mixer to compensate for differential delays in the system. The down-mixed DC signal was sent through a low-pass filter (Mini-circuits BLP-1.9) and then digitized by an oscilloscope (Tektronix TDS-754C).

OPTICALLY PUMPED EXCITED-STATE POPULATION

For the spin echo measurements, the laser was continuously sent through the sample, producing a large excited-state population. Over the timescale of the absorption and emission process, we expect the laser linewidth to be much broader than the optical homogeneous linewidth Γ_h of individual Er^{3+} ions in the crystal. Consequently, the absorption of the laser spectrum that overlaps each ion's resonance is described by the integrated absorption and emission cross section σ_0 [3], which can be calculated from the material properties presented earlier according to

$$\sigma_0 = \frac{\pi \Gamma_{inh,opt} \alpha_0}{2N} = 1.1 \times 10^{-8} \text{ cm}^2\text{Hz}. \quad (1)$$

The peak laser intensity within the sample is given by

$$I_p = \frac{2P}{\pi \omega_0^2}, \quad (2)$$

allowing us to calculate the equilibrium excited-state population n_e for the case of $\Gamma_h \ll \Delta\nu$ to be

$$n_e = \left(2 + \frac{h\nu \Delta\nu}{\sigma_0 I_p T_{1,opt}}\right)^{-1} = 0.5. \quad (3)$$

Thus, we expect equal Er^{3+} populations in the ground and excited state over the ~ 1 MHz bandwidth of the laser, but considering the much larger optical inhomogeneous linewidth of 390 MHz, overall there will still be a factor of ~ 800 greater total Er^{3+} population in the ground state than in the optical excited state.

Due to the strong optical pumping, once an Er^{3+} ion is in its excited state it will be driven back to the ground state by stimulated emission; however, the RF pulses applied during the spin echo sequence will transfer half of the Er^{3+} ions to their opposite spin state so that their optical resonance will be shifted by the difference Δ_Z between the Zeeman shifts of the ground and excited state spins given by

$$\Delta_Z = \pm \frac{|g_g - g_e| \mu_B B}{h}, \quad (4)$$

which is 71 MHz for our conditions. Since this shift is much larger than the laser linewidth $\Delta\nu$, after the RF excitation pulses are applied only the fraction of Er^{3+} ions remaining in their original spin state will be removed from the echo process by stimulated emission, reducing the spin echo amplitude by a factor two. The remaining spins relax to the ground state due to the optical spontaneous emission lifetime $T_{1,opt}$; however, if the laser light is sufficiently intense, stimulated emission can still occur due to the weak tails of the laser excitation spectrum at Δ_Z , resulting in an increased relaxation rate. If we assume a Lorentzian lineshape for the laser spectrum, the optical intensity I_Δ at Δ_Z is related to the peak intensity I_p according to

$$I_\Delta = \frac{\Delta\nu^2}{4\Delta_Z^2 + \Delta\nu^2} I_p, \quad (5)$$

resulting in a relaxation rate due to stimulated emission of

$$R_s = \frac{\sigma_0 I_\Delta}{h\nu \Delta\nu} = 540 \text{ s}^{-1}. \quad (6)$$

Together with spontaneous emission, this contributes a total spin relaxation rate of

$$R_{opt} = R_s + 1/T_{1,opt} \quad (7)$$

to the observed excited-state spin lifetime. For our conditions, this effect limits the observed lifetime to $T_{1e} < 1.5$ ms. This corresponds well with the plateau of $T_{1e} = 1.2$ ms for $T < 2$ K that we observe in our measurements (see Fig. 3B in main text).

SPIN ECHO DECAY MODELING

To study spectral diffusion and the different contributions to decoherence of the excited-state spin transition $|3\rangle \leftrightarrow |4\rangle$, we analyzed the 2- and 3-pulse echo results using the following procedure. First, the tails of the 3-pulse echo decays were fitted with an exponential decay

TABLE I. Decoherence model fit parameters.

Γ_0	Γ_{SD}	R_{ff}	$\alpha_{O,g}$	Δ_g
2.7×10^5 Hz	4.3×10^5 Hz	2.1×10^4 s $^{-1}$	50×10^{10} Hz	40 K

to determine the $|3\rangle \leftrightarrow |4\rangle$ spin-state lifetimes T_{1e} , with example results shown in Fig. 3 B). Next, all of the 3- and 2-pulse echo decays were fitted together using the model

$$I(t_{23}) = I_{3p} e^{(-\frac{t_{23}}{T_{1e}})} e^{(-2t_{12}\pi(\Gamma_0 + \frac{1}{2}\Gamma_{SD}[Rt_{12} + 1 - e^{-Rt_{23}}]))}, \quad (8)$$

with $t_{12} = 0.3 \mu\text{s}$ being a fixed delay for our 3-pulse decay measurements, and the dependence simplifying to

$$I(t_{12}) = I_{2p} e^{(-2t_{12}\pi(\Gamma_0 + \frac{1}{2}\Gamma_{SD}Rt_{12}))} \quad (9)$$

for 2-pulse decays where $t_{23} = 0 \mu\text{s}$.

The width Γ_0 represents decoherence caused by spin flips of Er^{3+} at site 2 that occur over timescales faster than the shortest times probed in our measurements (sub- μs). The width Γ_{SD} represents the magnitude of spectral diffusion caused by spin flips of Er^{3+} at site 1. The total spin-flip rate R for Er^{3+} spins at site 1 is composed of a spin flip-flop contribution R_{ff} that is independent of temperature for our conditions and a two-phonon Orbach relaxation component $R_{O,g} = \alpha_{O,g}/[e^{(\frac{\Delta_g}{T})} - 1]$ that depends strongly on temperature. Δ_g is the energy of the next crystal level above the ground state (in Kelvin) and $\alpha_{O,g}$ is the coupling strength. The two-phonon Raman and one-phonon direct terms are both negligible for our conditions. Example fit results for 3-pulse and 2-pulse decay measurements are presented in Fig. 3A and 3B, respectively, and the extracted parameters are given in Table I. The crystal field level splitting Δ_g of 57 K [1] is larger than the fitted value. However, it is known that this parameter is often observed to be significantly lower than expected due to approximations inherent in the simple exponential form of the temperature dependence [4–7].

ESTIMATION OF RELAXATION AND DECOHERENCE RATES

In this section, we investigate simple analytical estimates for spin dynamics and the resulting decoherence processes. To facilitate the discussion, notation for different groups of spins will be designated by subscripts. For example, $\Delta\omega_{1/2,1e1g}$ will designate the component

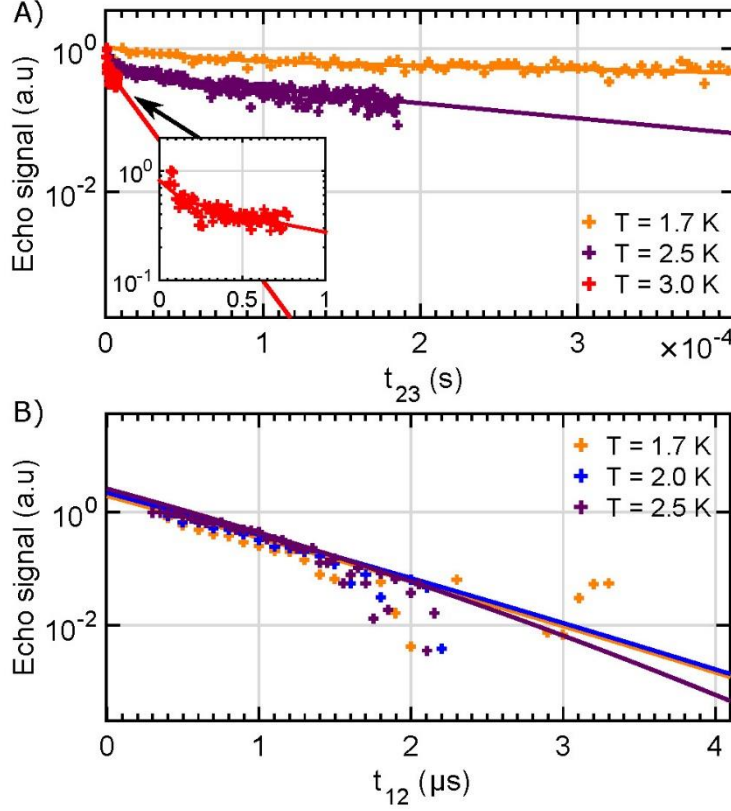


FIG. 2. Example of fits to the experimental A) 3-pulse and B) 2-pulse spin echo decays at several temperatures. All 2- and 3-pulse echo decays were fit together with shared fit parameters. For the sake of clarity in the figure, only a few selected decays are shown.

of the dipolar width (in angular frequency units) of Er^{3+} spins in the excited state of site 1 that is caused by other Er^{3+} spins in the ground state of site 1. For simplification, since we do not investigate the site 2 spin coherence lifetimes (i.e. $T_{2,2e}$ and $T_{2,2g}$), we will simply use T_{2g} and T_{2e} to represent the spin coherence lifetimes for the ground and excited state of Er^{3+} at site 1, respectively.

For our sample, the concentration of Er^{3+} spins at site 1 is $n = 4.7 \times 10^{17}$ ions/cm³, with the same concentration also at site 2. For the resonant processes (i.e. spin flip flops), the relevant concentration is half of that value because there are two magnetically inequivalent

sub-groups for each site. The effective g -factor of the optically excited state of site 1 is $g_{1e} = 3.3$ for the subsite and orientation studied here (see Fig 1B). For simplicity, the effective g -factors for the ground state of site 1 and 2 are taken as the average between the two subsites, giving values of $g_{1g} \approx 4.3$ and $g_{2g} \approx 14$. For the following estimates, we consider a sample temperature of $T = 2$ K and a magnetic field strength of $B = 8.7 \times 10^{-3}$ T.

According to Mims [8], the dipolar half-width of a single sub-group of spins A due to perturbations by a second sub-group of spins B can be estimated with the formula

$$\Delta\omega_{1/2,AB} = \frac{2\pi^2\mu_0\mu_B^2g_Ag_Bn}{(9\sqrt{3}h)}; \quad (10)$$

With g_A the gyromagnetic ratio of the studied A spins, g_B the gyromagnetic factor of the perturbing B spins, μ_0 the vacuum permeability, μ_B the Bohr Magnetron, and n the concentration of B spins (in spins/m³).

From Eq. 10, we can calculate the full-width at half maximum of the dynamic distribution of transition frequencies of A spins due to dipole-dipole interactions with B spins as

$$\Gamma_{AB} = \frac{\Delta\omega_{1/2,AB}}{\pi} \text{sech}\left(\frac{g_B\mu_B B}{2kT}\right)^2, \quad (11)$$

and estimate the spin flip-flop rate between B spins as [9]

$$R_{ff,BB} = \frac{2\pi(\Delta\omega_{1/2,BB})^2}{\Gamma_{inh}} \text{sech}\left(\frac{g_B\mu_B B}{2kT}\right)^2, \quad (12)$$

with B the magnetic field and k the Boltzman constant.

If the flip-flop rate for the B spins is much faster than the time evolution of the A spins, the dipolar contribution is partially reduced due to an averaging effect (motional narrowing [8]), and we can estimate the full-width at half maximum of the dynamic distribution of transition frequencies of A spins due to dipole-dipole interactions with B spins in that case as

$$\Gamma_{ff,AB} = \frac{(\Delta\omega_{1/2,AB})^2}{0.56\pi R_{ff,BB}} \quad (13)$$

Together, Eqs. 10 – 13 provide the following theoretical estimates for our model parameters:

- $\Gamma_{SD,theory} = \Gamma_{1e1g} = 4.4 \times 10^5$ Hz
- $R_{ff,theory} = R_{ff,1g1g} = 1.6 \times 10^5$ s⁻¹

- $R_{\text{ff},2g2g} = 1.8 \times 10^7 \text{ s}^{-1}$
- $\Gamma_{0,\text{theory}} = \Gamma_{\text{ff},1e2g} = 6.3 \times 10^5 \text{ Hz}$

These simple equations only give rough approximations—in particular, they do not account for the strong anisotropy of the $\mathbf{g}$ tensors; however, the theoretical estimates agree reasonably well with the experimental results determined from our global fit of the 2- and 3-pulse echo decays of $\Gamma_0 = 2.7 \times 10^5 \text{ Hz}$, $\Gamma_{\text{SD}} = 4.3 \times 10^5 \text{ Hz}$, and $R_{\text{ff}} = 2.1 \times 10^4 \text{ s}^{-1}$. To further confirm our theory, the variations of T_{2e} with temperature were estimated using the fitted parameters (see Table 1) and the relation [10] (see Fig. 2B in the main text):

$$T_{2e} = \frac{2\Gamma_0}{\Gamma_{\text{SD}}R} \times (-1 + \sqrt{1 + \frac{\Gamma_{\text{SD}}R}{\pi\Gamma_0^2}}) \quad (14)$$

The consistency between the experimental and theoretical values provides support for our overall interpretation of the population dynamics and decoherence mechanisms; nevertheless, further measurements for different magnetic field strengths and orientations will be required to fully test the predictions of this model.

EXCITED-STATE SPIN LIFETIME VS TEMPERATURE

The variations of the observed T_{1e} as a function of temperature (see above) can be modeled by the contribution of spin-phonon processes and optical excitation as

$$\frac{1}{T_{1e}} = \alpha_{D,e} g_e^3 B^5 \coth\left(\frac{h\nu}{2k_B T}\right) + \alpha_{R,e} T^9 + \alpha_{O,e} e^{(-\frac{\Delta E}{k_B T})} + R_{opt} \quad (15)$$

The first two terms, which represent the contribution from the one-phonon direct process and the off-resonant two-phonon Raman process are negligible at very low temperatures and magnetic field strengths. The variations in T_{1e} could be fit well using only the last two terms, which correspond to the resonant two-phonon Orbach process and the photon emission rate from the excited state (see section **Optically Pumped Excited-State Population** above). The resulting fit parameters are presented in Table II. The crystal-field splitting in the Orbach process that we determined is, once again, slightly smaller than the actual value [1] (see section **Spin Echo Decay Modeling**).

TABLE II. Fit parameters for T_{1e} .

$\alpha_{O,e}$	Δ_e	R_s	$T_{1,opt}$
1.0×10^{12} Hz	50 K	840 s^{-1}	9 ms

INSTANTANEOUS SPECTRAL DIFFUSION

To evaluate the effect of decoherence from ISD caused by a "hard" RF π pulse with a spectrum wider than the spin inhomogeneous linewidth (measured to be $\Gamma_{inh} = 10$ MHz for our conditions) so that all of the spins in the crystal are excited, we may simply use the dipolar width from Eq. 10 to derive the effective coherence lifetime as

$$T_{2,ISD,A} = \frac{1}{\Delta\omega_{1/2,AA}}. \quad (16)$$

If we consider the same conditions as in the earlier section **Estimation of Relaxation and Decoherence Rates**, Eq. 16 allows us to predict the ISD-limited coherence lifetimes for each of the spin transitions to be:

- $T_{2,ISD,1e} \leq 1.5$ ms
- $T_{2,ISD,1g} \leq 1.1$ μ s
- $T_{2,ISD,2g} \leq 100$ ns

Since these limits only depend on the excitation conditions (i.e. excitation-driven decoherence), the results show that ISD will severely limit the spin coherence lifetime in the ground state even at lower temperatures where other thermally driven spectral diffusion processes can be suppressed.

LOW-TEMPERATURE MODELING

In this section, we consider the same conditions as in the previous section **Estimation of Relaxation and Decoherence Rates** except for a much lower temperature of $T = 20$ mK and with a larger field of $B = 50$ mT applied along the same direction ($g_{1e} = 3.3$, $g_{1g} \approx 4.3$ and $g_{2g} \approx 14$).

For these conditions, the population ratios between $|2\rangle$ and $|1\rangle$ will be $r_{2g} = 8 \times 10^{-6}$ for site 2 and $r_{1g} = 2.5 \times 10^{-2}$ for site 1 at thermal equilibrium. Thus, there will be no significant

perturbation from the spin bath of Er^{3+} in site 2 due to their strong spin polarization, so at the lower temperature of 50 mK we expect Γ_0 to approach the value $\Gamma_{0,LT} = 0$ Hz.

We can estimate the low temperature spin coherence time T_{2e} for the optical excited state from the experimental fitted values between 1.6 K and 4 K (see section **Estimation of Relaxation and Decoherence Rates**) by using the equation :

$$T_{2e} = \frac{1.41}{\sqrt{R_{\text{ff},1\text{g}1\text{g}} \Delta\omega_{1/2,1\text{e}1\text{g}}}} \quad (17)$$

This equation comes from the model of Mims when the flip-flop rate of the perturbing spins is slower than the evolution time of the measured spins [8]. Since both the flip-flop rate and the spectral diffusion broadening depend on the degree of alignment of the perturbing spins, as the temperature and magnetic field are varied the coherence lifetime will change by a factor p given by the ratio of the hyperbolic secant squared factors in Eqs. 11 and 12. For our example, when we decrease the temperature from 2 K to 20 mK and increase the field from 8.7 mT to 50 mT, the coherence lifetime increases by the factor

$$p = \frac{\text{sech}\left(\frac{g_B \mu_B \times 0.0087}{2k \times 2}\right)^2}{\text{sech}\left(\frac{g_B \mu_B \times 0.05}{2k \times 0.02}\right)^2} \approx 350. \quad (18)$$

Using the fitted values of $R_{\text{ff},1\text{g}1\text{g}}$ and $\Delta\omega_{1/2,1\text{e}1\text{g}}$ in Eq. 17, we find $T_{2e, \text{High Temp}} = 8.4 \mu\text{s}$ and predict a low temperature value of $T_{2e, \text{Low Temp}} = 2.9$ ms.

In the ground state, however, the flip-flop rate for RF-excited spins increases due to the increase in the number of aligned spins in the environment that an excited spin can transfer energy to (see main text). This effect reduces the lifetime of RF-excited spins and results in an upper limit for the achievable ground-state spin coherence lifetime of $T_{2g, \text{Low Temp}} = 1/R_{\text{ff}}$, where R_{ff} is the ground-state spin flip-flop rate in the high-temperature limit. For our conditions, the high-temperature flip-flop rate is $R_{\text{ff}} = 2.1 \times 10^4 \text{ s}^{-1}$ and the corresponding maximum ground-state spin coherence lifetime is therefore only $\sim 48 \mu\text{s}$, which is significantly shorter than the excited-state spin coherence lifetime under the same conditions.

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- [1] T. Böttger, Y. Sun, C. W. Thiel, and R. L. Cone, Phys. Rev. B **74**, 075107 (2006).
 - [2] Y. Sun, T. Böttger, C. W. Thiel, and R. L. Cone, Phys. Rev. B **77**, 085124 (2008).
 - [3] R. C. Hilborn, Am. J. Phys. **50**, 982 (1982).
 - [4] B. A. Young and H. J. Stapleton, Phys. Lett. **21**, 498 (1966).

- [5] G. Wolfowicz, H. Maier-Flaig, R. Marino, A. Ferrier, H. Vezin, J. J. L. Morton, and P. Goldner, Phys. Rev. Lett. **114**, 170503 (2015).
- [6] T. Böttger, C. W. Thiel, R. L. Cone, Y. Sun, and A. Faraon, Phys. Rev. B **045134**, 1 (2016).
- [7] H.-J. Lim, S. Welinski, A. Ferrier, P. Goldner, and J. J. L. Morton, Phys. Rev. B **97**, 064409 (2018).
- [8] W. Mims, Phys. Rev. **168**, 370 (1968).
- [9] R. M. Macfarlane, R. Wannemacher, D. Boye, Y. P. Wang, and R. S. Meltzer, J. Lumin. **48-49**, 313 (1991).
- [10] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, Phys. Rev. B **73**, 075101 (2006).

CHAPTER 6

MEASUREMENT OF THE THULIUM ION SPIN HAMILTONIAN WITHIN A YTTRIUM
GALLIUM GARNET HOST CRYSTALContribution of Authors and Co-Authors

Manuscript in Chapter 6

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Measurement of the Thulium Ion Spin Hamiltonian Within a Yttrium Gallium Garnet Host Crystal

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We characterize the magnetic effects present for thulium ions in a $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (Tm:YGG) lattice with the goal to improve decoherence and line-width broadening caused by local host spins and crystal imperfections. More precisely, we measure hyper-fine tensors for the ground, $^3\text{H}_6$, and excited, $^3\text{H}_4$, states using a combination of spectral hole burning, absorption spectroscopy, and optically detected nuclear magnetic resonance. By rotating the sample through a series of angles with an external magnetic field we use these techniques to measure and fit the orientation dependence of the Tm^{3+} ion's spin-Hamiltonian. Using this spin-Hamiltonian we propose a set of orientations akin to zero first order Zeeman technique to improve material properties that are important for light-matter interaction and quantum information applications. Our results yield several important external field directions: some to extend optical coherence times, another to improve spin inhomogeneous broadening, and yet another that maximizes mixing of the spin states for specific sets of ions, which allows improving optical pumping and creation of lambda systems in this material.

I. INTRODUCTION

Rare earth ion-doped crystals (REIC) have long been studied for use in high frequency quantum and classical signal processing^{1,2}. The transitions of interest are those between electrons of the 4f shell which are weakly permitted, due to the mixing of the wavefunctions by the host crystal field. Additionally, these electrons lie spatially isolated behind a sheath of 5s and 5p shell electrons which are distributed farther from the nucleus. These transitions have shown optical and spin coherence times, up to hundreds of microseconds and minutes, that enable interesting applications in quantum and classical data processing and distribution^{3,4}. This coherence, and the associated applications are often limited only by time-varying electromagnetic fields in the local crystalline environment^{5,6}.

Thulium has received particular interest due to its simple level structure, long coherence time, and readily available diode lasers at the 795 nm optical transition wavelength^{7,8}. Of particular interest is Tm^{3+} embedded in Yttrium Gallium Garnet ($\text{Y}_3\text{Ga}_5\text{O}_{12}$, Tm:YGG) for which optical coherence times (T_2) on the order of milliseconds have recently been measured^{9,10}. This ion and host crystal combination is still relatively unexplored compared to Tm:YAG. For example, the difference in coherence times between these two structurally similar, yet chemically different, garnet materials is not yet completely understood^{3,9}. However, deeper understanding about the crystal dynamics, symmetry, and hyper-fine structure has led to huge improvements in spectroscopic properties of optical and microwave transitions in other rare earth doped materials. One such example is the possibility of transitions with zero first order Zeeman shift (ZEFOZ), which may be obtained by controlling the interplay of the measured terms of the ion's spin Hamiltonian, and can lead to orders of magnitude increase in

spin coherence times⁵. Additionally, the complete spin Hamiltonian can be used to improve and develop new experiments for applications of quantum networking and light matter interaction^{11,12}.

In this letter we present a complete characterization of the hyper-fine structure in the ground and excited states of the 795nm optical transition of Tm^{3+} ions. To perform these measurements we use, absorption spectroscopy, spectral hole burning (SHB), and optically detected nuclear magnetic resonance (ODNMR), isolate, measure, and confirm different terms of the spin Hamiltonian. These measurements individually produce information about the coupled behavior of these levels, and six magnetically equivalent, orientationally in-equivalent sites. Only by cross referencing the spectra from different sets of measurements are we able to decouple the information into the individual orientational behavior of each thulium ion in each individual site for each electronic level. Our results are then confirmed to be in good agreement with initial assumptions about crystalline structure⁹, and a pair of independent measurements of the spin Hamiltonian terms using a single crystalline direction of Tm:YGG. The new knowledge allows us to predict the presence of optical clock transitions in this material which may allow extending the optical coherence times for light storage and quantum memory.

This letter is presented in the following order: In Sec.II we give a brief overview of the Hamiltonian of the system and the remaining unknowns to be measured. In Sec.III we describe the general crystal geometry as well as the implications with regard to the Hamiltonian, and how to isolate the specific projections of an external field on a specific ion site. Section IV describes the experimental setups used to produce the results. In Secs. V and VI we describe how we gather spectra from hole burning and ODMNR measurements with different crystal orientations and which hyper-fine tensor values stem from the

results. Section VII contains details on a pair of independently conducted measurements that confirm these tensor values for a specific orientation of the external field. In Sec. VIII we discuss our results in the context of optical clock transitions and we identify a series of field orientations that may lead to improved optical coherence in this material.

II. SPIN HAMILTONIAN FOR THE ENHANCED ZEEMAN AND QUADRATIC ZEEMAN EFFECTS

For a non-Kramers ion contained in a crystal lattice of low symmetry, a six term Hamiltonian is often considered to describe the behavior of the ionic level structure^{13,14}.

$$H = (H_{FI} + H_{CF}) + H_{HF} + H_Q + H_{eZ} + H_{nZ} \quad (1)$$

The first pair of terms describes the energy structure of a free ion (H_{FI}) coupling to the local crystal field (H_{CF}), which determines the energies of the states differentiated by total electron spin angular momentum that we are interested in for this work. The remaining four terms, contributions from the hyperfine (H_{HF}), quadrupole (H_Q), electronic Zeeman (H_{eZ}) and nuclear Zeeman (H_{nZ}) interactions, are treated as small perturbations. The measurements conducted here focus on a specific pair of these electronic levels, specifically the $^3H_6 \leftrightarrow ^3H_4$ transition. Additionally, the only isotope of thulium (Tm^{169}) possesses a nuclear spin of $\frac{1}{2}$ which allows us to drop the quadrupole splitting term H_Q that is required to describe nuclei with lower magnetic symmetry^{7,15,16}.

The remaining terms of this Hamiltonian are magnetic in nature, corresponding to the hyper-fine, electronic Zeeman, and nuclear Zeeman interactions, and make up the "spin"-Hamiltonian of the system. By expanding these remaining terms to second order as in¹⁵ we arrive at a three term Hamiltonian,

$$H = \mathbf{B} \cdot (-g_n \beta_n \mathbb{I} - 2g_J \mu_B A_J \mathbf{\Lambda}_J) \cdot \mathbf{I} - g_J^2 \mu_B^2 \mathbf{B} \cdot \mathbf{\Lambda}_J \cdot \mathbf{B} \quad (2)$$

where g_n is the nuclear gyro-magnetic ratio of thulium, β_n is the nuclear magneton, g_J is electronic g factor for each level, μ_B is the Bohr magneton, A_J is the hyper-fine interaction constant, $\mathbf{I}$ the ion's nuclear spin, $\mathbf{B}$ the applied external field, and, finally, $\mathbf{\Lambda}_J$ the hyper-fine tensor. This tensor is given by second order perturbation theory as

$$\Lambda_{J,(\alpha,\beta)} = \sum_{n \neq 0} \frac{\langle 0 | J_\alpha | n \rangle \langle n | J_\beta | 0 \rangle}{E_n - E_0}, \quad \alpha, \beta \in \{x, y, z\} \quad (3)$$

where $\langle 0 | J_\alpha | n \rangle, \langle n | J_\beta | 0 \rangle$ are wave-function matrix elements for the electronic levels of interest and the sum is over the nearest crystal field levels with energies E_n ^{7,15,16}.

The first two terms in 2 describe the enhanced Zeeman effect that results from the second order coupling of the

hyper-fine interaction and the electronic Zeeman effect and the first order nuclear Zeeman interaction. The third term is the quadratic Zeeman effect that results from the expansion of the electronic Zeeman term where the orientation dependence is again determined by a scaled version of the same hyper-fine tensor, $\mathbf{\Lambda}^{17}$. Other terms that arise from the expansion to second order are small, and neglected. With this description in place the only unknowns in Eq.2 are the 18 matrix elements of the hyper-fine tensors $\mathbf{\Lambda}_{g,e}$ each a 3x3 matrix that complete the description of the magnetic interactions for Tm^{3+} ions in this material. The level structure with an applied magnetic field is shown in Fig. 2 a. The effect of the quadratic term can be seen as a shift of the whole electronic level, and the linear term (2 a.Inset) splits the pair of spin states. The number of unknown elements in this tensor drops further due to the local symmetry of the Tm^{3+} ions which replace yttrium in the YGG lattice.

III. CRYSTAL SYMMETRY AND SITE SELECTION

The location and symmetry of the yttrium sites is well understood for garnet crystals^{3,18,19}. YGG is a cubic crystal with space group symmetry O_h^{10} , and the thulium sites feature D_2 point group symmetry⁹. The site symmetry, as described for the similar case of $\text{Tm}:\text{YAG}^{20}$ and depicted in Fig. 1, allows for six crystallographically equivalent yet orientationally in-equivalent substitution sites.

The magnetic behavior in each of these sites is the same, due to the Tm^{3+} ion being locally surrounded by the same elemental cell units. However, the ion and its whole local environment can occur at six different orientations with respect to the cubic crystal cells of the garnet, leading to orientational in-equivalence between the sites. Here as in²⁰ and Fig 1, there are a few directions with respect to the cubic crystal axes that cast different subsets of the orientationally in-equivalent sites into classes of ions that share the same projections of applied electromagnetic fields ($\vec{E}, \vec{B}$) onto the local Tm^{3+} site axes. For fields ($\vec{E}, \vec{B}$) directed along the crystalline $\langle 111 \rangle$ and $\langle 001 \rangle$ sets of directions ($\langle 110 \rangle, \langle \bar{1}\bar{1}2 \rangle$ and $\langle 100 \rangle, \langle 010 \rangle$ respectively). These symmetric directions serve as a labeling convention for growth, dicing, and orientation of these crystals and are built into the models detailed below, which allows us to determine the relative projection of incident fields on each of the Tm ion sites throughout our experiments.

On a more microscopic level, the local D_2 symmetry for each site is quite high such that by using a set of axes around the Tm^{3+} ion defined by that site symmetry we can diagonalize the hyperfine tensor from Sec. II. This leaves only the six diagonal elements, $\Lambda_{J,(x,y,z)}$ (three for each electronic state J), which correspond to the tensor elements along the three axes shown in Fig.1 for "Site 1" of the six sites. Considering the crystal symmetry,

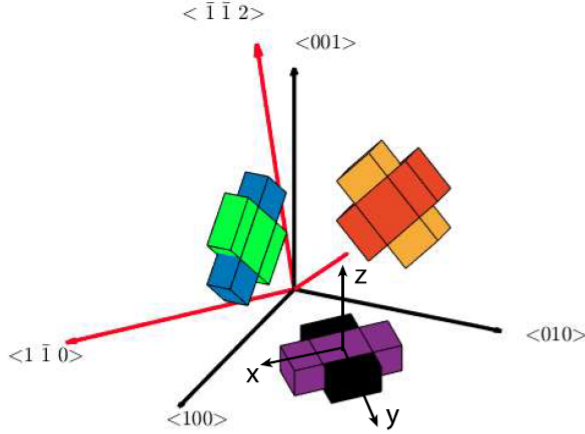


FIG. 1: Possible sites of Tm ions in a yttrium gallium garnet crystal. Black thick axes denote the cubic unit cell boundaries. Each of the 6 colored cuboids denotes the location as well as the direction of the ion's local Y-axis (along the cuboids largest dimension), expected to be the direction of the optical transition dipole moment of the thulium transition, relative to a cubic crystal cell. Each site is identified by a specific color throughout the remainder of this letter: "Site 1" (Black), "Site 2" (Purple), "Site 3" (Orange), "Site 4" (Yellow), "Site 5" (Green), "Site 6" (Blue). Red axes denote the symmetry axes along which the crystal is grown and oriented for these studies. Throughout this letter we will characterize rotations with respect to these directions $\langle 1\bar{1}0 \rangle$, $\langle 111 \rangle$, $\langle \bar{1}\bar{1}2 \rangle$, and rotations with respect to them. Finally, the labeled (x,y,z) thin black axes denote the local site axes as defined by the D_2 point group symmetry (shown is the example of Site 1).

the entire enhanced Zeeman term of Eqn. 2 for a given electronic level can be simplified to^{7,16}

$$H_{J,(x,y,z)} = -\hbar \sqrt{g_{J,x}^2 B_x^2 + g_{J,y}^2 B_y^2 + g_{J,z}^2 B_z^2} \cdot \mathbf{I} \quad (4)$$

for

$$g_{J,(x,y,z)} = -g_n \beta_n - 2g_J \mu_B A_J \Lambda_{J,(x,y,z)} \quad (5)$$

. The determination of the six remaining parameters (three per electronic level) will be discussed in two later sections.

To measure these parameters we gather data about the splittings of the ground and excited spin states for a series of different orientations of a Tm:YGG crystal sample. In spherical coordinates, each specific orientation (θ, ϕ) relative to the cubic crystal cell shown in Fig. 1, has a fixed set of projections on each of the 6 potential Tm^{3+} ion site axes. Thus for every angle of the magnetic field with a macroscopic, oriented sample, we can determine from the expected geometry the exact magnetic projection on each Tm ion axis. By matching sets

of these magnetic field projections to various measurements of the spin state splitting we determine the desired hyperfine tensor values.

IV. EXPERIMENTAL SETUP

To gather the data for our study, we used a total of five Tm:YGG crystals, all cut along with aspects relative to the crystal axes available for light propagation. In addition, we employed several experimental setups. While similar from an abstract point of view (Laser $\rightarrow$ Pulsing $\rightarrow$ Frequency Control $\rightarrow$ Cold Crystal in a magnetic field $\rightarrow$ Detector), they featured technological differences. For instance, we used different cryogenic systems –two helium flow cryostats reaching a base temperature of 2K, equipped with magnets that allow creating fields up to 7 T and fitted with a gearing system that allows rotating the cooled sample by up to 360 degrees around a fixed optical axis for each sample crystal; and an adiabatic demagnetization refrigerator reaching 500 mK temperature, equipped with a 2T magnet as well as a static crystal holder.

To address the center of the inhomogeneously broadened $^3\text{H}_6 \leftrightarrow ^3\text{H}_4$ transition of thulium at 795.325 nm wavelength, we used either a titanium sapphire laser or an external cavity laser. The light was subsequently directed through an acousto-optic modulator (AOM), which allowed creating pulses out of the continuous-wave laser light. Additionally, we used either an AOM in double-pass configuration, or a phase modulator driven by a serrodyne signal, to frequency modulate the light. The appropriately prepared pulses were then directed to the cooled Tm:YGG samples either free space or using a single-mode optical fiber. The beam diameter inside the samples were around 500 μm in case of the flow cryostat and free-space coupling, and around 200 μm in the other case. Finally, the light was sent into a photodetector, and the electrical signals were displayed on an oscilloscope and recorded for analysis.

The set of ODNMR experiments detailed in section VI also required the application of radio-frequency signals that vary between 20kHz and 10 MHz. Towards this end, one of the flow cryostats is equipped with a copper coil that allows creation of an adjustable frequency RF field around the crystal sample. This coil is driven using 5-10 W RF power, created by means of a RF signal generator, a pair of 40dB amplifiers as well as appropriate attenuation. For each needed frequency, the output from the signal generator was set to the desired value and mixed with RF noise, low passed to 100kHz before being sent to the coil, and terminated to 50 Ω . The added noise increases the RF tone bandwidth to provide a RF field capable of driving a larger population of spins, and in turn create signals with higher SNR.

Additional information about the experimental setups will be given in Sections V, VI, & VII along the description of the measurements.

V. SPECTRAL HOLE BURNING DESCRIPTION AND RESULTS

The six remaining tensor values appear in both the linear and quadratic terms of the above Hamiltonian such that measurements of either term's orientation dependence is sufficient to determine the entire spin-Hamiltonian. The linear splitting of spin levels in a system of ground and excited states can be observed through spectral hole burning measurements¹³. With a magnetic field applied, both the ground and excited electronic states split into spin up $+\frac{1}{2}$, ($|\uparrow\rangle$) and spin down $-\frac{1}{2}$, ($|\downarrow\rangle$) states creating a pair of levels seen in Fig.2 a. (Inset). Even at cryogenic temperatures, both ground state spin states are equally populated. Spectral hole burning drives atomic population through this level structure resulting in long lasting population differences between the different spin states⁸. The details of this optical pumping mechanism are well understood and are detailed in^{21,22}. The original pump pulse creates the main spectral hole, a reduction of the atomic absorption of the ensemble at the chosen pulse frequency within the in-homogeneous broadening of the crystal.

Considering only a single projection of the magnetic field on a site, ions in the selected bandwidth are pumped to the other ground state spin level and thereby create a feature with increased absorption, referred to as an anti-hole, at a frequency offset given by the ground state splitting, Δg . Due to the in-homogeneously broadened nature of the transition, additional anti-holes and a single side hole arise symmetrically around the main hole, at frequency offsets of $(\Delta g \pm \Delta e)$ and Δe , respectively. By sweeping weak laser light over the frequency region surrounding the main hole and recording the transmitted intensity these population differences are visible, shown in Fig.2 b. By measuring the frequency offset of side and anti-holes for a set of different orientations we can determine the hyperfine tensor in Eq.2.

As a complication, for an arbitrary orientation each site has a different projection of the external field on its local axes. Thus, based on that projection, is it possible that that the same spectral feature (e.g. the first anti-hole at $\Delta g - \Delta e$) from separate sites may be visible at different frequencies. In the worst case this could result in crowded spectrums which contain as many as 48 features that would need to be assigned to different sites and associated external field projections. Fortunately due to the fixed orientations of the sites with respect to the symmetric crystal axes, some orientations cast sites into equivalent subsets, making their spectral features appear at the same frequencies. This is the case in Fig.2 b. where the visible features belong to three different sites 1, 3, and 5 which all share the same field projection. However, for a differently oriented case of Figure 2 c. the visible features show only the $(\Delta g - \Delta e)$ anti-holes for a pair of Tm^{3+} sites with different magnetic field projections. Thus, with hole spectrums such as these from a series of different orientations, the problem then becomes in-

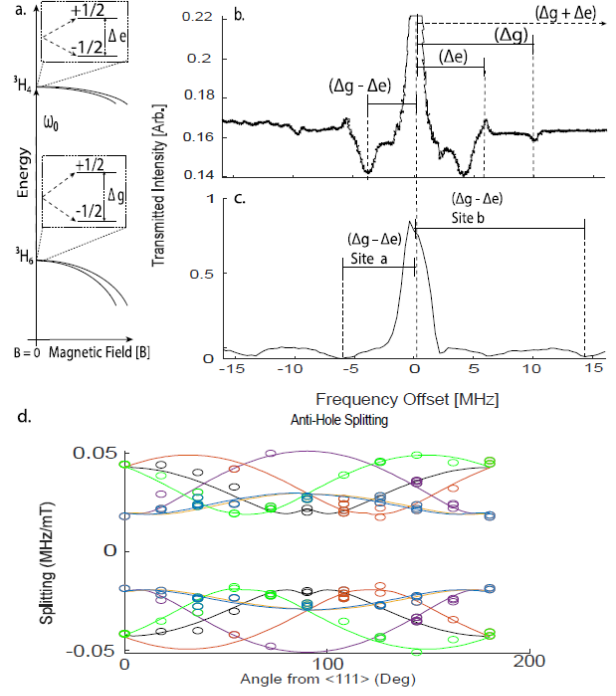


FIG. 2: **a.** Diagram of the level structure for the optical transition in Tm^{169} with increasing magnetic field.

Note that on a large scale the change in energy of all the spin states is dominated by the quadratic term, but for small fields it is linear. **b.** A detailed serrodyne scan of a spectral hole structure measured for a magnetic field of 90 mT applied along the crystalline $\langle 111 \rangle$ axis. The small feature at ~ 2 MHz is likely a spectral feature arising from the other set of sites for this orientation. **c.**

Double passed AOM frequency scan of a broader spectral hole at 300 mT. Only $\Delta g - \Delta e$ anti-holes are visible for a pair of differently oriented sites. **d.** Markers show the anti-hole frequencies plotted vs the angle between the external magnetic field and the crystal's $\langle 111 \rangle$ axis. Solid lines of each color are fits of a "difference" tensor to each of the six potential sites for the ions with a coefficient of determination $R^2 > 90\%$.

interpreting each spectrum, and making an assignment for each feature to a particular site, and its corresponding external field projection. This provides us with a set of splittings, which can be used to determine the tensor values for a given site at a given orientation.

This experiment was conducted in one of the flow cryostats mentioned in Sec.III. The $\text{Tm}:\text{YGG}$ sample was cooled to 2K and a fixed field of 300 mT was applied as the sample was rotated through a series of angles. To create a spectrum the experimental burning sequence at each angle involved a 1 ms hole burning pulse, a waiting period of 10 ms for population to decay from the excited state, and finally a 100 μs read pulse with a chirped frequency

over a 40MHz region centered at the main hole to reveal any side and anti-hole structure. This sequence used circularly polarized light and $\approx 100\text{mW}$ of power incident on the crystal and was averaged over many trials to produce a single spectrum at each angle. Due to a combination of pump laser linewidth, sample temperature, and limited AOM frequency shifting efficiency we were only able to monitor and record the frequency change of the first anti-hole, occurring at a frequency offset of $(\Delta g - \Delta e)$, for all sites during these rotational SHB measurements.

Though not a direct measurement of the tensor values of either the ground or excited state, these values contain valuable information that in conjunction with the ODNMR data from Section V is used to compute the spin-Hamiltonian. But tracking these splittings through the series of different angles between an external magnetic field and the symmetric crystal axes, we fit a "difference tensor" that best satisfies the measured $(\Delta g - \Delta e)$ splittings for all sites at all angles.

More specifically, for a specific angle of external field with respect to a particular crystalline direction, there is a known projection of the magnetic field on each of the six sites. Our fitting procedure fits $g_{(x,y,z)}$ values in 4 to a particular splitting which is assigned manually to a site, and determines the three associated magnetic field projections (B_x, B_y, B_z) at each angle. Thus, one set of fitted values match a whole matrix of magnetic projections, for a series of angles with regard to each site, to a set of splitting values assigned to each site. The spectral locations of the visible anti-holes at the series of angles compared to the results of this least squares tensor fitting procedure can be seen in Fig.2d. This fitting procedure and analysis were repeated for two differently oriented Tm:YGG crystals, and good agreement was found between the resulting "difference tensors". For more information regarding the fitting procedure, and plots of the fit for the second crystalline direction consult the supplementary material⁷.

VI. ODNMR MEASUREMENT AND RESULTS

In addition to SHB where optical pumping drives change in spin level population by way of the optical excitation to the excited state followed by spontaneous relaxation, it is also possible to alter the relative spin level populations by directly addressing the microwave transition between them. The relative population between the nuclear spin levels can then be observed optically in a double resonance experiment known as optically detected nuclear magnetic resonance (ODNMR), which has been carried out with a number of REICs^{13,23,24}. As opposed to SHB, ODNMR provides information directly about either Δg or Δe and thereby allows supplementing the results in the previous section to extract the hamiltonian in Eq.2. The strategy, shown in Fig. 3a, involves first creating a population difference between the two spin levels via SHB. While viewing this hole profile optically an RF

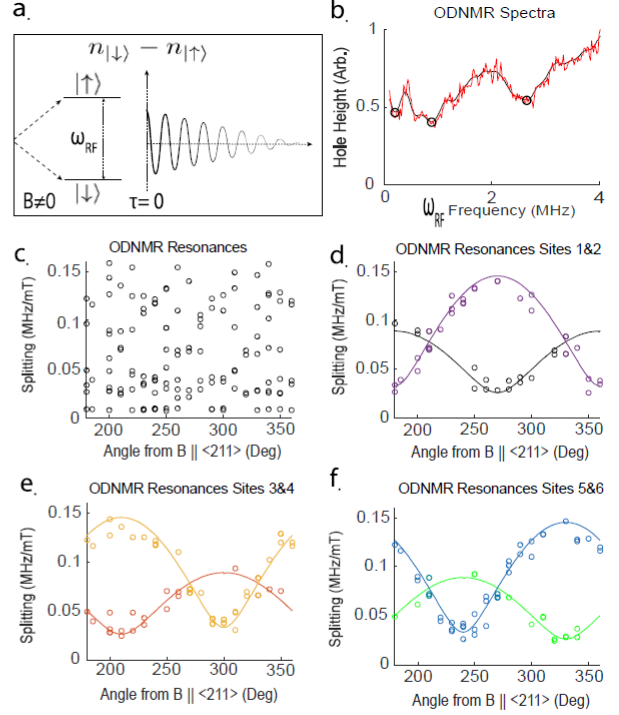


FIG. 3: **a.** Diagrammatic view of the ODNMR experiment, including the driven spin transition that appears at small magnetic fields, and the coherent RF drive that equalizes the population between the $\pm \frac{1}{2}$ spin states. **b.** The ω_{RF} frequencies that diminish the height of a spectral hole are identified as resonances by a smoothing and peak finding algorithm and then confirmed manually. A spectrum such as this one is generated for many angles between the field with the crystal || < 211 > axis. **c.** A plot of resonances from all spectrums at a series of angles between external field and the crystal < 211 > direction. **d,e,f** Site by site fitting of the tensors listed in I to the resonances from **c** across a series of angles.

pulse is created which, if resonant with the spin transition at frequency Δg , re-equalizes the spin population resulting in a change of the absorption depth of the spectral hole. Since the energy difference between spin states is unknown for a given external magnetic field the RF field is swept across a range of frequencies to find the resonance condition $\omega_{RF} = \Delta g$. The excited state splitting Δe can be measured with a similar approach using an altered sequence of optical and RF excitation pulses such that population can be addressed and viewed while in the excited state.

This experiment is carried out in one of the helium flow cryostats, equipped with a RF coil on a rotation mount to supply the RF fields. The Tm:YGG sample is cooled to 2K and an external magnetic field of 20-40mT

is applied perpendicular to the optical and rotational axis along the crystalline $\langle 211 \rangle$ direction. Using an altered SHB experimental sequence a spectral hole is prepared and read out, with burning and waiting times adjusted to ensure minimal contribution to the spectral hole depth from atomic population in the excited states while maximizing the repetition rate. Additionally the durations and relative powers of the burn and read pulses were adjusted to produce a slightly shallower hole that could be read with less noise from laser power fluctuations.

While repeating the hole burning experiment, 100 ms long RF pulses, are applied to the crystal. We tune the frequency of the RF field in 20 kHz steps from 100kHz-4 MHz and five repetitions are averaged to produce spectrums such as that seen in Fig.3 b. The broadening of the features is due to the convolution of the applied RF field linewidth of 100kHz and the spin resonance inhomogeneous linewidth. To ensure that these features showed indeed the ground state atomic resonances, we first confirmed that each resonance frequency had a linear shift with increasing external magnetic field, and were absent when no external field was applied. We optimized the generation of the ODNMR spectra over the parameter space of RF drive power, optical hole burning power, duration, sample temperature, SHB duty cycle, and experimental repetition rate.

This experiment was repeated for a series of different angles between the crystals $\langle 211 \rangle$ axis and the externally applied magnetic field. All resonance frequencies were determined with help of a peak finding algorithm; They are displayed in Fig. 3 c. As before, all six Tm sites contribute to this set of resonances.

Here again, each specific angle of external field with respect to a particular crystalline direction defines six projections of the magnetic field on each site. Each angle is associated with a series of ODNMR resonances as well, such that a vector of ground state tensor values must solve, as closely as possible, a matrix equation that includes magnetic projections on each site for many local angles, to fit over more than 200 equally weighted resonance points. The resulting tensor fits are shown in Fig. 3 d,e,f. Site assignment and fitting was repeated for two differently oriented cuts of Tm:YGG crystal which show good agreement with one another. The results of the second fit can be seen in the supplementary material. It is interesting to note that the calculated tensor values are comparable to those measured with Tm:GG²⁵. This gives us additional confidence in the results, as in the case of the confirmation between Tm:YAG and Tm:AG^{22,26}.

This fitting procedure produces the three ground state tensor values $\Lambda_{g,(x,y,z)}$, and in conjunction with the “difference tensor” fits from the previous section $\Lambda_{e,(x,y,z)}$ can also be determined. These results for the six spin-Hamiltonian components averaged over the four directional fits of sections V & VI are shown in Table I where the signs are given by convention. Unfortunately, both spectral hole burning and ODNMR yield only the magnitude but not the sign of the different parameters be-

	$^3\text{H}_6(\text{g})$	$^3\text{H}_4(\text{e})$
$g_n\beta_n$	-3.53(MHz/T)	-3.53(MHz/T) ²⁶
g_j	1.16	0.8
Λ_J	-470.3(MHz)	-678.3(MHz)
$\Lambda_J\Lambda_x$	-7.23×10^{-4}	-1.55×10^{-4}
$\Lambda_J\Lambda_y$	-4.47×10^{-3}	-3.95×10^{-3}
$\Lambda_J\Lambda_z$	-9.99×10^{-4}	-5.57×10^{-4}
g_x	27 ± 1.7 (MHz/T)	7 ± 2.5 (MHz/T)
g_y	146 ± 1.5 (MHz/T)	92 ± 2.8 (MHz/T)
g_z	36 ± 2.6 (MHz/T)	16 ± 3.1 (MHz/T)

TABLE I: Spin Hamiltonian values. The g_j values are calculated using the general formalism described in¹⁴. The Λ_J values are from⁷ and can be recalculated from¹⁴ as they depend only on the expectation value for electron radius for this Tm transition. $g_{x,y,z}$ values for the excited and ground states are measured in this work. Together with the listed constants they allow calculating all $\Lambda_{J,\alpha}$ values using Eqn.5.

cause we cannot differentiate one spin state from another. Nonetheless, and similarly to²⁷, for our purposes it is often enough to know the relative energy difference between the two spin states of each electronic level, and not whether it happens to be the spin up or spin down state since their energy shifts will be symmetric.

VII. VERIFICATION OF RESULTS

In the following, we will detail additional measurements based on alternative methods and on different Tm:YGG crystals. While being performed with a reduced set of parameters that does not allow independently establishing the Hamiltonian in Eq. 2, they nevertheless allow verifying the results presented in section VI.

A. Linear Zeeman shift

The enhanced Zeeman interaction given by the first two terms of Eq.(2) results in a linear splitting of the spin levels in both the ground and excited states. As discussed in section IV the Zeeman coefficient can be measured by first applying a magnetic field, then exposing the sample to narrow-band laser light, and finally probing the resulting sequence of holes and anti-holes by scanning a weak laser across the created spectral features.

This experiment was performed inside the ADR and at a temperature of 500 mK. In this case the magnetic field could only be applied along the crystal's $\langle 111 \rangle$ direction, resulting in magnetic projections of equal magnitude on the Y and Z components of sites 1,3 and 5, and X and Z components of sites 2,4 and 6. The hole burning laser was frequency locked to around 10 kHz linewidth by

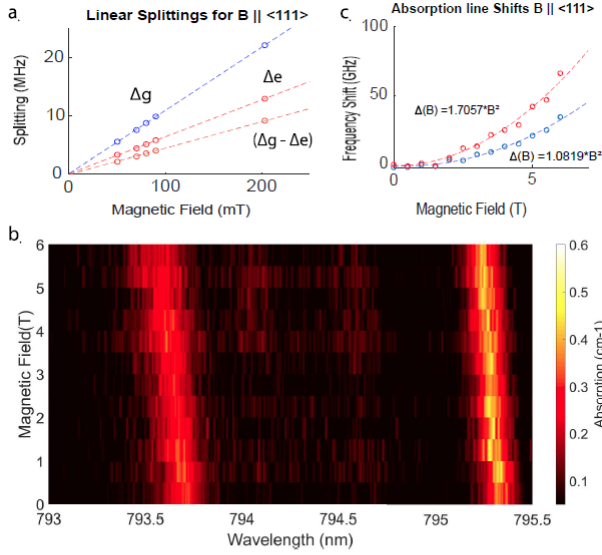


FIG. 4: **a.** The linear splitting of the anti-holes shown in Fig.2 b. for the $B \parallel \langle 111 \rangle$ orientation yields values of $45 \pm 108 \pm 2$ MHz/T and a side hole splitting of 63 ± 2 MHz/T. **b.** Absolute absorption frequency for the optical transitions from the lowest ground state crystal field level to the first (795.325 nm) and second (793.7 nm) excited state crystal field levels with increasing magnetic field. **c.** A closer look at the behavior of these transitions reveals the expected quadratic nature of the frequency shift.

means of a highly stable reference cavity and the Pound-Drever-Hall method, and we employed 1 mW of power incident on the crystal, burning pulses of 200ms duration, 10ms of waiting time to avoid spontaneously emitted signal, and a 1ms long read pulse. The lower temperature and narrower laser linewidth (compared to the measurements described before) allowed resolving all expected SHB features, including a pair of anti holes and a side hole, as seen in Fig. 2 b. for a field of 90 mT.

The splitting of these spectral features as a function of magnetic field in Fig.4 a. confirms the linear nature of the Zeeman interaction with splittings of the ground and excited states of 108 ± 2 MHz/T and 63 ± 2 MHz/T, respectively. This is in good agreement with the values calculated from the measured tensors, which we found to be $\Delta g = 106 \pm 2.2$ MHz/T, $\Delta e = 66 \pm 1.3$ MHz/T for sites 1,3 and 5 for this orientation.

B. Quadratic Zeeman shift

The quadratic Zeeman interaction given by the third term of Eq.(2) shifts each electronic crystal field level, characterized by the total angular momentum J , parabolically due to the so-called VanVleck paramagnetism²⁸.

Each J-manifold shifts with its own rate, as depicted in Fig.2 a. and described by its hyper-fine tensor. This creates an overall change to the optical transition frequency with a B^2 dependence that varies based on the external field direction. It can be calculated using the ground and excited state tensor values given in Table I.

To measure the quadratic Zeeman effect we used a flow cryostat operating at 5K and allowing the application of a magnetic field along the $\langle 111 \rangle$ direction of the Tm:YGG crystal. We performed white light absorption spectroscopy, similar to¹⁶, i.e. we directed collimated CW white light through the crystal and to an optical spectrum analyzer to observe the entire in-homogeneous line of the $^3H_6 \leftrightarrow ^3H_4$ transition at 795.325nm (see Fig.4b). The optical transition from lowest crystal field level of the ground state to the second crystal field level of the excited state at 793.7 nm was visible as well, confirming the expected crystal field spacing of 26 cm^{-1} in³. We monitored the absorption frequencies for this pair of transitions as the external magnetic field was increased from 0 to 6 T. The results are depicted in Fig. 4 c. A quadratic fit yields a frequency shift of $\Delta = 1.08 \pm 0.24$ GHz/T², which is in good agreement with the value of $\Delta_p = 1.09 \pm 0.25$ GHz/T² that we calculated from the measured spin tensors.

VIII. OPTICAL CLOCK TRANSITIONS AND SPECIAL DIRECTIONS

The frequency of the transition between two spin states—one belonging to the electronic ground state and one of the excited state—depends through the linear and quadratic Zeeman effects on the magnetic field. Small field fluctuations therefore cause spectral diffusion and hence a reduction of the optical coherence time. It is sometimes possible to chose a magnetic field magnitude and a crystal orientation for which the transition energy becomes, to first order, insensitive to fluctuations in the magnetic field. These transitions are referred to as optical clock transition and are quite similar to the ZEFOZ transitions from^{5,27,29,30}. Clock transitions are extremely powerful tools used for reducing decoherence due to noisy stray magnetic fields³¹. These clock transitions exist in Tm:YGG and can be found for a particular site using the procedure detailed below.

Inspecting the third term of Eq. 2 and taking into account that the elements of the hyperfine tensor Γ_J are larger in the ground state than in the excited state (see¹⁶ for a detailed explanation in Tm:YAG) the optical transition energy change caused by the quadratic Zeeman effect creates an increase in transition energy with magnetic field. This is depicted theoretically in Fig.2 a. and confirmed from the data in Fig. 4b.

Furthermore, looking at the first and second term of Eq. 2, which describe the linear Zeeman shift, we find that there exist ground and excited state pairs of spin states for which the optical transition frequency decreases

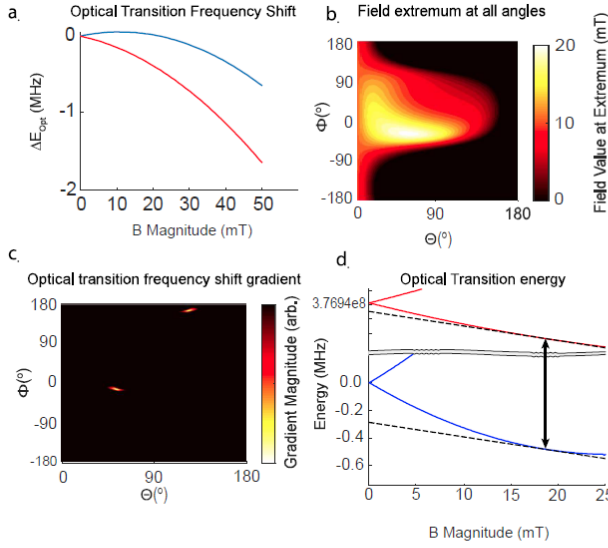


FIG. 5: **a.** The shift in the optical transition frequency follows a quadratic dependence with an extrema that, for every orientation, appears at a positive field for the spin conserving $-1/2 \leftrightarrow -1/2$ transition (blue) and at some negative field for the spin conserving $+1/2 \leftrightarrow +1/2$ transitions (red). **b.** For the $-1/2 \leftrightarrow -1/2$ spin conserving optical transition and for all angles, the magnetic field value of this extrema is identified. **c.** Angular gradient of the optical transition frequency at a field of 19mT. Two points are visible for which the angular gradient gets approaches zero. **d.** Energy shifts of the two $-1/2$ spin states at this particular direction vs. magnetic field magnitude. At 19mT the slope of the energy change for both states with change in field magnitude is equal (along with the other derivatives) and an optical clock transition occurs.

with applied magnetic field. Hence, for certain combinations of crystal orientation (or rather orientation of a local Tm site) with respect to the magnetic field, magnetic field strength and spin values, the linear and quadratic Zeeman effects oppose each other, and an optical clock transition can be observed³². This transition must have a field magnitude insensitive point, which is shown in Fig. 5 a as the shift in optical transition frequency $\Delta E_{opt}(|B|, \theta, \phi)$ vs. applied field magnitude.

In these cases, the spin-Hamiltonian terms form a quadratic function which must have an extremum, i.e. a field magnitude insensitive point, at some positive field magnitude. The first condition of an optical clock transition, a field magnitude $|B|$ such that $\frac{\partial \Delta E_{opt}}{\partial |B|} = 0$, is calculated for every orientation of magnetic field relative to the "Site 1" spin $-1/2$ conserving optical transition in Fig. 5 b using a mesh size of 1mT and 1 degree angular steps.

For the remaining angular derivatives

($\frac{\partial \Delta E_{opt}}{\partial B_\theta}, \frac{\partial \Delta E_{opt}}{\partial B_\phi} = 0$) there must also be angles for which ΔE_{opt} is also insensitive to first order angular change to complete each optical clock transition. Though all orientations have some field magnitude which results in an invariant point, only some orientations have angular gradients which simultaneously go to zero. Plotted in Fig 5 c is the magnitude of the angular gradient for both spin conserving optical transitions vs the optical transition frequency for all angles of magnetic field with respect to the crystalline axes. Two angular points stand out, one for each spin conserving transition, whose gradient value becomes exceedingly small. By cross referencing the points of small angular gradient with the field at which the magnitude extrema appears we can find an orientation that simultaneously brings all three derivatives to zero. In the case of the spin $-1/2$ conserving optical transition for "Site 1" we arrive at a set of coordinates $\vec{B}_{|B|, \theta, \phi} = (19mT, 55^\circ, -15^\circ)$ that correspond to an optical clock transition. The invariant energy levels of this transition at this field are shown in Fig.5d. This procedure can be repeated for the remaining sites and potential optical transitions (spin crossing or preserving) giving us the list of many optical clock transitions in this material shown in Table II.

Past studies characterize the benefit to coherence to be gained by moving to a field invariant direction using the definition of transition curvature given by²⁹. All transitions in Table II share the same curvature of $\approx 36Hz/G^2$. Other REIC samples previously brought to invariant points with this magnitude of curvature have resulted in improved spin coherence times by orders of magnitude. However, the amount of improvement in the case of Tm:YGG will depend heavily on the decoherence mechanisms involved in the optical transition.

Though the clock directions are important for maximizing optical coherence time, alternative crystal properties can also be optimized by choosing other external field directions. Following the arguments from³³ we have found other orientations that are capable of minimizing the spin in-homogeneous broadening for the ground state spin transition. Similarly, according to^{22,34} another orientation exists which allows maximizing the branching ratio of the available lambda system in this material. Details on the calculation of these orientations are available in the supplementary material.

IX. CONCLUSION

We conducted a series of spectroscopic studies that allowed us to measure the full spin-hamiltonian for Tm:YGG. Despite the multitude of sites, by using a combination of SHB and ODNMR we determined both the ground and excited state hyper-fine tensors. These tensors were confirmed to match the results of a pair of

Site #	$ B $	$\vec{B}_\theta$	$\vec{B}_\phi$	Spin Level Transition
1	19 mT	55°	-15°	-1/2 $\Leftrightarrow$ -1/2
1	19 mT	125°	166°	+1/2 $\Leftrightarrow$ +1/2
1	36 mT	64°	-150°	+1/2 $\Leftrightarrow$ -1/2
1	36 mT	117°	31°	-1/2 $\Leftrightarrow$ +1/2
2	19 mT	54°	76°	-1/2 $\Leftrightarrow$ -1/2
2	19 mT	125°	-105°	+1/2 $\Leftrightarrow$ +1/2
2	36 mT	116°	120°	-1/2 $\Leftrightarrow$ +1/2
2	36 mT	63°	-60°	+1/2 $\Leftrightarrow$ -1/2
3	19 mT	102°	54°	-1/2 $\Leftrightarrow$ -1/2
3	19 mT	79°	-127°	+1/2 $\Leftrightarrow$ +1/2
3	36 mT	64°	120°	+1/2 $\Leftrightarrow$ -1/2
3	36 mT	118°	60°	-1/2 $\Leftrightarrow$ +1/2
4	19 mT	38°	20°	-1/2 $\Leftrightarrow$ -1/2
4	19 mT	143°	-160°	+1/2 $\Leftrightarrow$ +1/2
4	36 mT	140°	-45°	-1/2 $\Leftrightarrow$ +1/2
4	36 mT	40°	135°	+1/2 $\Leftrightarrow$ -1/2
5	19 mT	38°	110°	-1/2 $\Leftrightarrow$ -1/2
5	19 mT	142°	-70°	+1/2 $\Leftrightarrow$ +1/2
5	36 mT	140°	45°	-1/2 $\Leftrightarrow$ +1/2
5	19 mT	40°	-135°	+1/2 $\Leftrightarrow$ -1/2
6	19 mT	78°	37°	-1/2 $\Leftrightarrow$ -1/2
6	19 mT	102°	-144°	+1/2 $\Leftrightarrow$ +1/2
6	36 mT	62°	30°	-1/2 $\Leftrightarrow$ +1/2
6	36 mT	118°	-150°	+1/2 $\Leftrightarrow$ -1/2

TABLE II: Optical clock transitions with angular coordinates of $\vec{B}$ given relative to the $\langle 100 \rangle, \langle 010 \rangle, \langle 001 \rangle$ crystalline axes. These positive and negative projections are based on the unit cell directions for the 6 sites for the Tm:YGG.

independent experiments with magnetic field directions limited to the $\langle 111 \rangle$ crystal axis. This new knowledge allowed us to determine a series of directions that should create optical clock transitions for specific thulium sites and in turn enhance the optical coherence of the transition in this material. This confirms the potential of Tm:YGG crystals for quantum networking and quantum memory applications.

Acknowledgements

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- ¹ W. R. Babbitt, Z. W. Barber, S. H. Bekker, M. D. Chase, C. Harrington, K. D. Merkel, R. K. Mohan, T. Sharpe, C. R. Stiffler, A. S. Traxinger, and A. J. Woidtke, "From spectral holeburning memory to spatial-spectral microwave signal processing," *Laser Physics*, vol. 24, p. 094002, aug 2014.
 - ² W. Tittel, M. Afzelius, T. Chanelière, R. Cone, S. Kröll, S. Moiseev, and M. Sellars, "Photon-echo quantum memory in solid state systems," *Laser & Photonics Reviews*, vol. 4, no. 2, pp. 244–267, 2010.
 - ³ Y. C. Sun, *Rare Earth Materials in Optical Storage and Data Processing Applications*, pp. 379–429. Berlin, Heidelberg: Springer Berlin Heidelberg, 2005.
 - ⁴ A. Kaplyanskii and R. McFarlane, *Spectroscopy of Crystals Containing Rare Earth Ions*. Elsevier, 2012.
 - ⁵ E. Fraval, M. J. Sellars, and J. J. Longdell, "Method of extending hyperfine coherence times in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$," *Phys. Rev. Lett.*, vol. 92, p. 077601, Feb 2004.
 - ⁶ R. MacFarlane, C. Yannoni, and R. Shelby, "Optical line narrowing by nuclear spin decoupling in $\text{Pr}^{3+}:\text{LaF}_3$," *Optics Communications*, vol. 32, no. 1, pp. 101 – 104, 1980.
 - ⁷ O. Guillot-Noël, P. Goldner, E. Antic-Fidancev, and J. L. Le Gouët, "Analysis of magnetic interactions in rare-earth-doped crystals for quantum manipulation," *Phys. Rev. B*, vol. 71, p. 174409, May 2005.
 - ⁸ N. Ohlsson, M. Nilsson, S. Kröll, and R. K. Mohan, "Long-time-storage mechanism for tm:yag in a magnetic field," *Opt. Lett.*, vol. 28, pp. 450–452, Mar 2003.
 - ⁹ C. W. Thiel, N. Sinclair, W. Tittel, and R. L. Cone, "Optical decoherence studies of $\text{Tm}^{3+}:\text{Y}_3\text{Ga}_5\text{O}_{12}$," *Phys. Rev. B*, vol. 90, p. 214301, Dec 2014.
 - ¹⁰ C. W. Thiel, N. Sinclair, W. Tittel, and R. L. Cone, " $\text{Tm}^{3+}:\text{Y}_3\text{Ga}_5\text{O}_{12}$ materials for spectrally multiplexed quantum memories," *Phys. Rev. Lett.*, vol. 113, p. 160501, Oct 2014.
 - ¹¹ M. Zhong, M. P. Hedges, R. L. Ahlefeldt, J. G. Bartholomew, S. E. Beavan, S. M. Wittig, J. J. Longdell, and M. J. Sellars, "Optically addressable nuclear spins in a solid with a six-hour coherence time," *Nature*, vol. 517, pp. 177–180, Jan 2015.
 - ¹² M. Rančić, M. P. Hedges, R. L. Ahlefeldt, and M. J. Sellars, "Coherence time of over a second in a telecom-compatible quantum memory storage material," *Nature Physics*, vol. 14, pp. 50–54, Jan 2018.
 - ¹³ R. Macfarlane and R. Shelby, "Chapter 3 - coherent transient and holeburning spectroscopy of rare earth ions in solids," in *Spectroscopy of Solids Containing Rare Earth Ions* (A. Kaplyanskii and R. Macfarlane, eds.), vol. 21 of *Modern Problems in Condensed Matter Sciences*, pp. 51 – 184, Elsevier, 1987.
 - ¹⁴ A. Abragam and B. Bleaney, "Electron paramagnetic resonance of transition ions," 2012.
 - ¹⁵ M. Teplov, "Magnetic resonance on pr 141 nuclei in a pr2 (s04) 3- 8h20 single crystal," *Zh. Eksp. Teor. Fiz.*, vol. 53,

- pp. 1510–1515, 1967.
- ¹⁶ L. Veissier, C. W. Thiel, T. Lutz, P. E. Barclay, W. Tittel, and R. L. Cone, “Quadratic zeeman effect and spin-lattice relaxation of Tm^{3+} :YAG at high magnetic fields,” *Phys. Rev. B*, vol. 94, p. 205133, Nov 2016.
 - ¹⁷ A. Abragam and B. Bleaney, “Enhanced nuclear magnetism: Some novel features and prospective experiments,” *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, vol. 387, no. 1793, pp. 221–256, 1983.
 - ¹⁸ J. F. Dillon and L. R. Walker, “Ferrimagnetic resonance in rare-earth doped yttrium iron garnet. ii. terbium substitution,” *Phys. Rev.*, vol. 124, pp. 1401–1413, Dec 1961.
 - ¹⁹ G. Menzer, “Xx. die kristallstruktur der granate,” *Zeitschrift für Kristallographie - Crystalline Materials*, vol. 69, no. 1, pp. 300 – 396, 01 Dec. 1929.
 - ²⁰ Y. Sun, G. M. Wang, R. L. Cone, R. W. Equall, and M. J. M. Leask, “Symmetry considerations regarding light propagation and light polarization for coherent interactions with ions in crystals,” *Phys. Rev. B*, vol. 62, pp. 15443–15451, Dec 2000.
 - ²¹ R. Lauro, T. Chanelière, and J. L. L. Gouët, “Slow light using spectral hole burning in a Tm^{3+} :YAG crystal,” *arXiv preprint arXiv:0902.2657*, 2009.
 - ²² A. Louchet, J. S. Habib, V. Crozatier, I. Lorgeré, F. Goldfarb, F. Bretenaker, J.-L. L. Gouët, O. Guillot-Noël, and P. Goldner, “Branching ratio measurement of a Λ system in Tm^{3+} : YAG under a magnetic field,” *Phys. Rev. B*, vol. 75, p. 035131, Jan 2007.
 - ²³ L. Erickson, “The nuclear quadrupole interaction in Pr^{3+} : LaF_3 — an optical-rf double resonance measurement of the ground electronic state,” *Optics Communications*, vol. 21, no. 1, pp. 147 – 149, 1977.
 - ²⁴ A. J. Silversmith, A. P. Radliński, and N. B. Manson, “Optical study of hyperfine coupling in the $^7\text{F}_0$ and $^5\text{D}_0$ states of two Eu^{3+} centers in CaF_2 and CdF_2 ,” *Phys. Rev. B*, vol. 34, pp. 7554–7563, Dec 1986.
 - ²⁵ E. Jones, “Observation of the $\text{tm}169$ nuclear magnetic resonance in thulium gallium garnet,” *Journal of Physics and Chemistry of Solids*, vol. 29, no. 8, pp. 1305 – 1308, 1968.
 - ²⁶ V. H. Schmidt and E. D. Jones, “Nuclear-magnetic-resonance study of thulium aluminum garnet,” *Phys. Rev. B*, vol. 1, pp. 1978–1986, Mar 1970.
 - ²⁷ D. L. McAuslan, J. G. Bartholomew, M. J. Sellars, and J. J. Longdell, “Reducing decoherence in optical and spin transitions in rare-earth-metal-ion-doped materials,” *Phys. Rev. A*, vol. 85, p. 032339, Mar 2012.
 - ²⁸ J. V. Vleck, *The theory of electric and magnetic susceptibilities*. Oxford: [s.n.], 1932.
 - ²⁹ J. J. Longdell, A. L. Alexander, and M. J. Sellars, “Characterization of the hyperfine interaction in europium-doped yttrium orthosilicate and europium chloride hexahydrate,” *Phys. Rev. B*, vol. 74, p. 195101, Nov 2006.
 - ³⁰ M. Lovrić, P. Glasenapp, D. Suter, B. Tumino, A. Ferrier, P. Goldner, M. Sabooni, L. Rippe, and S. Kröll, “Hyperfine characterization and spin coherence lifetime extension in Pr^{3+} : $\text{La}_2(\text{WO}_4)_3$,” *Phys. Rev. B*, vol. 84, p. 104417, Sep 2011.
 - ³¹ D. Kielpinski, V. Meyer, M. A. Rowe, C. A. Sackett, W. M. Itano, C. Monroe, and D. J. Wineland, “A decoherence-free quantum memory using trapped ions,” *Science*, vol. 291, no. 5506, pp. 1013–1015, 2001.
 - ³² R.-C. Tongning, T. Chanelière, J.-L. L. Gouët, and M. F. Pascual-Winter, “Optical clock transition in a rare-earth-ion-doped crystal: coherence lifetime extension for quantum storage applications,” *Journal of Physics: Conference Series*, vol. 605, p. 012037, apr 2015.
 - ³³ M. F. Pascual-Winter, R.-C. Tongning, T. Chanelière, and J.-L. Le Gouët, “Spin coherence lifetime extension in Tm^{3+} :YAG through dynamical decoupling,” *Phys. Rev. B*, vol. 86, p. 184301, Nov 2012.
 - ³⁴ F. de Seze, A. Louchet, V. Crozatier, I. Lorgeré, F. Bretenaker, J.-L. Le Gouët, O. Guillot-Noël, and P. Goldner, “Experimental tailoring of a three-level Λ system in Tm^{3+} : YAG,” *Phys. Rev. B*, vol. 73, p. 085112, Feb 2006.

Measurement of the Thulium Ion Spin Hamiltonian Within a Yttrium Gallium Garnet Host Crystal

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I. FITTING DETAILS

To fit the data present in each of the angular scans we begin with a simple linear regression problem of the form:

$$\mathbf{A}\vec{\lambda} = \vec{\Delta} \quad (1)$$

where $\mathbf{A}$ is a $m \times 3$ matrix of magnetic field projections, where each of the m rows, representing a particular ion site at a particular angle, is given by B_x, B_y, B_z . The $\vec{\Delta}$ is a vector that contains all the measured splittings from either ODNMR or SHB given the particular fit. Finally, the $\vec{\lambda}$ vector contains the hyperfine tensor values that solve this system of equations for the series of ion sites at a series of angles. Since no tensor values will fit the measured splittings with zero error and $\mathbf{A}$ may not be invertable, then the matrix equation in Eq. 1 must be generalized to its ordinary least squares version given by:

$$\vec{\lambda} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \vec{\Delta} \quad (2)$$

which gives the closest possible fit for the linear system of equations. Generalizing again, since the splittings do not depend linearly on the magnetic field projections, we solve the new matrix equation using the nonlinear modeling function of matlab for which the user supplies, the input vectors, $\vec{\lambda}$, and $\vec{\Delta}$, and the nonlinear model that describes their relationship, in this case,

$$\Delta_g = \sqrt{g_x^2 B_x^2 + g_y^2 B_y^2 + g_z^2 B_z^2} \quad (3)$$

or

$$\Delta_g - \Delta_e = \sqrt{g_x^2 B_x^2 + g_y^2 B_y^2 + g_z^2 B_z^2} - \sqrt{e_x^2 B_x^2 + e_y^2 B_y^2 + e_z^2 B_z^2} \quad (4)$$

for the ground and ground minus excited state splittings respectively. The only task that remaining is to make sure that each row of projections is associated with the correct resonance splitting to produce the final set of values. These associations were made manually by relating each resonance to the most likely sites and angles using similar initial measurements from [1].

All magnetic field projections are computed based on a unit vector magnetic field in relation to the site axes pictured in main text Figure 1. Each sites' axes given in the crystalline cubic cell frame are assumed to be:

Inverting the sign assumptions present in these directional definitions can result in some underlying changes to the signs but not the magnitudes of the determined tensor values and special directions relative to each defined axis [2].

Site	$\hat{x}$	$\hat{y}$	$\hat{z}$
1 (Black)	(1 -1 0)	(1 1 0)	(0 0 1)
2 (Purple)	(1 1 0)	(-1 1 0)	(0 0 1)
3 (Orange)	(0 1 -1)	(0 1 1)	(1 0 0)
4 (Yellow)	(0 1 1)	(0 -1 1)	(1 0 0)
5 (Green)	(-1 0 1)	(1 0 1)	(0 1 0)
6 (Black)	(1 0 1)	(1 0 -1)	(0 1 0)

TABLE I: Defined directions in the crystal. These directions were normalized to compute all projections of the magnetic fields. The positive and negative axes are assumed by convention to keep the site $\hat{z}$ directions pointing into the unit cell.

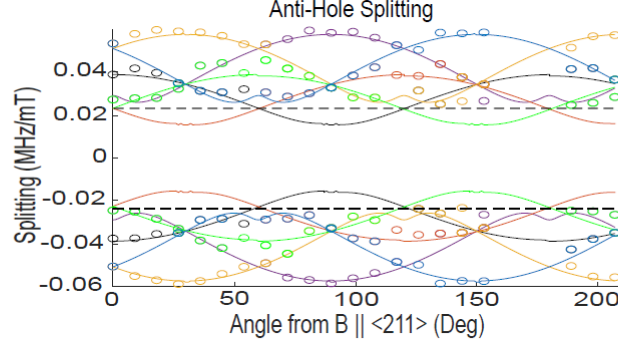


Fig. 1. Secondary SHB directional fit. **a.** Spectral hole burning anti hole splittings measured for an optical axis along the crystalline $\langle 110 \rangle$ axis. Dotted line indicate the minimum measurable splitting due to the width of the central spectral hole.

From the set of all the points for a particular measurement, resonance points which showed no angular dependence or extremely weak signatures were also omitted from the fits. Many of the omitted resonance points appeared at all angles of ODNMR with a splitting of 9-11 MHz/T and are assumed to be the gallium nuclear spin splittings of the host crystal. Finally, a fixed angular correction was made to all points for each particular set of data to account for the experimental uncertainty in the crystal orientation.

II. SECONDARY FIT OF THE SHB DIFFERENCE TENSOR

Given the experimental uncertainty in angles and orientation, and the manually conducted site assignment for each of the splittings it is important to verify the tensor values that are produced by our fitting procedure explain the splitting behavior for multiple crystalline directions. To account for this we rotated the crystal to a new optical axis, defining a new plane in which to rotate the B field, and repeated our angular rotation while collecting SHB data for the new direction. The fitting procedure described above was applied to the resonances of the new direction independently of the data from previous directions. The resulting tensor values, with fits pictured in Fig.1, show close agreement with the values produced by the fit of the first direction. The tensor values from both directions are averaged together to give the final values listed for the excited state splittings in the main text.

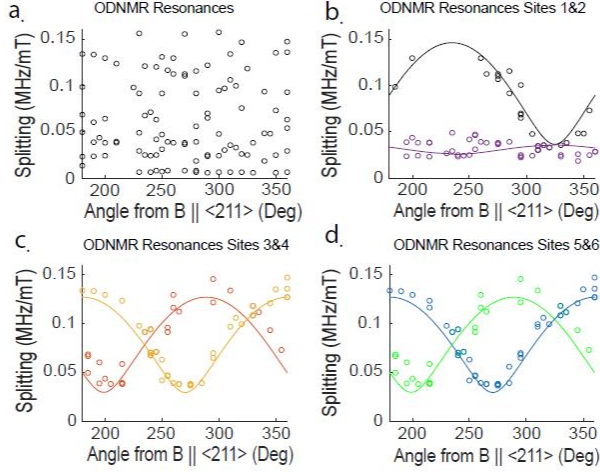
III. SECONDARY FIT OF THE ODNMR DIRECTIONAL TENSOR

Following the same logic for all rotational measurements, we conducted ODNMR measurements while rotating around a pair of different optical axes as well. The resulting tensor values, with fits pictured in Fig.2, also show good agreement with the values produced by the fit of the first direction. The tensor values from both directions are averaged together to give the final values listed for the ground state splittings in the main text.

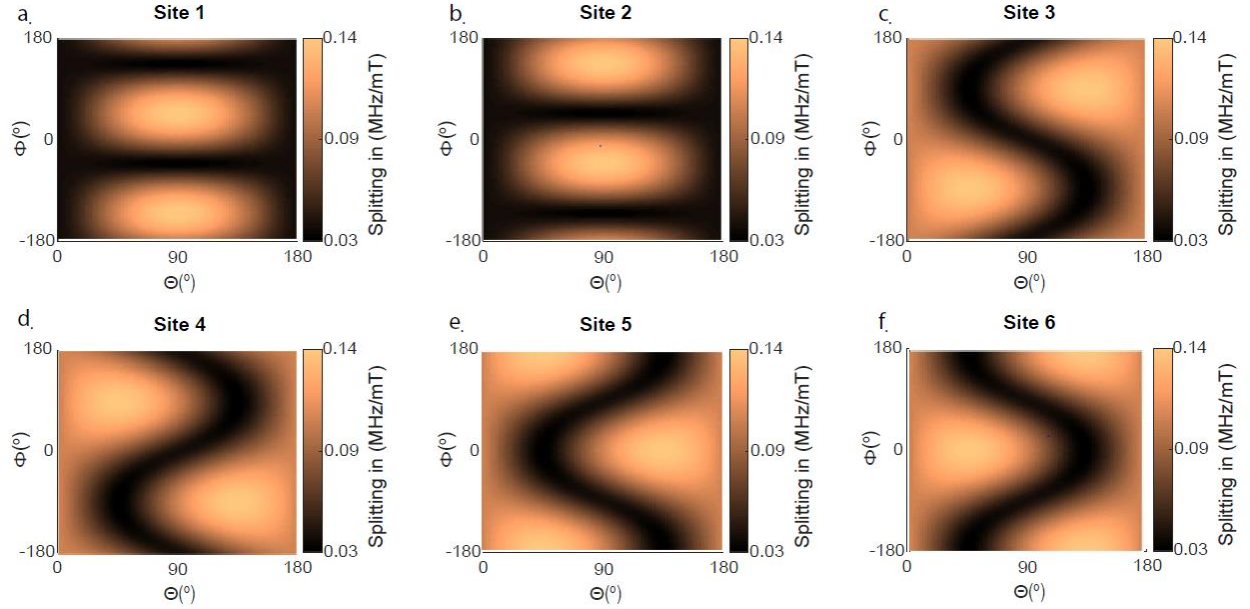
IV. MINIMIZE THE SPIN-INHOMOGENEOUS BROADENING

In the main text, the results for an optical clock transition are depicted to show an insensitive point between a pair of energy levels that belong to the optical transition for the Tm^{3+} ions in this material. The purpose of this point is to minimize the contribution of magnetic fluctuations to the uncertainty in optical transition energy. A similar analogy can be drawn to the pair of ground state spin levels if that is instead the transition of interest. Since the nuclear spin of thulium is $1/2$ however, these levels will always experience a linear splitting relative to the magnitude of the applied magnetic field. In other words, a complete ZEFOZ point is not accessible in this system. However, by choosing a specific orientation in the hyperfine tensor space, as in the case of [3], the effects on these spins due to orientation fluctuations of the local magnetic field can be minimized.

To improve future possibilities for spin control in Tm:YGG a crystal with similar spin coherence to Tm:YAG, but missing the complex cross relaxation mechanism caused by aluminum [4], we have conducted the same analysis as in

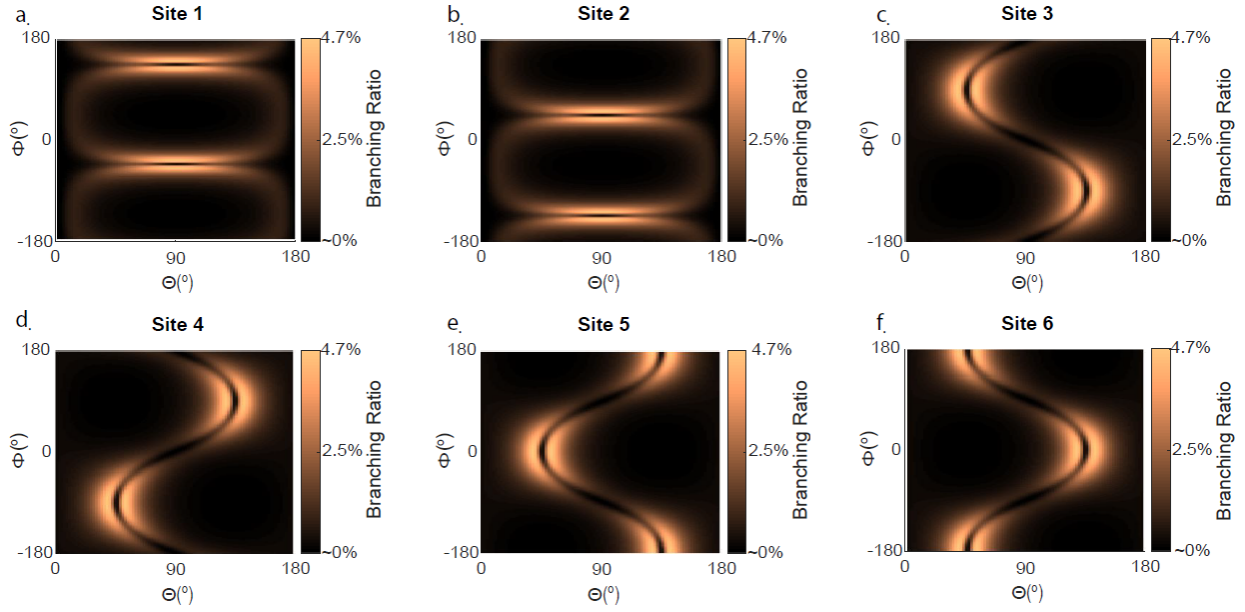


SIFig. 2. Secondary ODNMR directional fit using ODNMR data. **a.** All ODNMR resonances measured for an optical axis along the crystalline $\langle 110 \rangle$ axis. **b,c,d.** Site by site fitting of the tensors listed in the main text to the resonances from **a** across a series of angles.



SIFig. 3. a-f. Site by site orientation map of the ground state splittings. The highlighted extrema of each surface indicate the orientations of improved sensitivity to angular magnetic field fluctuations.

the case of [3]. We compute for some magnetic field amplitude, the magnitude at all angles of the splitting of the ground state spin levels. Finding for each of the present sites, extrema in this angular splitting landscape, we pinpoint orientations where the splitting between spin states has the smallest variation with respect to local angular change of an external magnetic field. The results of this computation are shown for each of the six sites in Fig.3. These external field orientations, computed from the tensors, will result in the narrowest possible spin transition in-homogeneous broadening in this material, and have potential to enable dynamical decoupling and spin control sequences.



SIFig. 4. a-f. Site by site orientation map of the branching ratio R as defined in [6]. Each site reaches a maximum branching ratio of 5% for certain angles close to the particular local $\hat{x}$ axis

V. BRANCHING RATIO SIMULATIONS AND DIRECTIONS

An additional aspect of interest in these rare earth ion-doped crystal systems is to create a lambda system where two lower energy levels are each connected via optical transition to a single excited state [5–7]. Such a system is relevant to a number of different quantum memory schemes. Since there are only a pair of degenerate spin levels in this spin 1/2 system, the pair of ground states that couple to a single excited level must be the $\pm 1/2$ ground state spin levels. According to selection rules, optical transitions should not be capable of creating nuclear spin flips making a lambda system with these couplings potentially impossible. However, due to the crystal field mixing of the electronic and nuclear wave-functions such spin crossing transitions become weakly allowed, alongside their spin preserving counterparts. By describing an effective magnetic field felt by the nuclear spin due to each of the nearest crystal field levels, the amount of spin mixing that is possible can be calculated from the hyperfine tensor values of Tm:YGG. Following the definition of an effective B field vector in the ground and excited states from [6], we compute the likely branching ratio for each ion site at all possible orientations to determine which angles may yield the best spin crossing transition probability for each site in Tm:YGG. Due to the lower anisotropy of the hyperfine tensors, the maximum branching ratios that appear possible in Tm:YGG is 5%, much lower than the optimal case of 25% in Tm:YAG.

VI. REFERENCES

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- [1] E. Jones, “Observation of the tm169 nuclear magnetic resonance in thulium gallium garnet,” *Journal of Physics and Chemistry of Solids*, vol. 29, no. 8, pp. 1305 – 1308, 1968.
 - [2] D. L. McAuslan, J. G. Bartholomew, M. J. Sellars, and J. J. Longdell, “Reducing decoherence in optical and spin transitions in rare-earth-metal-ion-doped materials,” *Phys. Rev. A*, vol. 85, p. 032339, Mar 2012.
 - [3] M. F. Pascual-Winter, R.-C. Tongning, T. Chanelière, and J.-L. Le Gouët, “Spin coherence lifetime extension in $\text{tm}^{3+}:\text{yag}$ through dynamical decoupling,” *Phys. Rev. B*, vol. 86, p. 184301, Nov 2012.

- [4] R. L. Ahlefeldt, M. F. Pascual-Winter, A. Louchet-Chauvet, T. Chanelière, and J.-L. Le Gouët, “Optical measurement of heteronuclear cross-relaxation interactions in tm:yag,” Phys. Rev. B, vol. 92, p. 094305, Sep 2015.
- [5] A. Louchet, J. S. Habib, V. Crozatier, I. Lorgeté, F. Goldfarb, F. Bretenaker, J.-L. L. Gouët, O. Guillot-Noël, and P. Goldner, “Branching ratio measurement of a Λ system in tm^{3+} : YAG under a magnetic field,” Phys. Rev. B, vol. 75, p. 035131, Jan 2007.
- [6] F. de Seze, A. Louchet, V. Crozatier, I. Lorgeté, F. Bretenaker, J.-L. Le Gouët, O. Guillot-Noël, and P. Goldner, “Experimental tailoring of a three-level Λ system in tm^{3+} : YAG,” Phys. Rev. B, vol. 73, p. 085112, Feb 2006.
- [7] O. Guillot-Noël, P. Goldner, E. Antic-Fidancev, and J. L. Le Gouët, “Analysis of magnetic interactions in rare-earth-doped crystals for quantum manipulation,” Phys. Rev. B, vol. 71, p. 174409, May 2005.

CHAPTER 7

CHARACTERIZATION OF $^{171}\text{YB}^{3+}:\text{YVO}_4$ FOR
PHOTONIC QUANTUM TECHNOLOGIESContribution of Authors and Co-Authors

Manuscript in Chapter 7

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Contributions: Designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

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Characterization of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ for photonic quantum technologiesJonathan M. Kindem,^{1,2} John G. Bartholomew,^{1,2} Philip J. T. Woodburn,³ Tian Zhong,^{1,2,4} Ioana Craiciu,^{1,2} Rufus L. Cone,³ Charles W. Thiel,³ and Andrei Faraon^{1,2,*}¹*Kavli Nanoscience Institute and Thomas J. Watson, Sr., Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125, USA*²*Institute for Quantum Information and Matter, California Institute of Technology, Pasadena, California 91125, USA*³*Department of Physics, Montana State University, Bozeman, Montana 59717, USA*⁴*Institute of Molecular Engineering, University of Chicago, Chicago, Illinois 60637, USA*

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Rare-earth ions in crystals are a proven solid-state platform for quantum technologies in the ensemble regime and attractive for new opportunities at the single-ion level. Among the trivalent rare earths, $^{171}\text{Yb}^{3+}$ is unique in that it possesses a single $4f$ excited-state manifold and is the only paramagnetic isotope with a nuclear spin of $1/2$. In this work, we present measurements of the optical and spin properties of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ to assess whether this distinct energy-level structure can be harnessed for quantum interfaces. The material was found to possess large optical absorption compared to other rare-earth-doped crystals owing to the combination of narrow inhomogeneous broadening and a large transition oscillator strength. In moderate magnetic fields, we measure optical linewidths less than 3 kHz and nuclear spin linewidths less than 50 Hz. We characterize the excited-state hyperfine and Zeeman interactions in this system, which enables the engineering of a Λ system and demonstration of all-optical coherent control over the nuclear-spin ensemble. Given these properties, $^{171}\text{Yb}^{3+}:\text{YVO}_4$ has significant potential for building quantum interfaces such as ensemble-based memories, microwave-to-optical transducers, and optically addressable single rare-earth-ion spin qubits.

DOI: [10.1103/PhysRevB.98.024404](https://doi.org/10.1103/PhysRevB.98.024404)**I. INTRODUCTION**

Future quantum networks will incorporate a number of different quantum technologies, such as stationary qubits for high-fidelity logic operations and quantum memories for synchronization and long-term storage [1–3]. A successful network will require robust interfaces to coherently map quantum information between the best technologies, which may be based on disparate physical systems. For example, quantum transducers between the microwave and optical domains could be used to interface superconducting processors over long distances through optical networks [4].

Rare-earth ions (REIs) doped into crystalline hosts have demonstrated significant progress in implementing solid-state quantum technologies. REIs possess some of the longest optical and spin coherence lifetimes in the solid state [5–8], which has provided the foundation for numerous demonstrations of quantum memories and quantum interfaces [9–14]. For interfaces involving both microwave and optical photons, REIs with an odd number of electrons (i.e., Kramers ions), such as erbium, neodymium, and ytterbium, are of interest due to their electron-spin transitions. The large magnetic moments of these ions allow for strong interactions with microwaves, enabling fast operations and the potential for interfacing with superconducting qubits. Isotopes of these ions with nonzero nuclear spin also offer the possibility of long-term quantum storage [8]. This combination of properties creates the potential

for building interfaces between microwave photons, optical photons, and long-lived nuclear spins.

Among the Kramers ions, ytterbium is an attractive choice due to its simple level structure consisting of only two electronic multiplets. The optical transition between the lowest energy levels of these multiplets occurs around 980 nm, which is readily accessible by standard diode lasers. Furthermore, the $^{171}\text{Yb}^{3+}$ isotope is unique among the trivalent REIs as the only Kramers ion with a nuclear spin of $1/2$. This gives the simplest possible hyperfine energy structure allowing for both electron- and nuclear-spin degrees of freedom, reducing the complexity of optical preparation and manipulation of spin states [15,16]. Recent work in $^{171}\text{Yb}^{3+}:\text{Y}_2\text{SiO}_5$ [17–20], $\text{Yb}^{3+}:\text{LiNbO}_3$ [21], and $\text{Yb}^{3+}:\text{YAG}$ [22] highlights the interest in this ion. In this work, we investigate $^{171}\text{Yb}^{3+}$ doped into the host crystal YVO_4 . YVO_4 is an attractive choice for implementing quantum interfaces [23,24] due to the ability to fabricate nanoscale devices [25] and high site symmetry in this material. Furthermore, previous work points to the potential for high oscillator strength transitions for Yb^{3+} doped into YVO_4 [26].

We present an initial survey of the properties of optical and nuclear-spin transitions in $^{171}\text{Yb}^{3+}:\text{YVO}_4$ at cryogenic temperatures. To determine whether this material can be used for efficient interactions with light, we characterized the strength and inhomogeneity of the optical transitions using high-resolution optical spectroscopy. Large hyperfine couplings and narrow optical inhomogeneous lines in this material result in resolved optical transitions between the hyperfine states, which allowed for characterization of the excited-state

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spin Hamiltonian directly from absorption measurements in an applied magnetic field. Knowledge of the spin Hamiltonian enables the identification of magnetic-field orientations that create strongly spin-conserving transitions (for cyclic transitions) or strongly spin-mixing optical transitions (allowing for efficient lambda systems). To assess the possibility of storage and manipulation of quantum information in this material, we measured the coherence properties of the optical and nuclear-spin transitions as a function of applied magnetic field. To demonstrate the potential for all-optical control of the nuclear spin states, we also measured spin echoes using bichromatic Raman pulses.

This paper is organized as follows: Section II presents the material properties of the samples used in this work and the spin Hamiltonian used to model this system. Section III describes the experimental methods and apparatus. Section IV presents the experimental results and discussion. This section is further divided into subsections: A (optical-absorption spectroscopy), B (optical transition strengths), C (excited-state lifetime), D (optical coherence measurements), E (nuclear-spin measurements), and F (all-optical spin coherence measurements).

II. BACKGROUND

A. Material properties

YVO₄ (also called yttrium orthovanadate or YVO) forms a zircon tetragonal crystal with D_{4h} symmetry [27]. Ytterbium substitutes for yttrium in sites of local D_{2d} point-group symmetry. The z axis of the site coincides with the crystalline fourfold axis (the c axis of the crystal). The uniaxial nature of this site reduces the number of parameters needed to characterize the system compared to a lower symmetry crystal such as Y₂SiO₅ [17,18].

The majority of measurements presented in this paper were performed in samples cut from a boule of YVO₄ doped with isotopically enriched ¹⁷¹Yb³⁺ custom grown by Gamdan Optics. The concentration of ¹⁷¹Yb was measured to be 100 ppm using secondary ion mass spectrometry (SIMS). The samples were cut and polished to various thicknesses appropriate to each measurement. Fluorescence lifetime measurements were performed using a nominally undoped sample of YVO₄ (Gamdan Optics), which was measured using SIMS to have a residual ¹⁷¹Yb³⁺ concentration of approximately 2 ppm.

B. Spin Hamiltonian

The $4f^{13}$ configuration of Yb³⁺ consists of two electronic multiplets: $^2F_{7/2}$ and $^2F_{5/2}$. In the crystal field of YVO₄, the ground-state multiplet ($^2F_{7/2}$) splits into four Kramers doublets and the excited-state multiplet ($^2F_{5/2}$) splits into three Kramers doublets. The energies of these crystal-field levels have been measured previously [28] and are shown in Fig. 1(a). At liquid-helium temperatures, only the lowest energy doublet of the ground state is thermally occupied. The optical transition of interest for quantum interfaces is between the lowest energy doublets of the ground state and excited state [$^2F_{7/2}(0) \rightarrow ^2F_{5/2}(0)$]. This transition occurs at approximately 984.5 nm for Yb³⁺ doped into YVO₄.

In this work, we focus on the ¹⁷¹Yb isotope, which has a nuclear spin $I = 1/2$. Treating the Kramers doublets as

effective spins with $S = 1/2$, we can describe the system with the following spin Hamiltonian [29]:

$$H_{\text{eff}} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - \mu_n \mathbf{B} \cdot \mathbf{g}_n \cdot \mathbf{I}. \quad (1)$$

The first term is due to the electronic Zeeman interaction, where μ_B is the Bohr magneton, $\mathbf{B}$ is the applied magnetic field, $\mathbf{g}$ is the electronic Zeeman tensor, and $\mathbf{S}$ is the spin-1/2 operator. The second term describes the coupling between the electron spin and nuclear spin via the hyperfine interaction, where $\mathbf{I}$ is the nuclear-spin operator and $\mathbf{A}$ is the hyperfine interaction tensor. The last term arises from the nuclear Zeeman interaction, where μ_n is the nuclear magneton and $\mathbf{g}_n$ is the nuclear Zeeman tensor. For ¹⁷¹Yb in YVO₄, the nonzero components of $\mathbf{g}_n$ will be of the order of the gyromagnetic moment of the free nucleus $g_n = 0.987$, which leads to a nuclear Zeeman interaction ~ 2000 times smaller than the electronic Zeeman term. For the magnetic-field values used in this work, we treat this interaction by incorporating it into the electronic Zeeman tensor.

The energy structure in the absence of an external magnetic field ($\mathbf{B} = 0$) is determined by the hyperfine interaction $\mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$. In the site symmetry of YVO₄, the degeneracy of these levels is partially lifted and the Hamiltonian has the following eigenvalues at zero field: $E = \frac{A_{\perp}}{4}, \frac{A_{\parallel}}{4}, \frac{-A_{\parallel}+2A_{\perp}}{4}, \frac{-A_{\parallel}-2A_{\perp}}{4}$, where $A_{\perp}$ and $A_{\parallel}$ are the components of the hyperfine tensor $\mathbf{A}$ perpendicular and parallel to the crystal symmetry axis (the c axis) [29]. The order of the energies is determined by the signs of these components, which we have determined to be $A_{\parallel}^g < 0$ and $A_{\perp}^g, A_{\parallel}^e, A_{\perp}^e > 0$ (see Sec. IV A) with the superscript g (e) denoting the ground (excited) state. The corresponding eigenstates numbered from lowest to highest energy are

$$|1\rangle_g = |\uparrow\uparrow\rangle_g, \quad |1\rangle_e = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_e - |\downarrow\uparrow\rangle_e), \quad (2)$$

$$|2\rangle_g = |\downarrow\downarrow\rangle_g, \quad |2\rangle_e = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_e + |\downarrow\uparrow\rangle_e), \quad (3)$$

$$|3\rangle_g = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_g - |\downarrow\uparrow\rangle_g), \quad |3\rangle_e = |\uparrow\uparrow\rangle_e, \quad (4)$$

$$|4\rangle_g = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_g + |\downarrow\uparrow\rangle_g), \quad |4\rangle_e = |\downarrow\downarrow\rangle_e. \quad (5)$$

We denote the electron-spin components as $|\uparrow\rangle \equiv |S_z = \frac{1}{2}\rangle$, $|\downarrow\rangle \equiv |S_z = -\frac{1}{2}\rangle$ and the nuclear-spin components as $|\uparrow\rangle \equiv |I_z = \frac{1}{2}\rangle$, $|\downarrow\rangle \equiv |I_z = -\frac{1}{2}\rangle$.

For high magnetic fields applied along the c axis, the electronic Zeeman interaction dominates over the hyperfine interaction. In this regime, mixing between the electron and nuclear spin is greatly reduced and the states effectively become

$$|1'\rangle_g \approx |\uparrow\uparrow\rangle, \quad |1'\rangle_e \approx |\downarrow\uparrow\rangle, \quad (6)$$

$$|2'\rangle_g \approx |\uparrow\downarrow\rangle, \quad |2'\rangle_e \approx |\downarrow\downarrow\rangle, \quad (7)$$

$$|3'\rangle_g \approx |\downarrow\downarrow\rangle, \quad |3'\rangle_e \approx |\uparrow\downarrow\rangle, \quad (8)$$

$$|4'\rangle_g \approx |\downarrow\uparrow\rangle, \quad |4'\rangle_e \approx |\uparrow\uparrow\rangle. \quad (9)$$

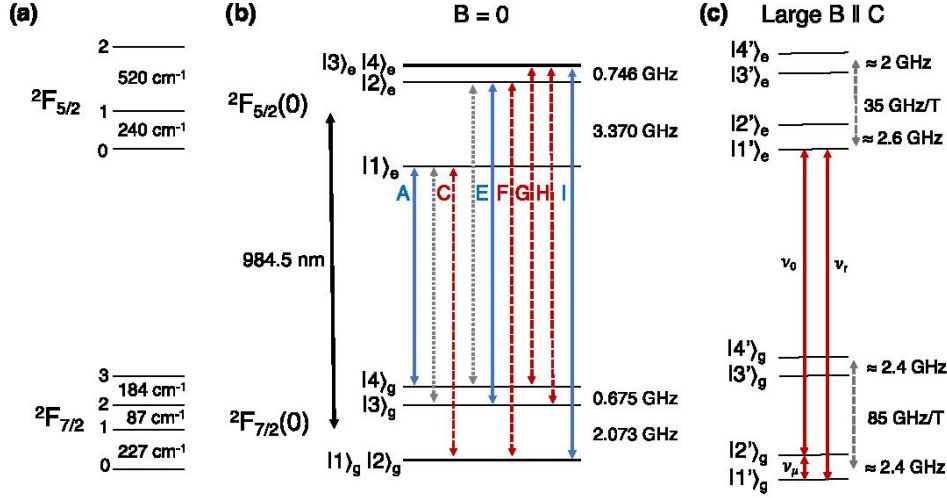


FIG. 1. Energy-level diagram for $^{171}\text{Yb}^{3+}:\text{YVO}_4$. (a) Crystal-field splittings of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ reproduced from [28]. (b) Zero-field energy-level diagram for the $2F_{7/2}(0) \rightarrow 2F_{5/2}(0)$ transition of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ at 984.5 nm studied in this paper. Energy splittings in the ground and excited state are extracted from the excited-state hyperfine tensor determined in this work and previous measurements of the ground-state hyperfine tensor [30]. The transitions corresponding to the observed absorption spectrum in Fig. 2 for $E \parallel c$ ($E \perp c$) are shown in solid blue (dashed red). The dotted grey lines correspond to transitions that are forbidden by symmetry. (c) Energy-level diagram for the linear Zeeman regime with $B \parallel c$ with arrows denoting the transitions studied in this work.

We have again numbered the states from lowest to highest energy using the fact that $g_{\parallel} < 0$ for the ground state and $g_{\parallel} > 0$ for the excited state (see Sec. IV A). The prime is used to distinguish between the high-field and zero-field state labels. In this work, we focus on the coherence properties of the optical and nuclear-spin transitions in the regime where the linear Zeeman interaction is dominant.

III. EXPERIMENTAL METHODS

High-resolution laser absorption scans with a home-built external-cavity diode laser (ECDL) using the design from [31] were performed to measure the inhomogeneous linewidth and absorption of the $2F_{7/2}(0) \rightarrow 2F_{5/2}(0)$ transition. The energies of the optical transitions were extracted from absorption scans taken with magnetic fields applied along the crystal symmetry axes and used to determine the excited-state spin Hamiltonian. For this purpose, we used a 90- μm -thick a -cut sample of $^{171}\text{Yb}^{3+}:\text{YVO}_4$. This thickness was chosen such that the sample was not overabsorbing at 2 K. The sample was mounted in a custom sample mount and masked to avoid spurious light leakage around the crystal that could lead to inaccurate measurements of the optical depth. For the data presented here, the probe light propagated parallel to the a axis of the crystal and perpendicular to the applied magnetic field ($\mathbf{k} \perp \mathbf{B}, c$). Additional axial spectra ($\mathbf{k} \parallel c$) were taken to confirm the electric dipole nature of the optical transitions [32]. The absorption was determined by measuring the transmission of the ECDL on a photodetector (New Focus 2031) as the frequency of the laser was scanned across resonance. The center frequency of the scan was calibrated with a wave meter (Burleigh WA-1500) and the frequency detuning of the scan was calibrated using a Fabry-Perot reference cavity. The absorption experiments were

performed in an Oxford Spectromag cryostat at a temperature of 2 K with an applied magnetic field of up to 6 T.

For measurements of the excited state, optical coherence, and spin coherence lifetimes, the optical transitions were addressed using a single frequency Ti:sapphire laser (M-Squared Solstis) that was gated by an 80-MHz acousto-optic modulator in a double-pass configuration to create the required pulse sequence. For measurements of the coherence properties and inhomogeneity of the nuclear-spin transition, the nuclear-spin transition was addressed directly using a coaxial transmission line mounted directly next to the sample.

The excited-state lifetime was measured from the time-resolved fluorescence decay. We performed pulsed excitation on the $2F_{7/2}(0) \rightarrow 2F_{5/2}(0)$ transition and collected the resulting fluorescence to the upper crystal-field levels of the ground state [i.e., $2F_{5/2}(0) \rightarrow 2F_{7/2}(1-3)$] using a 1000-nm long-pass filter. The fluorescence counts as a function of time were recorded using a silicon avalanche photodiode (Perkin-Elmer). Fluorescence measurements were performed in a 500- μm -thick sample that was nominally undoped (residual $^{171}\text{Yb}^{3+}$ concentration of ~ 2 ppm) and a 200- μm -thick 100-ppm sample of $^{171}\text{Yb}^{3+}:\text{YVO}_4$. These measurements were performed at 4 K with zero applied magnetic field in a Montana Instruments cryostat using a home-built confocal microscope setup.

The coherence properties of the optical transition were investigated using two-pulse photon echo decays as a function of magnetic field strength. For this purpose, two-pulse photon echoes on the $|1'\rangle_g \rightarrow |1'\rangle_e$ transition were measured using heterodyne detection. During the echo sequence, a fiber-based phase modulator EOM (IXBlue NIR-MPX-LN-20) was driven by a microwave source (Windfreak Synth HD) at 500 MHz to create an optical sideband resonant with the optical transition. The resulting echo was detected as a beat at the sideband

frequency using an InGaAs photodiode (Thorlabs DET08CFC, 5 GHz bandwidth). Typical π pulses for this measurement were 4 μ s long.

Optical coherence measurements were performed with the sample mounted on the still plate of a Bluefors dilution refrigerator at a temperature of 650 mK. These measurements used a 500- μ m-thick *c*-cut 100-ppm sample with $\mathbf{k} \parallel c$. The light entered the refrigerator via single-mode optical fiber and was focused onto the back surface of the sample, which was coated in gold to enhance reflection. The reflected light was coupled back into the fiber and directed to the photodetector with a fiber beam splitter. A variable magnetic field of up to 1.5 T was applied along the crystal *c* axis using a home-built superconducting solenoid.

The inhomogeneous linewidth of the nuclear-spin transition was measured using continuous-wave Raman heterodyne detection [33]. Frequency-swept microwave tones from a tracking generator (Anritsu) were amplified and applied to the sample. The coherence generated on the $|1'\rangle_g \rightarrow |2'\rangle_g$ nuclear-spin transition was mapped to an optical coherence by applying a continuous-wave laser to the $|2'\rangle_g \rightarrow |1'\rangle_e$ optical transition at frequency ν_0 , which resulted in coherent Raman scattering on the $|1'\rangle_g \rightarrow |1'\rangle_e$ optical transition at ν_r . This signal was detected on the transmitted optical beam as a beat at the microwave transition frequency ($\nu_0 - \nu_r$) using an InGaAs photodiode.

The nuclear-spin coherence was measured using two-pulse spin echoes. Coherent manipulation on the nuclear-spin state was performed with both direct microwave excitation and all-optical excitation with bichromatic Raman pulses [34–37]. The ions were first initialized into the $|1'\rangle_g$ state via optical pumping on the $|2'\rangle_g \rightarrow |1'\rangle_e$ transition. For direct manipulation, the echo sequence was performed using tones generated by a microwave source tuned to the $|1'\rangle_g \rightarrow |2'\rangle_g$ nuclear spin transition. Pulses were generated using microwave switches (Minicircuits ZASWA-2-50DR+) with typical π pulse lengths of 100 μ s. For all-optical spin echoes, the nuclear-spin transition was coherently manipulated via the shared excited state $|1'\rangle_e$ by applying bichromatic pulses to the $|2'\rangle_g \rightarrow |1'\rangle_e$ and $|1'\rangle_g \rightarrow |1'\rangle_e$ transitions as depicted in Fig. 1(c). Typical spin π pulses for the all-optical sequence were 8 μ s. The two optical frequencies were generated by driving a fiber-based phase modulator with a microwave source tuned to the nuclear-spin transition frequency. The relative power of the two optical frequencies was chosen to maximize the echo signal. The resulting spin echo was optically detected via Raman heterodyne scattering by applying a readout pulse to the $|2'\rangle_g \rightarrow |1'\rangle_e$ transition at the time of the echo. The signal was detected as a beat on the probe laser at the nuclear-spin transition frequency.

Nuclear-spin coherence measurements were performed at approximately 700 mK. These measurements were done in transmission through a 2-mm-thick *a*-cut sample with $\mathbf{k} \perp c$. **B.** The polarization of the input light was set using a fiber polarization controller to maximize the echo signal. A variable magnetic field was applied to the crystal using a set of home-built superconducting Helmholtz coils. For the direct microwave measurements, the magnetic field was applied along the *c* axis. For the all-optical measurements, the magnetic field was applied $\sim 20^\circ$ from the *c* axis. As described in Sec. IV,

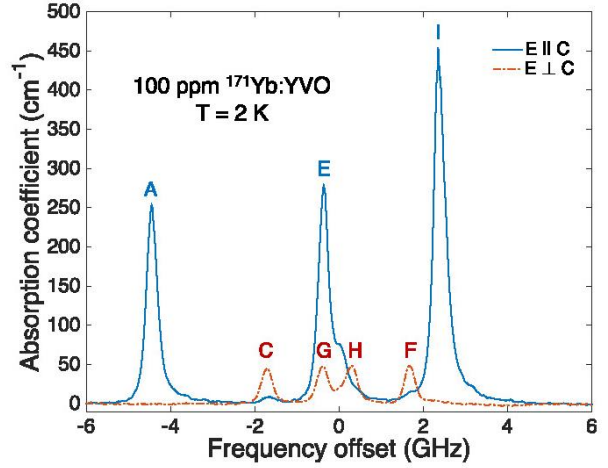


FIG. 2. Optical-absorption spectra of the $^2F_{7/2}(0) \rightarrow ^2F_{5/2}(0)$ transition of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ at 2 K and zero applied magnetic field for light polarized parallel (solid blue) and perpendicular (dashed red) to the crystal *c* axis.

this was done to help equalize the strengths of the optical transitions used in the measurement.

IV. OPTICAL AND SPIN PROPERTIES OF $^{171}\text{Yb}:\text{YVO}_4$

A. Optical-absorption spectroscopy

The zero-field absorption spectra for the $^2F_{7/2}(0) \rightarrow ^2F_{5/2}(0)$ transition of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ at 2 K is shown in Fig. 2. We observed narrow inhomogeneous linewidths [the average full width at half maximum (FWHM) is 275 MHz], which allowed us to resolve and address individual optical-hyperfine transitions. For $\mathbf{E} \parallel c$, we observed three resolved transitions with a peak absorption coefficient for the strongest transition of 450 cm^{-1} . For $\mathbf{E} \perp c$, we observed four resolved transitions with a peak absorption of 50 cm^{-1} . The corresponding transitions on the energy diagram are labeled in Fig. 1(b). The strong polarization selection rules between the optical hyperfine transitions observed in Fig. 2 are consistent with those derived for electric-dipole transitions based on the site's point-group symmetry [38].

We observed a peak at zero detuning, which corresponds to the presence of zero-spin isotope in the sample (measured to be <10 ppm from SIMS). We also noted the presence of additional satellite lines due to the 173 isotope.

The ground-state Zeeman and hyperfine tensors of $^{171}\text{Yb}^{3+}:\text{YVO}_4$ have been determined using electron paramagnetic resonance [30], so a description of the system requires finding the corresponding values for the excited state. For a uniaxial crystal, this reduces to four parameters: the components of $\mathbf{g}$ and $\mathbf{A}$, parallel and perpendicular to the crystal symmetry axis. The values for $\mathbf{A}$ can be determined by the energy-level structure in the absence of a magnetic field, while $\mathbf{g}$ can be determined from the energy-level structure as magnetic fields are applied parallel and perpendicular to the crystal's *c* axis.

Fitting to the energy-level splittings extracted from the absorption spectra, we find agreement with previously published

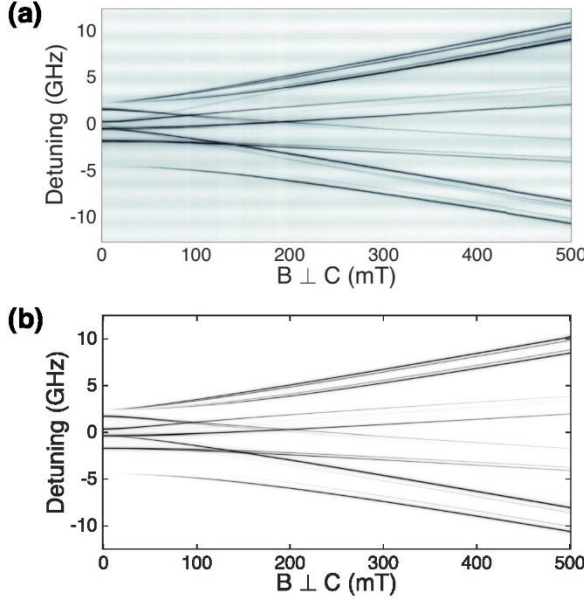


FIG. 3. (a) Typical high-resolution absorption spectra for a magnetic field ramp with $B, \mathbf{k} \perp c$ and $\mathbf{E} \perp c$ showing resolved optical hyperfine transitions. Darker regions correspond to higher absorption. (b) Simulated absorption spectra using the experimentally determined spin Hamiltonian for magnetic field ramp with $B, \mathbf{k} \perp c$ and $\mathbf{E} \perp c$. The simulated absorption spectra take into account a slight misalignment ($\sim 1^\circ$) between the crystal a axis and the applied magnetic field.

data for the ground-state $\mathbf{A}$ tensor [30] ($A_{\parallel}^g/h = -4.82$ GHz, $A_{\perp}^g/h = 0.675$ GHz) and we determine the principal values of the excited-state hyperfine tensor to be $A_{\parallel}^e/h = 4.86 \pm 0.05$ GHz and $A_{\perp}^e/h = 3.37 \pm 0.05$ GHz.

The excited-state $\mathbf{g}$ tensor was determined by measuring the frequency of the optical transitions with magnetic fields applied parallel and perpendicular to the crystal's c axis. Figure 3(a) shows an example of one such measurement in which the absorption was recorded while the magnetic field perpendicular to the crystal c axis was continuously ramped. By fitting to the energy levels extracted from this spectra and similar measurements for other field orientations, we determine $g_{e,\parallel} = 2.51 \pm 0.1$ and $g_{e,\perp} = 1.7 \pm 0.1$. Figure 3(b) shows the absorption spectra expected from the spin Hamiltonian, which we see enables accurate predictions of the energy-level splittings and relative transition absorption oscillator strengths in this case.

B. Optical transition strengths

The strength of the optical transitions can be characterized by assigning an oscillator strength to each individual transition. The absorption oscillator strength for a transition $|i\rangle \rightarrow |j\rangle$ for a polarized spectrum is given by [39,40]

$$f_{ij} = 4\pi\epsilon_0 \frac{m_e c}{\pi e^2 N} \sum_i \frac{9n_i}{(n_i^2 + 2)^2} \int \alpha_i(\nu) d\nu, \quad (10)$$

where ϵ_0 is the vacuum permittivity, m_e is the mass of the electron, e is the charge on the electron, c is the speed of

TABLE I. Absorption properties of the $^{171}\text{Yb}^{3+}:\text{YVO}_4$ transitions as labeled in Fig. 2, including the transition polarization [38], integrated absorption coefficient, oscillator strength, and radiative decay rate at zero magnetic field.

Trans.	Pol.	$\int \alpha(\nu) d\nu$ (GHz/cm)	f (10^{-6})	$1/\tau_{\text{rad}}$ (kHz)
A	π	97.3	5.4	1.3
C	σ	16.4	1.0	0.3
E	π	102.7	5.5	1.4
F	σ	17.4	1.1	0.4
G	σ	20.2	2.6	0.2
H	σ	19.9	2.6	0.2
I	π	189.7	4.9	1.2

light, N is the number density, and the summation is over the three orthogonal polarizations states with α_i and n_i absorption coefficient and index of refraction, respectively. For YVO_4 , $n_{\parallel} = 2.17$ and $n_{\perp} = 1.96$ at 984 nm [41].

Assuming a doping density of 100 ppm, the number density of Yb^{3+} in YVO_4 is calculated to be $N = 1.24 \times 10^{18} \text{ cm}^{-3}$, which is distributed between the four ground-state levels according to Boltzmann statistics at 2 K. The integrated absorption coefficient and corresponding oscillator strengths for the observed transitions are summarized in Table I. We measure an average oscillator strength of 5.3×10^{-6} for transitions allowed for $\mathbf{E} \parallel c$ (transitions A, E, I in Fig. 2) and 1.8×10^{-6} for transitions allowed for $\mathbf{E} \perp c$ (transitions C, F, G, H in Fig. 2).

The radiative lifetime for the $^2F_{5/2}(0) \rightarrow ^2F_{7/2}(0)$ transitions can be determined from the absorption measurements. The radiative lifetime for a transition $|j\rangle \rightarrow |i\rangle$ is related to the oscillator strength by [39,40]

$$\frac{1}{\tau_{\text{rad}}} = \frac{2\pi e^2}{\epsilon_0 m_e c} \frac{(n^2 + 2)^2}{9n} \frac{n^2}{\lambda_0^2} \frac{f_{ji}}{3}, \quad (11)$$

where n is the index of refraction, λ_0 is the wavelength in vacuum, and f_{ji} is the emission oscillator strength. The emission oscillator strength is related to the absorption oscillator strength f_{ij} by $f_{ji} = \frac{g_i}{g_j} f_{ij}$, where g_i (g_j) is the degeneracy of state $|i\rangle$ ($|j\rangle$). The calculated emission rates for the observed transitions are included in Table I. From these rates, we obtain an average radiative rate of $1/\tau_{\text{rad}} = 1/(590 \text{ } \mu\text{s})$ for the $^2F_{5/2}(0) \rightarrow ^2F_{7/2}(0)$ transitions.

C. Excited-state lifetimes

The excited-state lifetime is important for optical preparation of population among the spin states and sets the upper limit on the optical coherence time. The measured excited-state lifetime allow us to determine the optical branching ratio between the crystal-field levels, which is important in the context of Purcell enhancement in nanophotonic cavities [42]. Here, we measure the excited-state lifetime through fluorescence decay.

To avoid the problem of radiation trapping [43] observed in previous measurements of excited-state lifetimes in Yb-doped materials [22,26,44], the excited-state lifetime was measured in a nominally undoped sample of YVO_4 , which had

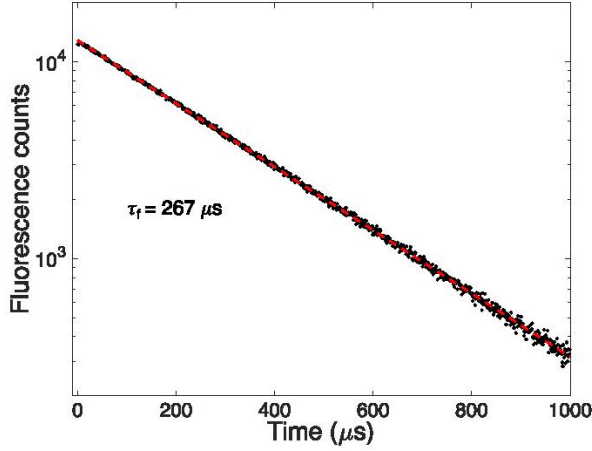


FIG. 4. Excited-state lifetime measurement via fluorescence decay. An exponential fit (dashed line) gives $\tau_f = 267 \pm 1 \mu s$.

a residual $^{171}\text{Yb}^{3+}$ concentration of approximately 2 ppm. In this sample, we did not see variations in the optical lifetime within the inhomogeneous line or other signs of radiation trapping. A typical fluorescence decay in this sample is shown in Fig. 4. Fitting to a single exponential gives a fluorescence lifetime of $\tau_f = 267 \pm 1 \mu s$. The branching ratio back to the same crystal-field level [$^2F_{5/2}(0) \rightarrow ^2F_{7/2}(0)$] is then given by $\beta = \tau_f / \tau_{\text{rad}}$, where τ_f and τ_{rad} are the fluorescence and radiative lifetimes. Using the radiative lifetime obtained from the absorption measurements, we determine the branching ratio to be $\beta = 0.45$.

We also note that in a 200- μm -thick 100-ppm sample we observed lifetimes longer than 500 μs in the center of the inhomogeneous distribution that decreased to less than 300 μs when the excitation pulse was detuned by 200 MHz from the center of the line. This behavior is attributed to radiation trapping due to the high optical depth and strong transition strengths of these ions.

D. Optical coherence measurements

To assess the ability to store quantum states in the material, we first investigate the coherence of the optical transition using two-pulse photon echoes (2PPEs). For Kramers ions, we expect a dominant source of decoherence to be magnetic fluctuations due to magnetic dipole-dipole interactions between Yb ions [45]. One way to minimize this source of decoherence is to freeze-out the electron spins by achieving a ground-state splitting much larger than $k_b T$ [45]. For $^{171}\text{Yb}^{3+}:\text{YVO}_4$, the energy-level splitting is maximized for a magnetic field along the crystal c axis. Here, we present measurements of the optical coherence in the linear Zeeman regime with the magnetic field along the c axis. While a comprehensive study is warranted to fully understand the decoherence mechanisms in this system, a large magnetic field applied parallel to c provides insight on the maximum achievable coherence times in this material and the dominant decoherence mechanisms.

Figure 5(a) shows typical photon echo decays for magnetic fields ranging from 340 mT to 1.36 T along the crystal c

axis. We observed strong nonexponential decays, which can be attributed to spectral diffusion and described by a Mims decay [46]. For heterodyne detection, the decay of the echo field is given by [46]

$$E(t_{12}) = E_0 e^{-2t_{12}/T_m^x}, \quad (12)$$

where t_{12} is the delay between the two pulses used in the photon echo experiment, x is the Mims parameter describing the spectral diffusion, and T_m is phase memory time (the time at which the echo field amplitude decays to e^{-1} of its initial value). Fits to the Mims decay are shown as solid lines in Fig. 5(a). From T_m , we can extract an effective homogeneous linewidth as $\Gamma_{\text{h,eff}} = (\pi T_m)^{-1}$. The effective linewidth as a function of applied magnetic field along the c axis is shown in Fig. 5(b).

We observed a decrease in the linewidth with applied magnetic field from ~ 5.5 kHz at 340 mT to ~ 3 kHz at 1.5 T, which was the maximum magnetic field achievable for this measurement. The reduction in linewidth for increasing magnetic field is expected for dephasing dominated by Yb-Yb spin flips and similar to that observed in other Kramers ions [45,47]. At the highest magnetic fields, we saw that the coherence no longer increased with applied field. The nonexponential decay and saturation of coherence time in the high-field limit are typical signs of the superhyperfine limit [48]. In this limit, magnetic fluctuations due to the electron spins are effectively frozen out and the main contribution to dephasing is interactions with the nuclei of the host material.

We note that recent work in $^{171}\text{Yb}^{3+}:\text{Y}_2\text{SiO}_5$ [20] and $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ [49] demonstrated an increase in coherence time due to reduced sensitivity to magnetic fluctuations at zero first-order Zeeman (ZEFOZ) points at $\mathbf{B} = 0$. While we did not explore the low-field regime in this work, Eq. (1) predicts similar zero-field ZEFOZ transitions in $^{171}\text{Yb}^{3+}:\text{YVO}_4$ between levels $|3\rangle_g$ and $|4\rangle_g$ of the ground state and $|1\rangle_e$ and $|2\rangle_e$ of the excited state.

E. Nuclear-spin measurements

The coherence times of the $^2F_{7/2}(0)$ nuclear-spin transitions will determine the feasibility of long-term quantum information storage in this system. In this section, we present measurements on the inhomogeneous linewidth and coherence properties of the $|1'\rangle_g \rightarrow |2'\rangle_g$ nuclear-spin transition in the linear Zeeman regime.

The inhomogeneous broadening of the nuclear-spin transition was measured using continuous-wave Raman heterodyne spectroscopy [33]. Figure 6 shows a typical trace of the normalized Raman heterodyne signal power as the microwave frequency is swept across the resonance. Fitting this peak to a Lorentzian gives a FWHM of 250 kHz, which serves as an upper bound on the inhomogeneous broadening of the spin transition since the width of the observed signal can be power broadened by the Rabi frequencies of the optical and microwave fields used in the measurement [50]. The inhomogeneity of the nuclear-spin transition can be attributed to variations in the crystal field due to strain and defects in the crystal and variations in the local magnetic field arising from spin-spin interactions [51], as well as inhomogeneity of the applied magnetic field along the beam path. This measurement

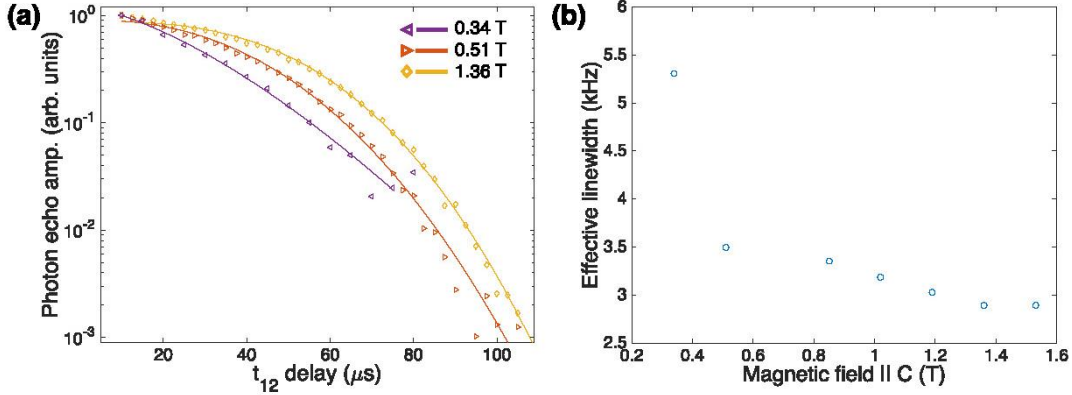


FIG. 5. (a) Typical photon echo decays for $B \parallel c$ showing an increase of coherence time and strong nonexponential decays with increasing magnetic field. Fits to a Mims decay are shown for each field value as a solid line (see main text for details). (b) Effective linewidth extracted from the fits to the photon echo decays for $B \parallel c$.

was done with a field of 440 mT along c , but is typical of what was obtained for other magnetic field amplitudes applied along this direction.

The nuclear-spin coherence was measured by spin-echo decays with direct microwave manipulation of the $|1'\rangle_g \rightarrow |2'\rangle_g$ spin transition and optical detection via coherent Raman scattering. Figure 7 shows typical nuclear-spin echo decays for increasing magnetic fields along the c axis. For the higher field decays, we observed nonexponential decays resulting from time-varying dephasing mechanisms that can again be described by the Mims decay using Eq. (12). We measured coherence times of 250 μ s at 60 mT that increased up to 6.6 ms at a field of 440 mT, which was the maximum achievable magnetic field for the experimental configuration at the time of the measurement. Time-resolved measurements of the decay of the area of spectral holes prepared in the inhomogeneous line [51] gave spin-relaxation times longer than 200 ms in this field configuration, indicating that these coherence times are not lifetime limited.

F. All-optical spin coherence measurements

In addition to direct microwave excitation of the nuclear spins, we are interested in performing coherent all-optical control on the nuclear spins. All-optical control allows us to take advantage of relatively strong optical transitions to perform faster manipulations on the spin. This approach also removes the need for a microwave circuit to be incorporated next to the sample, which reduces the complexity of the experimental setup and prevents additional heating of the sample through the microwave excitation. As an initial demonstration of the potential for all-optical control in this system, we use an all-optical Raman echo technique [52] to measure the coherence of the nuclear-spin transition. The $|1'\rangle_g \rightarrow |2'\rangle_g$ transition is addressed by applying bichromatic pulses to the lambda system formed by the $|2'\rangle_g \rightarrow |1'\rangle_e$ and $|1'\rangle_g \rightarrow |1'\rangle_e$ optical transitions. Efficient rephasing of coherence on the spin transition using bichromatic pulses in this fashion requires that the Rabi frequencies of the two transitions of the lambda system are

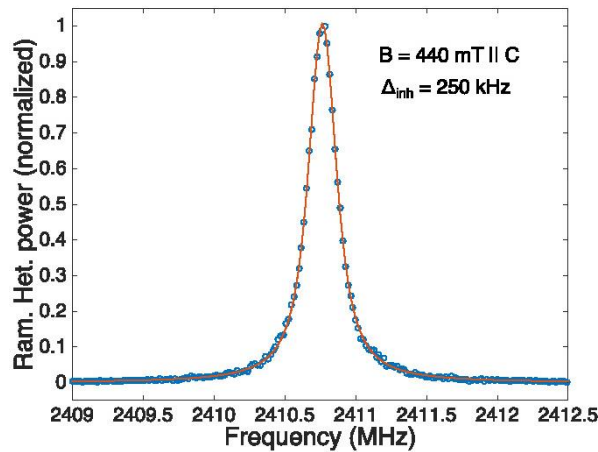


FIG. 6. Continuous-wave Raman heterodyne measurement of the nuclear-spin inhomogeneity with $B = 440 \text{ mT}$ parallel to the c axis. A Lorentzian fit gives a FWHM of 250 kHz.

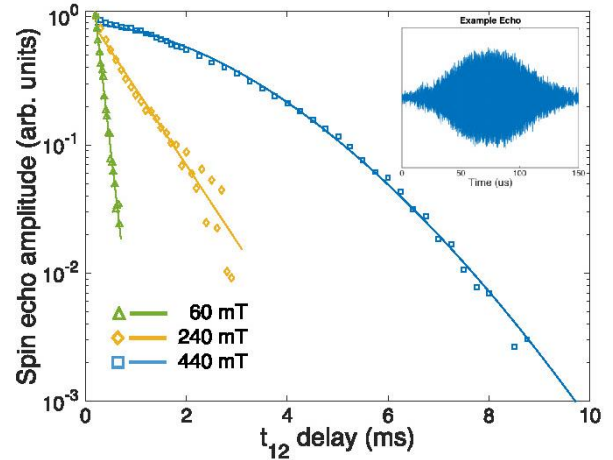


FIG. 7. Typical nuclear-spin echo decays for increasing applied magnetic field along the c axis. The echo sequence is performed with direct microwave excitation and read out optically.

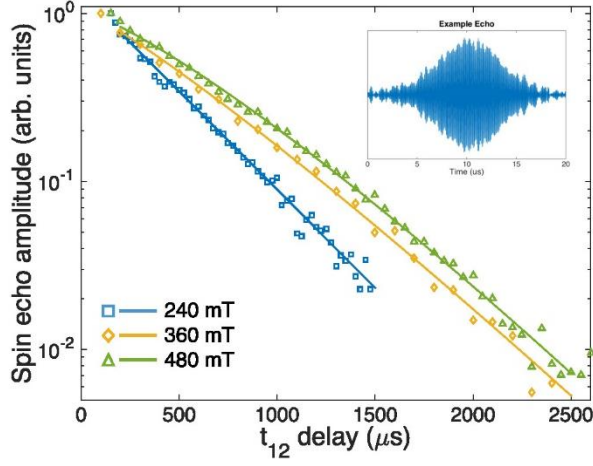


FIG. 8. Typical nuclear-spin-echo decays for increasing magnetic fields applied 20° from the c axis. Here, the entire sequence is performed using all-optical manipulation of the spins.

equal [35]. For magnetic fields applied parallel to the c axis, one transition of the lambda system is weak because the wave functions have approached separability and the optical transition cannot flip the nuclear spin. Moving the field off axis induces mixing of the nuclear and electronic states, which allows for a more favorable branching ratio between the two arms of the lambda system.

Figure 8 shows representative all-optical Raman echo decays for increasing applied magnetic fields applied 20° from the c axis. Fitting to a Mims decay to describe the observed nonexponential behavior gave spin coherence times up to 1 ms at 480 mT, which was the maximum field available for this experiment. We note that moving the field off axis increases the magnetic sensitivity of the transition and therefore we expect a decrease of the spin coherence time in this regime. This configuration also reduces the ground-state splitting, which would increase the contribution from Yb-Yb electron-spin interactions. We expect to extend this coherence time with increasing magnetic fields as observed in the optical coherence measurements.

V. SUMMARY AND CONCLUSION

In this work, we have presented measurements assessing $^{171}\text{Yb}^{3+}:\text{YVO}_4$ for use in quantum interfaces focusing on the strength of the optical transitions, the energy level structure, and the coherence properties of the optical and spin transitions.

From optical-absorption measurements, we extract oscillator strengths in the upper range of those observed in REIs and larger than those observed for $^{171}\text{Yb}^{3+}$ doped into Y_2SiO_5 and YAG [17,22]. This oscillator strength is promising for detecting and manipulating single ions coupled to nanophotonic cavities. The combination of large oscillator strengths and narrow inhomogeneous broadening in this material gives rise to exceptionally large absorption coefficients for this material. Significantly, the peak absorption of 450 cm^{-1} is within a factor of 2 of the absorption in recently studied stoichiometric rare-earth crystals [53], even though the ion concentration

is a factor of 10^4 more dilute. This absorption coefficient is promising for ensemble-based memories in bulk samples and reaching the impedance-matched regime necessary to achieve high-efficiency nanophotonic quantum memories. We observe a large branching ratio for relaxation directly to the ground state for the $^2F_{5/2}(0) \rightarrow ^2F_{7/2}(0)$ transition, which is appealing in the context of Purcell enhancement of the emission rate in a nanocavity [24,54].

The large hyperfine couplings and narrow inhomogeneous linewidths give rise to resolved optical-hyperfine transitions. This is useful for addressing and manipulating single transitions and states without additional preparation. The large nuclear-spin transition splittings are also useful in the context of off-resonance memory schemes and high-bandwidth spin-wave storage. We completed a characterization of the energy-level structure by determining the excited-state spin Hamiltonian. The knowledge of the full spin Hamiltonian is essential for designing optimal quantum interfaces because it facilitates the prediction and engineering of lambda systems or highly cyclic transitions. The symmetry of the crystal gives rise to the strong selection rules on the optical transitions. These selection rules are advantageous for engineering cyclic transitions [55], especially in the context of a nanocavity that can preferentially enhance emission along one polarization.

For protocols requiring additional nuclear-spin states, the ^{173}Yb isotope could be of interest because it has a nuclear spin of $5/2$. The knowledge of the spin Hamiltonian for the ^{171}Yb isotope allows the spin Hamiltonian for the ^{173}Yb isotope to be approximated by scaling the hyperfine splittings by the ratio of the nuclear magnetic moments of the isotopes [56].

The optical coherence times are already sufficient for use in quantum applications and are promising from the perspective of reaching transform-limited photons in a nanocavity setting. The observed spin coherence properties show potential for use in spin-wave quantum memories and for single rare-earth ion qubits. In the linear Zeeman regime, the optical coherence times are limited by the superhyperfine interaction in the material. While a higher magnetic field regime was not available for the experimental configuration at the time of measurement, we expect the spin coherence times to increase with applied magnetic field as we completely freeze-out the electron-spin contribution. Further extension of the nuclear-spin coherence time is predicted through the use of dynamic decoupling techniques [7]. We note that the doping density used in these measurements (100 ppm) is relatively high compared to many of the materials used for REI quantum technologies. We expect that by going to lower doping density samples we will reduce the contribution from Yb spin-spin interactions and observe longer optical and spin coherence times in the low-field regime. Furthermore, by moving to lower temperatures, we can hope to freeze-out the electron spins at lower magnetic fields. While this work focused on the optical and nuclear-spin coherence properties in the linear Zeeman regime, we calculate that a zero-field ZEFOZ transition exists for one of the ground-state transitions, which is expected to lead to an enhancement of coherence [20,49]. This configuration would also have the advantage of a strong electron-spin transition between the ground states. Future studies are warranted to investigate the spin coherence properties of this material at lower

doping densities, temperatures, and different magnetic field regimes.

In summary, we find that $^{171}\text{Yb}^{3+}:\text{YVO}_4$ is a promising material for REI-based quantum interfaces, such as ensemble-based quantum memories, microwave-to-optical transduction, and single REIs in nanophotonic cavities.

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- [1] H. J. Kimble, *Nature (London)* **453**, 1023 (2008).
 - [2] T. E. Northup and R. Blatt, *Nat. Photonics* **8**, 356 (2014).
 - [3] J. L. O'Brien, A. Furusawa, and J. Vučković, *Nat. Photonics* **3**, 687 (2009).
 - [4] R. W. Andrews, R. W. Peterson, T. P. Purdy, K. Cicak, R. W. Simmonds, C. A. Regal, and K. W. Lehnert, *Nat. Phys.* **10**, 321 (2014).
 - [5] R. W. Equall, Y. Sun, R. L. Cone, and R. M. Macfarlane, *Phys. Rev. Lett.* **72**, 2179 (1994).
 - [6] T. Böttger, C. W. Thiel, R. L. Cone, and Y. Sun, *Phys. Rev. B* **79**, 115104 (2009).
 - [7] M. Zhong, M. P. Hedges, R. L. Ahlefeldt, J. G. Bartholomew, S. E. Beavan, S. M. Wittig, J. J. Longdell, and M. J. Sellars, *Nature (London)* **517**, 177 (2015).
 - [8] M. Rančić, M. P. Hedges, R. L. Ahlefeldt, and M. J. Sellars, *Nat. Phys.* **14**, 50 (2017).
 - [9] W. Tittel, M. Afzelius, T. Chanelière, R. Cone, S. Kröll, S. Moiseev, and M. Sellars, *Laser Photonics Rev.* **4**, 244 (2009).
 - [10] M. P. Hedges, J. J. Longdell, Y. Li, and M. J. Sellars, *Nature (London)* **465**, 1052 (2010).
 - [11] M. Sabooni, Q. Li, S. Kröll, and L. Rippe, *Phys. Rev. Lett.* **110**, 133604 (2013).
 - [12] E. Saglamyurek, N. Sinclair, J. A. Slater, K. Heshami, D. Oblak, and W. Tittel, *New J. Phys.* **16**, 065019 (2014).
 - [13] M. Gündogan, P. M. Ledingham, K. Kutluer, M. Mazzer, and H. de Riedmatten, *Phys. Rev. Lett.* **114**, 230501 (2015).
 - [14] C. Laplane, P. Jobez, J. Etesse, N. Timoney, N. Gisin, and M. Afzelius, *New J. Phys.* **18**, 013006 (2016).
 - [15] B. Lauritzen, S. R. Hastings-Simon, H. de Riedmatten, M. Afzelius, and N. Gisin, *Phys. Rev. A* **78**, 043402 (2008).
 - [16] E. Baldit, K. Bencheikh, P. Monnier, S. Briaudeau, J. A. Levenson, V. Crozatier, I. Lorgeré, F. Bretenaker, J. L. Le Gouët, O. Guillot-Noël, and P. Goldner, *Phys. Rev. B* **81**, 144303 (2010).
 - [17] S. Welinski, A. Ferrier, M. Afzelius, and P. Goldner, *Phys. Rev. B* **94**, 155116 (2016).
 - [18] A. Tiranov, A. Ortu, S. Welinski, A. Ferrier, P. Goldner, N. Gisin, and M. Afzelius, *arXiv:1712.08616*.
 - [19] H.-J. Lim, S. Welinski, A. Ferrier, P. Goldner, and J. J. L. Morton, *Phys. Rev. B* **97**, 064409 (2018).
 - [20] A. Ortu, A. Tiranov, S. Welinski, F. Fröwis, N. Gisin, A. Ferrier, P. Goldner, and M. Afzelius, *arXiv:1712.08615*.
 - [21] Z. Kis, G. Mandula, K. Lengyel, I. Hajdara, L. Kovacs, and M. Imlau, *Opt. Mater.* **37**, 845 (2014).
 - [22] T. Böttger, C. W. Thiel, R. L. Cone, Y. Sun, and A. Faraon, *Phys. Rev. B* **94**, 045134 (2016).
 - [23] H. de Riedmatten, M. Afzelius, M. U. Staudt, C. Simon, and N. Gisin, *Nature (London)* **456**, 773 (2008).
 - [24] T. Zhong, J. M. Kindem, J. G. Bartholomew, J. Rochman, I. Craiciu, E. Miyazono, M. Bettinelli, E. Cavalli, V. Verma, S. W. Nam, F. Marsili, M. D. Shaw, A. D. Beyer, and A. Faraon, *Science* **357**, 1395 (2017).
 - [25] T. Zhong, J. Rochman, J. M. Kindem, E. Miyazono, and A. Faraon, *Opt. Express* **24**, 536 (2016).
 - [26] C. Kränkel, D. Fagundes-Peters, S. T. Fredrich, J. Johannsen, M. Mond, G. Huber, M. Bernhagen, and R. Uecker, *Appl. Phys. B* **79**, 543 (2004).
 - [27] R. Wyckoff, *Crystal Structures*, 2nd ed. (John Wiley & Sons, New York, 1963).
 - [28] E. V. Pestryakov, V. V. Petrov, V. I. Trunov, A. V. Kirpichnikov, M. A. Merzliakov, A. V. Laptev, and V. N. Matrosov, *Proc. SPIE* **6054**, 60540I (2006).
 - [29] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford, 1970).
 - [30] U. Ranon, *Phys. Lett. A* **28**, 228 (1968).
 - [31] E. C. Cook, P. J. Martin, T. L. Brown-Heft, J. C. Garman, and D. A. Steck, *Rev. Sci. Instrum.* **83**, 043101 (2012).
 - [32] *Spectroscopic Properties of Rare Earths in Optical Materials*, Springer Series in Materials Science Vol. 83, edited by G. Liu and B. Jacquier (Springer-Verlag, Berlin, 2005).
 - [33] C. Wei, S. A. Holmstrom, N. B. Manson, J. P. D. Martin, X. F. He, and P. T. H. Fisk, *Appl. Magn. Reson.* **11**, 521 (1996).
 - [34] T. Blasberg and D. Suter, *Opt. Commun.* **109**, 133 (1994).
 - [35] T. Blasberg and D. Suter, *Phys. Rev. B* **51**, 6309 (1995).
 - [36] A. Walther, A. N. Nilsson, Q. Li, L. Rippe, and S. Kröll, *Eur. Phys. J. D* **70**, 166 (2016).
 - [37] D. Serrano, J. Karlsson, A. Fossati, A. Ferrier, and P. Goldner, *Nat. Commun.* **9**, 2127 (2018).
 - [38] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (MIT Press, Cambridge, MA, 1963).
 - [39] B. Di Bartolo, *Optical Interactions in Solids* (Wiley, New York, 1968).
 - [40] B. Henderson and G. Imbush, *Optical Spectroscopy of Inorganic Solids* (Oxford University Press, New York, 2006).
 - [41] H.-S. Shi, G. Zhang, and H.-Y. Shen, *J. Synth. Cryst.* **30**, 85 (2001).
 - [42] E. M. Purcell, *Phys. Rev.* **69**, 681 (1946).
 - [43] D. S. Sumida and T. Y. Fan, *Opt. Lett.* **19**, 1343 (1994).

- [44] V. E. Kisel, S. E. Troshin, N. S. Tolstik, V. G. Shcherbitsky, N. V. Kuleshov, V. N. Matrosov, T. S. Matrosova, and M. I. Kupchenko, *Opt. Lett.* **29**, 2491 (2004).
- [45] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, *Phys. Rev. B* **73**, 075101 (2006).
- [46] W. Mims, *Phys. Rev.* **168**, 370 (1968).
- [47] Y. Sun, C. W. Thiel, R. L. Cone, R. W. Equall, and R. L. Hutcheson, *J. Lumin.* **98**, 281 (2002).
- [48] J. Ganem, Y. P. Wang, D. Boye, R. S. Meltzer, W. M. Yen, and R. M. Macfarlane, *Phys. Rev. Lett.* **66**, 695 (1991).
- [49] J. V. Rakonjac, Y.-H. Chen, S. P. Horvath, and J. J. Longdell, [arXiv:1802.03862](https://arxiv.org/abs/1802.03862).
- [50] P. T. H. Fisk, X. F. He, K. Holliday, and N. B. Manson, *J. Lumin.* **45**, 26 (1990).
- [51] R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Solids Containing Rare Earth Ions*, edited by A. A. Kaplyanskii and R. M. Macfarlane (Elsevier Science BV, North-Holland, New York, 1987), pp. 51–184.
- [52] J. Karlsson, N. Kunkel, A. Ikesue, A. Ferrier, and P. Goldner, *J. Phys.: Condens. Matter* **29**, 125501 (2017).
- [53] R. L. Ahlefeldt, M. R. Hush, and M. J. Sellars, *Phys. Rev. Lett.* **117**, 250504 (2016).
- [54] T. Zhong, J. M. Kindem, E. Miyazono, and A. Faraon, *Nat. Commun.* **6**, 8206 (2015).
- [55] J. G. Bartholomew, R. L. Ahlefeldt, and M. J. Sellars, *Phys. Rev. B* **93**, 014401 (2016).
- [56] R. J. Elliott and K. W. H. Stevens, *Proc. R. Soc. London A* **218**, 553 (1953).

CHAPTER 8

OPTICAL SPECTROSCOPY AND DECOHERENCE STUDIES OF
ERBIUM-DOPED $\text{Y}_3\text{Al}_5\text{O}_{12}$ AT 1.5 MICRONSContribution of Authors and Co-Authors

Manuscript in Chapter 8

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Contributions: Prepared and synthesized material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

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Optical spectroscopy and decoherence studies of erbium-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ at 1.5 microns

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We report on the optical and magnetic properties of the 1.5 micron $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition of erbium-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ at cryogenic temperatures for quantum information, photonic signal processing, and spectral filtering applications. We measured the crystal field energy levels of the $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ states and characterized the linear and quadratic Zeeman shifts and thermal broadening and shift for the lowest $^4\text{I}_{15/2}$ to lowest $^4\text{I}_{13/2}$ transition relevant for applications. Results and analysis of the temperature and magnetic field dependence of the coherence lifetime and spectral diffusion decoherence processes are presented. We compare these dependencies with a model that allows us to identify the processes responsible for decoherence and spectral diffusion under different operation conditions. We find that two processes limit coherence, spin flip-flop processes at low magnetic fields and direct phonon processes at high magnetic field. Furthermore, we find that unlike many other Er^{3+} -activated materials, the coherence lifetime only weakly depends on the crystal orientation for the conditions studied here, suggesting that this system is well suited for applications using powders or transparent ceramics where the individual grains are randomly oriented. Overall, the narrowest linewidth observed is 6.5 kHz at a temperature of 1.6 K and a magnetic field of 6 T. Finally, we show that the inhomogeneous linewidth can be increased from 8 GHz up to 255 GHz in the mixed garnet $\text{Y}_{1.5}\text{Lu}_{1.5}\text{Al}_5\text{O}_{12}$ material, providing a significantly larger bandwidth for applications that employ spectral multiplexing.

In addition to traditional luminescence applications, rare-earth-ion-doped materials are one of the leading physical systems in the fields of photonic signal processing [1–3] and quantum information[4–7]. They are particularly attractive due to their long optical coherence lifetimes and the ability to spectrally tailor their inhomogeneously broadened absorption lines. For example, atomic frequency comb based quantum memories as well as classical RF spectrum analyzers rely on the ability to create high finesse frequency gratings within the inhomogeneously broadened absorption lines. These same properties also make them ideal candidates for ultra-narrow, high-attenuation spectral filters [8–13] as well as optical frequency references for laser local oscillators [14–17].

Of all the rare-earth ions, erbium is particularly appealing for applications because its $^4\text{I}_{15/2}$ to $^4\text{I}_{13/2}$ transition occurs at 1.5 microns i.e. within the C-band of current telecommunications technology. This would allow erbium-based devices to integrate seamlessly into existing telecommunications infrastructure. Consequently, interest in developing erbium-based quantum information processing technologies has grown rapidly in recent years [4, 7]. However, no single erbium-doped material can meet the requirements of different applications and implementations. Therefore, it is essential to characterize new materials to assess their suitability for different information processing approaches and to provide a diverse toolbox of available materials. With this motivation, we

present a spectroscopic characterization of the promising system erbium-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ ($\text{Er}^{3+}:\text{YAG}$). While only a few initial studies of coherence properties have been reported previously, [1, 18] $\text{Er}^{3+}:\text{YAG}$ is a well-known commercially produced laser crystal that is extensively used in surgical and dental applications. The YAG host crystal offers many desirable properties for photonic applications, and thulium-doped YAG has proven to be one of the most successful systems for high-bandwidth signal processing applications [1–3].

Most previous studies of $\text{Er}^{3+}:\text{YAG}$ have focused on magnetism, [19, 20] laser applications, [21, 22] and crystal field structure [23, 24]. Here, we carry out high-precision, low-temperature measurements of the electronic structure of the $^4\text{I}_{15/2}$ ground and $^4\text{I}_{13/2}$ excited Stark multiplets as well as the linear and quadratic Zeeman interaction that affects decoherence mechanisms for the lowest-to-lowest transition between these states. We also present a detailed study and analysis of the magnetic field and temperature dependence of the decoherence dynamics for the lowest-to-lowest transition relevant to optical and quantum signal processing applications.

CRYSTAL FIELD LEVEL STRUCTURE OF $^4I_{15/2}$ AND $^4I_{13/2}$

As the first step in characterizing $\text{Er}^{3+}:\text{YAG}$, we measured the electronic structure of the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets. While there have been a number of past studies of the energy levels in $\text{Er}^{3+}:\text{YAG}$ as well as fitting of crystal field parameters, [18, 20, 23–30] there still remains some disagreement in the literature between different reported values for the positions. High resolution optical absorption spectra were measured to determine the $^4I_{13/2}$ energy level structure and transition absorption coefficients α , while fluorescence spectra were measured to determine the $^4I_{15/2}$ energy level structure and the relative relaxation branching ratios β to each level from $^4I_{13/2}$. All measurements were performed on a 0.1% $\text{Er}^{3+}:\text{YAG}$ crystal (Scientific Materials Corp., Bozeman, MT) held in a Cryomech PT405 closed-cycle optical cryostat at a temperature of 3.4 K measured at the crystal. The energy level structure of $^4I_{15/2}$ was determined by exciting the sample with a broadband tungsten-halogen lamp and recording the fluorescence spectra using a SPEX1000M spectrometer with 3 GHz resolution and a liquid-nitrogen-cooled germanium photodiode. The structure of $^4I_{13/2}$ was determined from absorption measurements using the same tungsten-halogen source and an Advantest Q8347 optical spectrum analyzer with 900 MHz frequency resolution. A calibrated laser source was used to determine the absolute frequency of both the spectrometer and spectrum analyzer. The resulting energy level structure is shown in Table I along with the values reported in Refs. [18, 24, 26–28, 30].

EXCITED-STATE LIFETIME OF $^4I_{13/2}$

For applications that rely on long-lived optical coherence, the transition between the lowest crystal field levels of the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets is of most interest since higher lying energy levels generally decay rapidly through spontaneous emission of acoustic phonons. Thus, when an Er^{3+} ion is optically excited to an upper level of $^4I_{13/2}$, it relaxes to the lowest level $^4I_{13/2}(Y_1)$ on the timescale of nanoseconds or faster, and then decays radiatively to all $^4I_{15/2}(Z_i)$ levels over the timescale of milliseconds. The excited state lifetime T_1 ultimately limits the maximum coherence lifetime T_2 through the relation $T_2 \leq 2T_1$. The $^4I_{13/2}$ in $\text{Er}^{3+}:\text{YAG}$ has previously been reported to be 6.9 ms by Payne et al. [22] and 10 ms by Zhang et al. [18]. The lifetime has also been previously measured for the closely related mixed garnet $\text{Er}^{3+}:\text{Y}_{1.5}\text{Lu}_{1.5}\text{Al}_5\text{O}_{12}$, where a value of 9.9 ms was reported, [31] suggesting that the value in $\text{Er}^{3+}:\text{YAG}$ is nearer to the 10 ms indicated by Zhang et al.

To determine the $^4I_{13/2}$ excited-state lifetime, we measured time-resolved fluorescence decays as well as spec-

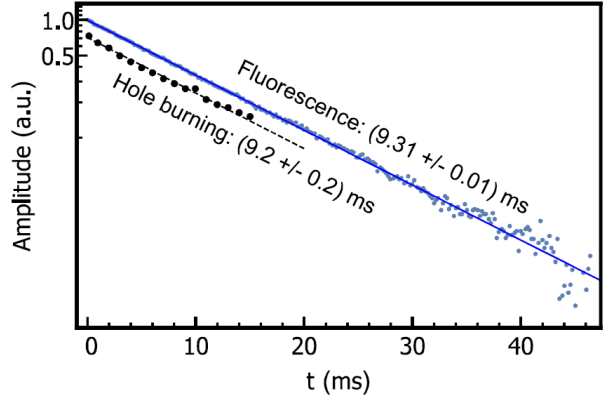


FIG. 1. Fluorescence decay and decay of spectral hole area of the $^4I_{13/2}$ (Y_1) excited state. Both experimental data sets are fit to an exponential decay to extract the levels lifetime

tral hole decays at a temperature of 3 K. For the fluorescence measurements, the diode laser was tuned into resonance with one of the upper $^4I_{13/2}$ levels and gated with an amplitude modulator to provide a short ($< \mu\text{s}$) excitation pulse. The resulting $1.5 \mu\text{m}$ fluorescence decay shown in Fig. 1 was detected using a fast ($> \text{MHz}$) amplified photodiode. Fitting the exponential decay indicated a lifetime of 9.3 ms. To further verify the observed lifetime, we carried out time-resolved spectral hole decay measurements. In particular, it is well known that fluorescence lifetime measurements can give artificially long values due to the effects of reabsorption of the resonant fluorescence, an effect known as radiation trapping [32]. Consequently, one potential explanation for the discrepancy between the results of Payne et al. and the results of Zhang et al. and those reported here could be radiation trapping. To investigate this possibility, spectral hole burning techniques were also used since they have been shown to be much less sensitive to radiation trapping due to the frequency selective nature of the measurement [33]. For these experiments, a gated laser pulse resonant with the $Z_1 \rightarrow Y_1$ transition is used to prepare a narrow spectral hole due to frequency-selective excitation of Er^{3+} ions into the excited state. After a fixed delay, the change in spectral hole depth due to population relaxation is recorded by scanning the laser frequency across the entire hole spectrum, mapping out the population decay as a function of the readout delay. The resulting exponential decay is plotted in Fig. 1, indicating a lifetime of 9.2 ms, in good agreement with the fluorescence decay measurements.

	Hellwege 1966 [26]	Zverev [27]	Gruber [24]	Devi [28]	Zhang [18]	Ter-Gabrielyan [30]	This Work	
$^4\text{I}_{15/2}$	0	0	0	0	0	0	0.063	
	26.6	23	22	22	22	22	22.6	0.67
	58.4	60	60	61	61	61	61.1	0.009
	78.8	78	80	79	-	79	79.6	0.043
	422.8	426	417	417	-	418	417.8	0.137
	436.1	433	432	430	-	425	431.3	0.004
	530.1	527	-	526	-	527	526.7	0.039
	574.3	572	574	573	-	573	574.0	0.036
$^4\text{I}_{15/2}$	-	6549	6549	-	6549	6548	6547.5	2.48
	-	6598	6599	-	6599	6598	6597.1	2.71
	-	6603	6606	-	6606	6604	6603.7	3.68
	-	6788	6786	-	6786	6785	6784.1	0.73
	-	6807	6805	-	6806	6804	6803.6	2.20
	-	-	6883	-	-	6823	6824.7	0.10
	-	6887	6889	-	6886	6886	6883.6	1.27

TABLE I. Crystal field levels of the ground $^4I_{15/2}(Z_i)$ and excited state $^4I_{13/2}(Y_j)$ multiplets in 0.1 % $\text{Er}^{3+}:\text{YAG}$ (in cm^{-1}), including previously reported values from Refs.[18, 26–28, 30?]. The last column shows our measurements of the relative strength of the transitions, with the branching ratio (i.e. the relative intensity I/I_{tot}) for the $^4I_{13/2}(Y_1) \rightarrow ^4I_{15/2}(Z_i)$ fluorescence and the peak absorption coefficient in cm^{-1} for the $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_j)$ absorption transitions.

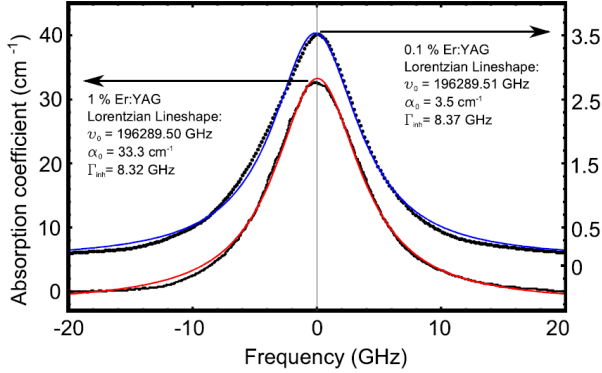


FIG. 2. Absorption spectrum of the $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_1)$ transition in 0.1% $\text{Er}:\text{YAG}$ and 1% $\text{Er}:\text{YAG}$ at zero field and 3.4 K. The peak absorption coefficients are 3.5 cm^{-1} (0.1% $\text{Er}:\text{YAG}$) and 33.3 cm^{-1} (1% $\text{Er}^{3+}:\text{YAG}$).

INHOMOGENEOUS BROADENING OF THE $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_1)$ TRANSITION

The inhomogeneous broadening Γ_{inh} of the optical transition is a key parameter for optical signal processing applications since it determines the maximum signal bandwidth that the transition may process as well as the spectral multiplexing capacity of the material. Rare-earth-ion transitions in YAG often exhibit large inhomogeneous broadenings of $>10 \text{ GHz}$, [1] and the linewidth for the $Z_1 \rightarrow Y_1$ transition of $\text{Er}^{3+}:\text{YAG}$ has previously been reported as 20 GHz by Zhang et al. [18] and 30

GHz by Sun [1]. Our measured laser absorption spectra for both 0.1% $\text{Er}^{3+}:\text{YAG}$ and 1% $\text{Er}^{3+}:\text{YAG}$ are shown in Fig. 2, revealing a much narrower inhomogeneous linewidth of only 8.3 GHz for both samples. Interestingly, there is no measurable increase in the inhomogeneous linewidth with dopant concentration, indicating that the strain caused by the dopant ion is not the dominant broadening source even at the 1% doping level. The transition has a center frequency of 196289.5 GHz and a Lorentzian lineshapes with peak absorption of 3.5 cm^{-1} for the 0.1% crystal and 35 cm^{-1} for the 1% crystal.

Because the inhomogeneous linewidth was significantly narrower in this material than what was expected, we also investigated approaches for increasing the linewidth to meet the needs of potential spectral multiplexing applications. [34] It is known that the static strain in the crystal lattice, and the resulting doping the material with ions that have a large ionic radius mismatch with the normal host constituents. [35] This approach has been demonstrated for $\text{Tm}^{3+}:\text{YAG}$ by introducing Lu^{3+} into the lattice, producing $>100 \text{ GHz}$ of broadening when the crystal is grown with equal amounts of Y^{3+} and Lu^{3+} . [36] Consequently, we examined the inhomogeneous broadening for the material $\text{Er}^{3+}:\text{Y}_{1.5}\text{Lu}_{1.5}\text{Al}_5\text{O}_{12}$ ($\text{Er}^{3+}:\text{YLuAG}$). This material has also been previously studied for $\text{Er}^{3+}:\text{YAG}$ laser applications to provide increased gain bandwidths. [31] The absorption spectrum of the $Z_1 \rightarrow Y_1$ transition of 0.05% $\text{Er}^{3+}:\text{YLuAG}$ at 3 K is shown in 3. We find that the absorption is shifted to higher frequency by 249 GHz and has a much broader full-width at half maximum of 255 GHz , a nearly two or-

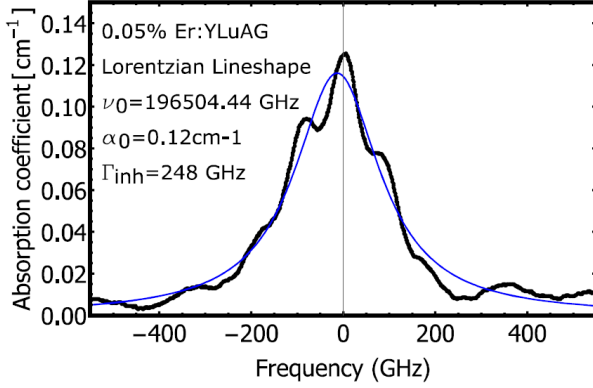


FIG. 3. Absorption spectrum of the ${}^4I_{15/2}$ (Z_1) $\rightarrow$ ${}^4I_{13/2}$ (Y_1) transition in 0.05% $\text{Er}^{3+}:\text{YLuAG}$.

ders of magnitude increase relative to $\text{Er}^{3+}:\text{YAG}$. However, unlike $\text{Tm}^{3+}:\text{YLuAG}$ where the broadened absorption is smooth and exhibits no structure, [36] the transition in $\text{Er}^{3+}:\text{YLuAG}$ shows clear structure and appears to be composed of at least five overlapping peaks with individual widths on the order of ≈ 100 GHz each. This suggests that Er^{3+} ions with different local distributions of neighboring Y^{3+} and Lu^{3+} are partially resolved in the spectrum. A similar effect has been previously observed for Cr^{3+} ions in YLuAG, [37] although not for Ce^{3+} ions in the same crystals [38].

THERMAL BROADENING AND FREQUENCY SHIFT

The temperature dependence of the transition energy and linewidth is important for spectral filtering and optical frequency reference applications since it directly affects the thermal stability of the system. [8–17] Consequently, we measured the broadening and frequency shift of the $Z_1 \rightarrow Y_1$ transition in 1% $\text{Er}^{3+}:\text{YAG}$ over a wide temperature range of 3 K to 87 K, with the results plotted in 4. The transition shifts to lower frequency by only 18 GHz over this range, and the absorption line becomes homogeneously broadened for temperatures above 50 K. To describe the observed thermal shift and broadening, we employ a simple semi-empirical model for the effect of phonon excitation to upper crystal field levels in ${}^4I_{15/2}$ and ${}^4I_{13/2}$. For this direct phonon process, both the frequency shift and broadening are proportional to the occupation of the resonant phonon modes, resulting in a shift with the form

$$E(T) = E_0 + \sum_i \frac{a_i}{e^{\frac{\Delta_i}{kT}} - 1} \quad (1)$$

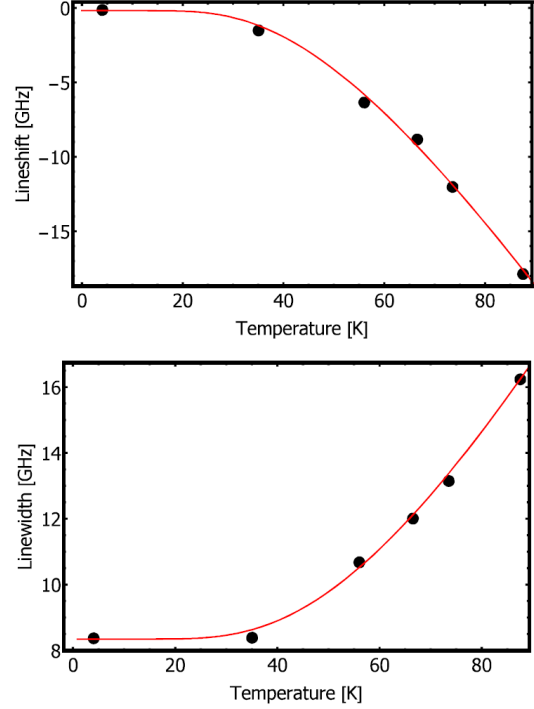


FIG. 4. Observed thermal frequency shift (top) and thermal broadening (bottom) of the ${}^4I_{15/2}$ (Z_1) $\rightarrow$ ${}^4I_{13/2}$ (Y_1) transition for 0.1% $\text{Er}^{3+}:\text{YAG}$.

and a broadening of

$$\Gamma(T) = \Gamma_{inh} + \sum_i \frac{b_i}{e^{\frac{\Delta_i}{kT}} - 1} \quad (2)$$

where the summations are over all crystal field levels in both ${}^4I_{15/2}$ and ${}^4I_{13/2}$ with energies Δ_i relative to the lowest level. [39?] Due to the relatively weak temperature dependence observed in Fig. 4 and the large number of potential resonant phonon frequencies, we find that Eqs. 1 and 2 describe the measured dependence well if only a single effective phonon mode is used, as shown by the solid lines in Fig. 4. Using this approach, we obtain values of $a = -82$ GHz with $\Delta = 110 \text{ cm}^{-1}$ for the frequency shift, and $b = 59$ GHz with $\Delta = 130 \text{ cm}^{-1}$ for the broadening, where the values of Δ extracted from the fitting represent empirical effective values.

LINEAR AND QUADRATIC ZEEMAN EFFECTS

The $4f^{11}$ configuration of Er^{3+} ion has an odd number of electrons and therefore all electronic states must be at least doubly degenerate in the absence of a magnetic field. For the D_2 point symmetry of the Er^{3+} sites

in YAG, all other degeneracy is removed by the crystal field so that when a magnetic field is applied, both ground and excited state crystal field levels split into two levels due to the Zeeman effect. As the field strength is increased, mixing between crystal field levels further shifts the energy levels, giving rise to the second order quadratic Zeeman effect. The linear electronic Zeeman shift in Er^{3+} -doped materials is generally quite large for the $^4I_{15/2}$ and $^4I_{13/2}$ states due to the large total angular momentum, exceeding the inhomogeneous broadening at relatively weak magnetic fields (around 0.1 T), while the quadratic Zeeman effect tends to become important at fields of a few Tesla for materials with typical crystal field level splittings on the order of tens of cm^{-1} . Consequently, characterizing the linear and quadratic Zeeman shifts is required before performing any other experiment involving magnetic fields in order to identify the different transitions observed and to predict the precise transition frequency for a specific field magnitude and orientation. Furthermore, measuring the Zeeman effect is also essential for understanding the strong magnetic dipole-dipole interactions between Er^{3+} ions and other ions or nuclear spins in the lattice.

To characterize the Zeeman effect for the $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_1)$ (lowest-to-lowest) transition, we measured the absorption spectrum for different magnetic field strengths and orientations. For these measurements, the sample is cooled in an Oxford Spectromag cryostat, with spectra collected at temperatures of 1.6 K with the sample in superfluid liquid helium and 5.0 K with the sample in a constant flow of He exchange gas. A superconducting solenoid provides magnetic fields up to 7 T. In order to record high-resolution absorption spectra, we use a tunable Newport velocity external cavity diode laser with ≈ 200 kHz linewidth that is scanned between 1522 and 1530 nm at a scan rate of 5 nm/sec. We calibrate the scan using a fiber Mach-Zehnder interferometer with a free spectral range of 7.94 GHz. The absolute frequency of the velocity laser is measured by observing a beat signal with a second laser whose frequency is monitored using a wavemeter (Burleigh WA-1500). Finally, the transmission through the sample is measured using a New Focus NF 1811 photo receiver.

While the Er^{3+} ions occupy a single crystallographic site with D_2 point symmetry in YAG, this site has six magnetically inequivalent orientations related to each other through the overall cubic symmetry of the crystal as illustrated by Fig. 5. There are four transitions possible between the Zeeman-split ground and excited state doublets for each site, and for an arbitrary orientation of the magnetic field all four transitions are allowed in all polarizations, yielding a maximum of 24 lines. However, particular orientations of the magnetic fields some sites are magnetically equivalent (called site subsets or subsites), which reduces the number of lines. A typical absorption spectrum is shown in Fig. 6(b). Due to a

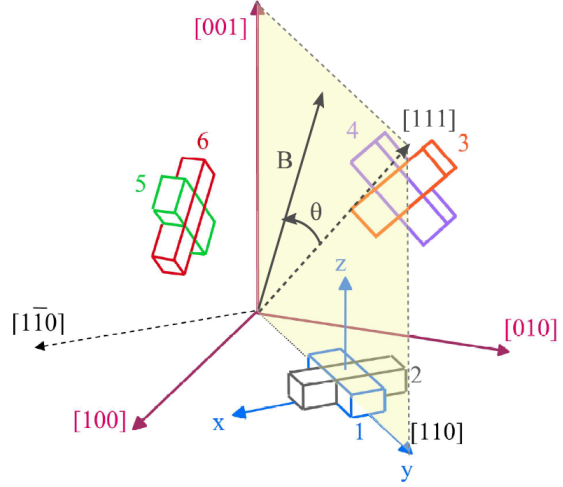


FIG. 5. Diagram illustrating the relative orientation of the six magnetically inequivalent sites in YAG that are occupied by erbium ions. [40, 41]

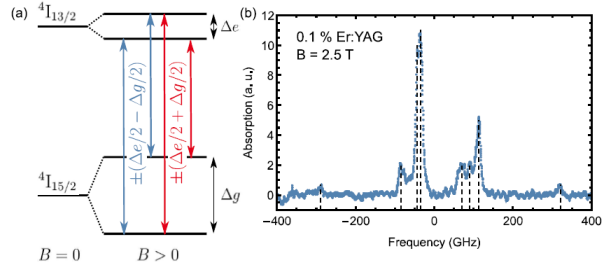


FIG. 6. (Splitting of the $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_1)$ transition in a magnetic field. (a) Relevant energy level structure. The degeneracy of both the $^4I_{15/2}(Z_1)$ ground and $^4I_{13/2}(Y_1)$ excited state is lifted by the application of a magnetic field B , leading to the appearance of 4 transitions for one site. (b) Example absorption spectrum for $B = 2.5$ T and $T = 1.6$ K. The magnetic field, as well as the light polarization were orientated along the X axis of the crystal, X corresponding to 16 deg off the $[-1-12]$ crystalline axis by a rotation about the $[1-10]$ axis.

faceting error, the crystallographic axes $[\bar{1}\bar{1}2]$ and $[111]$ are rotated by 16 degrees about $[1\bar{1}0]$ from the crystal faces of our 0.1% Er:YAG crystal, which was confirmed by x-ray diffraction; These directions are labeled X , Z , and Y respectively for convenience. Consequently, the absorption spectrum in Fig. 6(b) is for the magnetic field B oriented along the X -axis, where there are nearly 4 subsets of Er^{3+} ions. Only eight transitions (marked with dashed lines) of the expected 16 lines were observed. To extract the Zeeman shift of the lines, the spectrum was fitted by a sum of Lorentzian functions from which we obtained the central position of each peak.

Magnetic field strength dependence

We first varied the magnetic field strength B and followed the Zeeman shifts. The results are shown in Fig. 7 for the magnetic field oriented along the X -axis (see definition above). Four pairs of lines were identified in each spectrum, where each pair is the set of spin-preserving, or cross transitions for one of the two probed subsets. The pairs are indicated on the figure by different colors. The two transitions of a pair exhibit a symmetric splitting from the linear Zeeman effect, but the center of mass is also shifted as the field increases due to the quadratic Zeeman effect. The extracted linear and quadratic Zeeman coefficients are presented in Tab. II.

For the D_2 point symmetry of Er^{3+} in YAG, the linear Zeeman effect for each electronic state is characterized by a g -tensor with principle axes aligned along the $[1-10]$, $[110]$, and $[001]$ directions with corresponding values of g_x , g_y , and g_z , respectively. Ball et al. determined the g -factor for the ground state to be $g_{g,x} = 3.71$, $g_{g,y} = 7.75$, and $g_{g,z} = 7.35$ [19]. Using those results, we could determine the effective g -values for the four inequivalent subsets when $B \parallel X$: $g_{g,1} = 7.59$ (site 1), $g_{g,2} = 5.43$ (site 2), $g_{g,3,5} = 5.11$ (site 3 and 5), and $g_{g,4,6} = 7.62$ (site 4 and 6). Because some g -values are close, as a first approximation, we effectively grouped the ions in two subsets: subset a (sites 1, 4 and 6) with $g_{g,a} = 7.6$ and subset b (sites 2, 3 and 5) with $g_{g,b} = 5.3$.

From the theoretical g -values in the ground state for each subsets, we uniquely attributed each pair of lines to a subset. Table II shows the averaged Δg corresponding to each pair. This Δg value is equal to either $g_g + g_e$ in case of cross transitions or $|g_g - g_e|$ in case of spin-preserving transitions (see Fig. 6). Because only the red lines in Fig. 7 have a Δg larger than $g_{g,a} = 7.6$, we could determine that the red lines correspond to ions in subset a with an excited-state g -value $g_{e,a} = 10$ (see Table II). In the same way we determined that the blue lines correspond to ions in subset b with an excited-state g -value $g_{e,b} = 0.7$. These lines are cross transitions, while the green and black lines correspond to spin-preserving transitions. From the green and black lines coefficients, we could guess similar g_e values, which confirm the validity of our approximation.

While orientation dependent measurements and complex fitting, as shown below, is required to fully characterize the excited state g -tensor, the large magnetic anisotropy revealed by our results for this magnetic field direction allow us to place limits on what the maximum values of the principle g -factor components can be. Because of the small value of $g_{e,b}$, we could estimate that $g_{e,x} \approx 1$ and $g_{e,z} \approx 1$ so that the excited-state magnetism is dominated by the value of $g_{e,y}$, which must be much larger than the other two values ($g_{e,y} \approx 12$). These estimations provided a useful starting point for the anal-

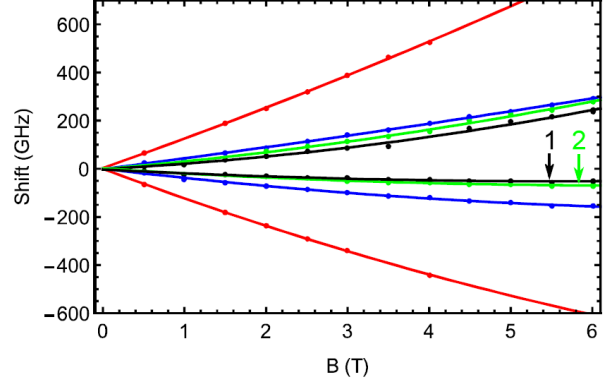


FIG. 7. Frequency shift of the eight lines observed on the $^4I_{15/2}(Z_1) \rightarrow ^4I_{13/2}(Y_1)$ transition as a function of magnetic field strength, for $B \parallel X$. Each pair of lines, corresponding to a set of spin-preserving or of cross transitions for a particular subset, is represented by one color. The experimental points are fitted by polynomial functions up to the second order (solid lines). Parameters are given in Table II. Zero shift corresponds to 1526.66 nm.

ysis of full orientation-dependent Zeeman measurements.

A quadratic shift of the optical lines was also observed. Since the quadratic Zeeman shift corresponds to the displacement of the crystal field levels, the 2 pairs of transitions for a subset of sites are expected to experience an identical quadratic shift, but generally different than for another subset. The fit parameters (see Table II) are given with too large uncertainties to make a difference between the two subsets and give a specific value to each of them. However, our experimental data give the order of magnitude of the quadratic shift, which is about 2 GHz/T^2 in average for this orientation. This quadratic shift probably comes from a quadratic displacement of the ground state due to its interaction with the next crystal-field level located at 22.6 cm^{-1} above (see Table I).

Orientation dependence

In order to fully determine the linear excited state g -tensor, we recorded absorption spectra for various orientation of the magnetic field and keeping $B = 1 \text{ T}$. The magnetic field was rotated in a plane defined by the X and Y axes of the crystal, nearly the $[-1-12]$ and $[1-10]$ crystallographic axes. We extracted the central position of each line, and Figure 8 shows the orientation dependence of the shifts.

We first needed to identify the shifts we measured and associate each of them with a specific site. Thus, we started with the first estimation of the excited state g -tensor we got from the magnetic field strength dependence and could see a rough overlap between the predicted line shifts and our experimental data. This is how

pair	linear (GHz/T)	quadratic (GHz/T ²)	averaged Δg	attributed g_g	deduced g_e
red	+119.2 / -127.4	+3 / +4.4	17.6	7.6	10
blue	+43.6 / -40.8	+0.8 / +2.4	6.0	5.3	0.7
green	+18.4 / -17.2	+3.7 / +1.5	3.7	5.3	1.6
black	+29.5 / -22.2	+2.9 / +1.75	2.5	7.6	10.1

TABLE II. Linear and quadratic Zeeman coefficients determined from Fig.7 for each pair of transitions (positive and negative number) for $B \parallel X$. From the linear part we calculated an averaged Δg that can be equal either to $g_g + g_e$ or $|g_g - g_e|$ for respectively the cross and spin-preserving transitions. We attributed g_g values to each pair of transitions and deduced the g_e values for the excited state doublets. See main text for more details.

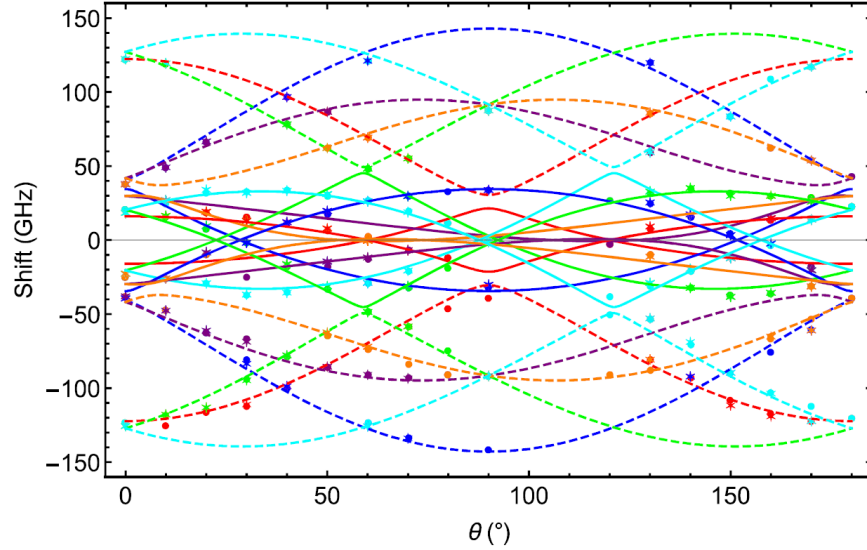


FIG. 8. Shifts of the optical transitions as a function of the magnetic field orientation for $B = 1$ T in 0.1% Er:YAG. The magnetic field was applied in the X - Y plane, where X corresponds to the crystalline axis $[-1-12]$ rotated by 16 deg about $[1-10]$ and Y corresponds to $[1-10]$. The rotation of the magnetic field was about the Z axis of the crystal, Z corresponding to the crystalline axis $[111]$ rotated by 16 deg about $[1-10]$, and $\theta = 0$ corresponding to B along X . We observed various lines that we identified to originate from site 1 (blue), site 2 (red), site 3 (purple), site 4 (green), site 5 (orange) and site 6 (cyan). Experimental data were taken at 1.6 K (dots) and at 5.0 K (stars). The lines (solid for spin-preserving and dashed for cross) represent our fit, which gives us the components of the excited state g -tensor (see main text).

we obtained four data sets per site. Then, we performed one high-dimensional fitting of all the data sets, with the only 3 free parameters being the principal g -values of the excited state g -factor. The fit gave: $g_{e,x} = 0.66$, $g_{e,y} = 12.67$, $g_{e,z} = -3.86 \times 10^{-9}$. These values were finally confirmed through comparisons of Zeeman hole burning spectra along each crystal face to the predicted energy shifts of site.

Hole burning spectra

We used spectral hole burning in order to probe the excited state Zeeman structure and therefore verify the results of the orientation dependence fit. In a spectral hole burning sequence, a strong and spectrally-narrow laser burns a hole in the absorption profile, which is then

probed by a weak frequency-scanned pulse. As shown in Figure 9, because of the lack of ions in the ground state for this class of ions, the probe pulse experience less absorption also when it is detuned by the excited-state splitting Δ_e . This is often called a sidehole. This phenomena can be observed when Δ_e remains smaller than the inhomogeneous broadening, i.e. for small magnetic fields. Here, the ground state structure is not considered because of the fast relaxation rate that erases any population difference within the two Zeeman levels in the ground state. Therefore, this method allows one to observe without ambiguity the excited state structure. As shown in Figure 10, we measured hole burning spectra as a function of the magnetic field strength for $B \parallel X$, Y , and Z . For each orientation, we simulated the position of the sideholes at $\pm\Delta_e$ for all sites using the g -tensor obtained above from the orientation dependence fit. In

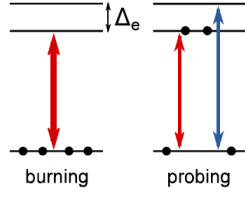


FIG. 9. Scheme of spectral hole burning with structured excited-state. First, a strong burning pulse excites ions which are on-resonance, creating a spectrally narrow hole in the absorption profile. In a second step, the frequency-scanned weak probe pulse experiences less absorption when it is on resonance with the first burning pulse, but also when it is detuned by the excited state splitting Δ_e , because of the lack of ions in the ground state. The later is called a sidehole.

Figure 10, the dashed lines represent the center of the expected sideholes, after applying a correction rotation of the magnetic field orientation of less than 10 degrees. Depending on the orientation, we observe a different number of site subsets. Overall, the agreement between the measured and the calculated positions of the sideholes is good. This confirms the g -tensor for the excited state given by the orientation dependence fit.

OPTICAL COHERENCE LIFETIME MEASUREMENTS

The large magnetic moment of Er^{3+} in solids means that it is very sensitive to changes in its magnetic environment. In the context of coherence lifetime, this means that optical transitions in Er^{3+} are strongly influenced by perturbations in their local environment, e.g. spin flips of neighboring Er^{3+} ions. In assessing an Er^{3+} material for information processing applications, it is vital to understand the decoherence and spectral diffusion. Therefore, we study the behavior of the coherence properties of the $^4\text{I}_{15/2} (Z_1) \rightarrow ^4\text{I}_{13/2} (Y_1)$ transition of $\text{Er}^{3+}:\text{YAG}$ with varying magnetic field strengths and temperatures using two-pulse photon echoes [42]. Photon echo measurements on this transition in 0.1% $\text{Er}^{3+}:\text{YAG}$ have been previously reported by Zhang et al. [18] where very short coherence lifetimes of only up to 50 ns were found for an applied field of 100 G. Very little variation in coherence time was observed for temperatures ranging from 1 K up to 7 K. Sun [1] also reported measurements for much higher applied fields of up to 4 T, finding non-exponential coherence decays with coherence lifetimes as long as 80 μs observed.

For the measurements reported here, transition number 1 in Fig.7 was chosen since the corresponding subset of ions has the smallest Zeeman splitting for the X field orientation and can therefore be expected to have a lower sensitivity to spectral diffusion caused by the magnetic fluctuations in the crystal. To investigate this transi-

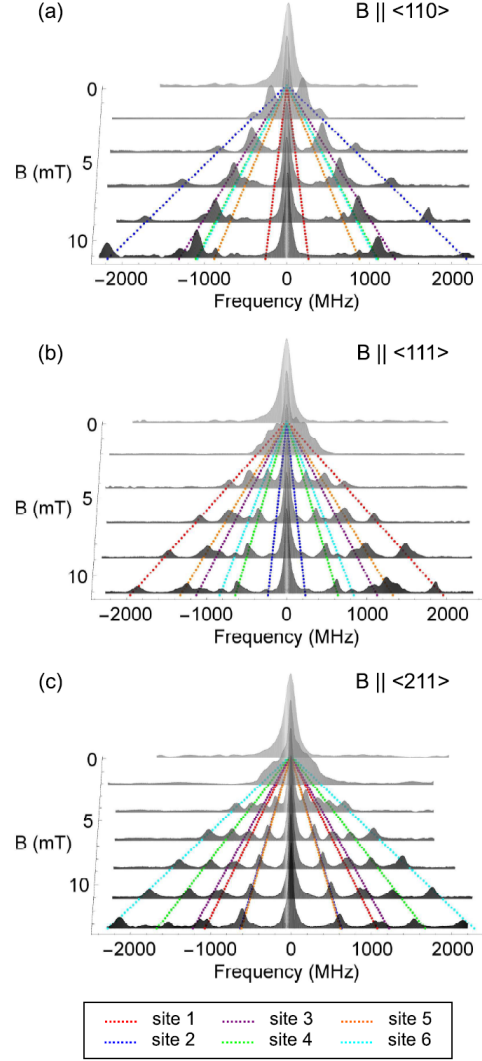


FIG. 10. Hole burning spectra exhibiting sideholes at the excited state splitting for magnetic fields between 0 and 10 mT and for 3 orientations: (a) $B \parallel Y$, (b) $B \parallel Z$, and (c) $B \parallel X$ in 0.1% $\text{Er}:\text{YAG}$. The experimental data are shown together with the theoretical position of the sideholes, predicted by the excited state g -tensor obtained by the orientation dependence fit, after applying a correction rotation of the magnetic field orientation of less than 10 degrees.

tion we use a tunable diode laser amplified by an erbium doped fiber amplifier (ILX Lightwave LDC3700B or Optilab EDFA-I-23-B) cascaded with a semiconductor optical amplifier (Thorlabs S9FC1004P). This configuration provides roughly 100 mW of optical power. The continuous wave laser is then amplitude modulated using an acousto-optic modulator in order to create the necessary pulses. The light is focused onto the crystal in the cryostat and the transmitted light as well as the emitted echo

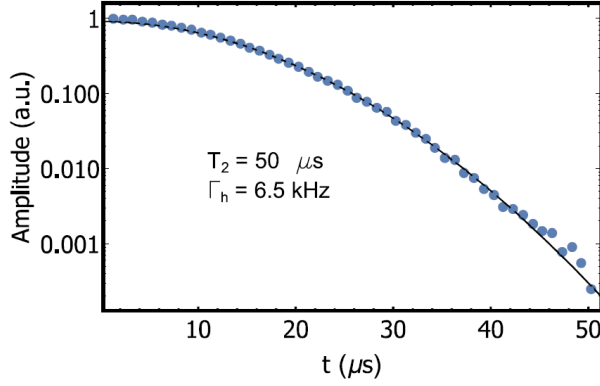


FIG. 11. Example of a typical two pulse photon echo decay at $B = 6$ T and $T = 1.6$ K.

are detected using a New Focus 1811 photoreceiver. For this measurement the magnetic field and the light polarization are both oriented along X , with the light propagating along the Z axis. The laser was centered on the appropriate transition using the Zeeman characterization data presented in the previous section.

Due to spectral diffusion, all our measured echo decays are non exponential. We thus use the empirical description proposed by Mims [43] to fit our data and to extract the effective memory time T_M and effective homogeneous linewidth $\Gamma_{eff} = 1/\pi T_M$.

$$I(t_{12}) = I_0 \exp \left\{ -2 \left(\frac{2t_{12}}{T_M} \right)^m \right\} \quad (3)$$

Here m is the so called Mims exponent determining the shape of the decay. The echo decay for $B = 6$ T and $T = 1.6$ K that shows the longest coherence time of $50 \mu s$ (i.e. Γ_{eff} of 6.5 kHz) is presented in Figure 11.

To investigate the processes causing spectral diffusion and to find optimal operation parameters, we measured effective linewidth at fields between 0.7 and 6 T and temperatures between 1.6 and 3.5 K. The measurement results are summarized in Figure 12.

To determine the underlying processes limiting the coherence properties, we adapted a model developed by Böttger et al. [44] for $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ to fit our data obtained with $\text{Er}^{3+}:\text{YAG}$. According to this model, the effective linewidth can be written as

$$\Gamma_{eff}(B, T) = \frac{\Gamma_{SD} R}{-2\Gamma_0 + 2\sqrt{\Gamma_0^2 + \frac{\Gamma_{SD} R}{\pi}}}. \quad (4)$$

Γ_{eff} is composed of the homogeneous linewidth Γ_0 without spectral diffusion and of additional broadening Γ_{SD} , caused by interactions between Er^{3+} ions. The latter has a full width at half maximum

$$\Gamma_{SD}(B, T) = \Gamma_{max} \operatorname{sech}^2 \left(\frac{g_{env} \mu_B B}{2k_B T} \right), \quad (5)$$

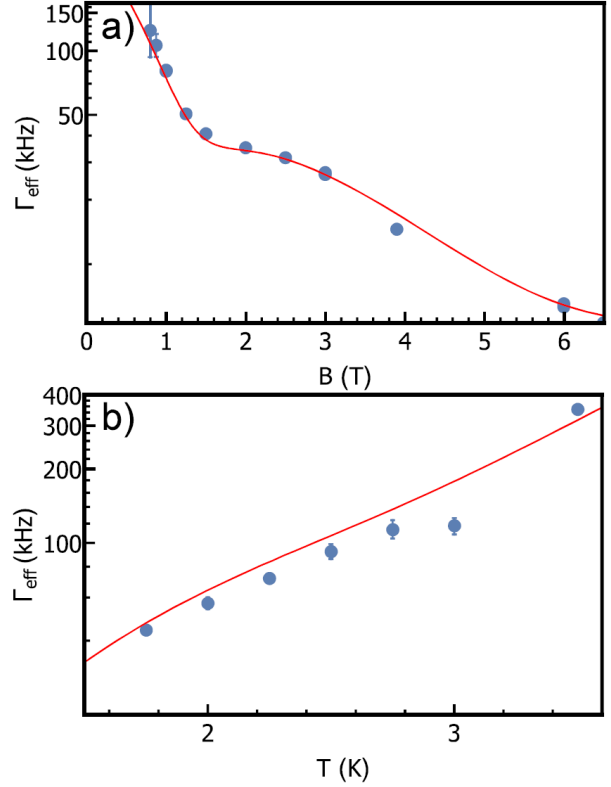


FIG. 12. a) Magnetic field dependence of the effective homogeneous linewidth, b) temperature dependence of the effective homogeneous linewidth.

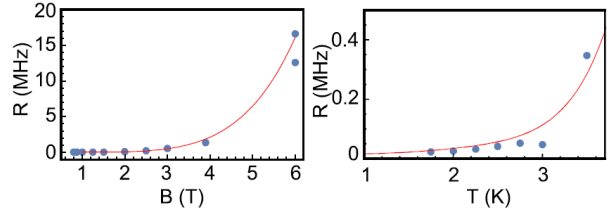


FIG. 13. (a) Magnetic field and (b) temperature dependence of the spectral diffusion rate (see Eq. 6).

where Γ_{max} is the maximum broadening due to the magnetic dipole-dipole interaction, $g_{env} \mu_B B$ is the splitting of the two Er^{3+} spin states, and the second part of Eq. (5) describes the suppression of spectral diffusion at high magnetic fields due to the increased magnetic ordering.

Spectral diffusion occurs at a rate R characterizing the relaxation of the perturbing Er^{3+} spins, and which is

Parameter	Value
Γ_0	$(1.75 \pm 0.3) \text{ kHz}$
$\Gamma_{\max}$	$(880 \pm 2) \text{ kHz}$
α_D	$(2.11 \pm 0.2) \text{ kHz/T}^5$
α_{ff}	$(105 \pm 16) \text{ kHz}$
α_R	$(2.7 \pm 0.5) \text{ Hz/K}^9$

TABLE III. Parameters for transition 1 (see Fig. 7), extracted from the fits to the two pulse photon echo experiments of Fig. 12.

given by

$$R(B, T) = \alpha_D g_{\text{env}}^3 B^5 \coth\left(\frac{g_{\text{env}} \mu_B B}{2k_B T}\right) + \alpha_{\text{ff}} \text{sech}\left(\frac{g_{\text{env}} \mu_B B}{2k_B T}\right) + \alpha_R T^9. \quad (6)$$

We assume that three processes, described by the different terms in Eq. 6, are causing the Er^{3+} spin flips, which in turn lead to spectral diffusion. Each process has a characteristic magnetic field and temperature dependence. The first term with coefficient α_D describes broadening resulting from direct phonon processes in which spins are flipped by the interaction with a resonant phonon of the lattice. This process dominates the rate at high fields. The second term with coefficient α_{ff} describes the so-called flip-flop process in which two neighboring Er^{3+} ions in opposite spin states exchange their spin orientation. This process is dominant at low fields. Finally, the last term describes the off-resonant Raman process in which two phonons cause a spin-flip via a transition to a virtual, higher lying, e.g. crystal field, level. The contribution of this process increases very rapidly with temperature.

Using a two dimensional fit, we fit this model simultaneously to the measured magnetic field and temperature dependence of Γ_{eff} . This allows us to quantify the spectral diffusion and to determine the relative importance of the different processes. The extracted parameters are given in Table III, and the corresponding magnetic field and temperature dependencies of the rate are shown in Figure 13.

From these values and the fits plotted in Figures 12 (a) and (b) and 13, one can see that similarly to many other erbium doped materials [44, 45] mainly two processes drive spectral diffusion. At low magnetic fields flip flop processes dominate. However, they are strongly suppressed even at intermediate fields of around 1.5 T. As the magnetic field is further increased, the direct phonon processes start to take over, giving rise to a local maximum of Γ_{eff} around 2.5 T. Finally, at fields of around 5 T the increasing amount of spin polarization almost completely suppresses spectral diffusion. This spin polarization at high fields arises from the fact

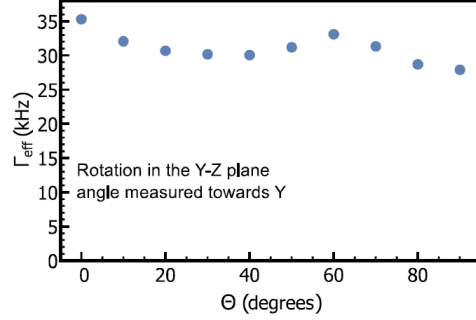


FIG. 14. Orientation dependence of the measured homogeneous linewidth at a field of 2 T and 1.6 K for fields in the Y-Z plane (relative to $B||Z$ at zero degrees). Error bars are smaller than the size of the data points.

that at high fields the resulting Zeeman splittings are so large that at the given temperature (1.6 K), no phonons that can cause spin flips are available. From the temperature dependence one can see that Raman processes only contribute at temperatures above around 3 K. At all lower temperatures the linewidth is limited by the direct phonon process. Overall we note that the obtained values for Γ_0 and $\Gamma_{\max}$ in 0.1% $\text{Er}:\text{YAG}$ are very similar to the ones obtained for 0.005% $\text{Er}:\text{Y}_2\text{SiO}_5$ [44], even though the doping concentration is different by two orders of magnitude. However, we observe faster spectral diffusion rates in $\text{Er}^{3+}:\text{YAG}$.

Besides the magnetic field and temperature, the orientation of the crystal with the magnetic field often affects the observed coherence properties since the sensitivity of the Er^{3+} ion to the magnetic environment is orientation-dependent. To study this, we looked at Γ_{eff} for transition 1 in Figure 7 for different orientations of the magnetic field. To determine if an optimal orientation indeed exists, the crystal was rotated in the field around X from the Z direction to the Y direction. Since the selection rules allow all transitions regardless of the orientation of the electric field, we do not rotate the electric field with the crystal. The orientation dependence, shown in Figure 14, is measured at 2 T and a temperature of 1.6 K. Furthermore, we only monitor the transition that gives rise to the longest coherence time since our objective is to find optimal operation parameters for the material.

The optimal coherence properties are achieved with the magnetic field along Y i.e. at 90 degrees. However, from Figure 14 one can see that there is no significant dependence of the homogeneous linewidth on the orientation of the magnetic field. Its overall value only varies by 20 %. Note that many more orientations of the magnetic and electric fields are possible and might lead to better properties. Further studies in crystals with different cuts will allow us to determine it.

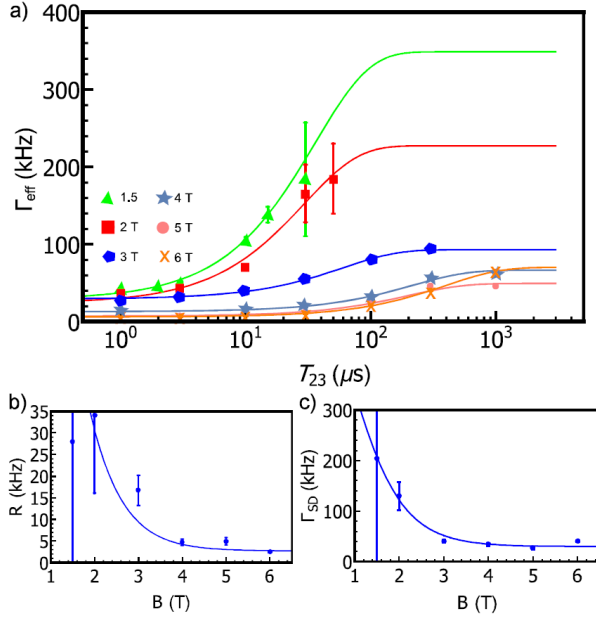


FIG. 15. Spectral diffusion measurements on line 2 of the $15/2(Z_1) \rightarrow 4I_{13/2}(Y_1)$ transition using three-pulse photon echoes. a) Homogeneous linewidth as a function of t_{23} for various B fields. b) Dependence of the spectral diffusion rate R on the B field, fitted using Eq. (6). c) Dependence of the spectral diffusion linewidth Γ_{SD} on the B field, fitted using Eq. (5).

SPECTRAL DIFFUSION AT LONG TIMESCALES

The two-pulse photon echo measurements above provided a way of studying the spectral diffusion dynamics on short timescales, of the order of the memory time T_M . Understanding the effect of spectral diffusion on the homogeneous linewidth over long timescales, comparable to the optical excited state lifetime, is also important for some applications such as AFC quantum memories or optical radio frequency spectrum analyzers, which rely on narrow lines over long timescales. We use three pulse photon echo measurements in order to access those timescales. Using this technique a frequency grating is created within the inhomogeneous absorption line by the first two $\pi/2$ pulses separated by a delay t_{12} . A third pulse then probes that grating after a time t_{23} and an echo is emitted at a time t_{12} after this third pulse. In our three pulse photon echo experiments, we record t_{12} decays for various t_{23} . The decay of the echo intensity is fit using equation 3. This allows us to extract the effective homogeneous linewidth at various t_{23} . Note that this time we monitored a different transition (labeled 2 in Figure 7). The t_{23} dependence of the homogeneous linewidth for various magnetic fields is shown in Figure 15. One can see that almost regardless of the magnetic field, signifi-

Parameter	Value
Γ_{max}	$(519 \pm 137) \text{ kHz}$
g_{env}	(3.6 ± 0.5)
α_{D}	0 kHz/T^5
α_{ff}	$(154 \pm 79) \text{ kHz}$
α_{R}	$(2.6 \pm 2) \text{ kHz/K}^9$

TABLE IV. Spectral diffusion parameters extracted from the fits to the three pulse echo data for transition 2 shown in Figure 7.

cant spectral diffusion sets in at around $10 \mu\text{s}$. However, the overall magnitude and maximum broadening depends strongly on the magnetic field. To extract the spectral diffusion rate $R(B)$, shown in Figure 15 b), as well as the broadening through spectral diffusion $\Gamma_{\text{SD}}(B)$ (Figure 15 c)), we fit a generalized form of equation Equation 4 [44]

$$\Gamma_{\text{eff}} = \frac{\Gamma_{\text{SD}} R}{-2a + 2\sqrt{a^2 + 2b/\pi}}$$

$$a = \Gamma_0 + \frac{1}{2}\Gamma_{\text{SD}}(1 - e^{-RT_2^3})$$

to our experimental data. We then fit this data to Eq. (6) and Eq. (5) respectively. From these fits we extract the maximum spectral diffusion linewidth Γ_{max} , the average g -factor of the surrounding spin bath as well as the coefficients for the processes contributing to spectral diffusion, shown in Table IV.

One can see, that although this is a different transition, the value for the maximum possible linewidth Γ_{max} and the coefficient of the flip flop process α_{ff} are very close to the values for transition 1 in Fig 7 measured using two pulse echoes. However, for transition 2, we cannot see any contribution from the direct phonon process to spectral diffusion. The spectral diffusion rates (Figure 15 inset) do not increase at high magnetic field which would be the case if there was any significant direct phonon process present. Compared to transition 1, this should result in narrower linewidths at intermediate magnetic fields; however, the optimal linewidth of this transition is not significantly narrower.

CONCLUSION

In this paper we quantified the linear and quadratic Zeeman shifts in of the lowest-to-lowest transition between the $4I_{15/2}$ ground state and the $4I_{13/2}$ excited state in erbium-doped YAG. We also measured coherence lifetimes at various magnetic fields and temperatures and investigated the importance of spectral diffusion in the material. We found that two processes are limiting coherence, flip-flop processes and direct phonon processes. The relative importance of both depends on the transition that is investigated. In addition, we found that the

coherence lifetime in our material is only weakly orientation dependent which might be of advantage for applications and materials such as powders or ceramics, in which a deterministic orientation is not possible. Overall, the narrowest observed homogeneous linewidth in erbium-doped YAG was 6.5 kHz.

ACKNOWLEDGMENTS

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- [1] Y. C. Sun, in *Spectroscopic Properties of Rare Earths in Optical Materials*, P. R. Hull, P. J. Parisi, P. R. M. O. Jr, P. H. Warlimont, D. G. Liu, and P. B. Jacquier, eds. (Springer Berlin Heidelberg, 2005), no. 83 in Springer Series in Materials Science, pp. 379–429.
 - [2] L. Menager, I. Lorgere, J.-L. Le Gouet, D. Dolfi, and J.-P. Huignard, *Optics Letters* **26**, 1245 (2001).
 - [3] W. R. Babbitt, Z. Barber, S. Bekker, M. Chase, C. Harrington, K. Merkel, R. K. Mohan, T. Sharpe, C. Stiffler, A. Traxinger, and A. Woidtke, *Laser Physics* **24**, 094002 (2014).
 - [4] B. Lauritzen, J. Min??, H. de Riedmatten, M. Afzelius, and N. Gisin, *Physical Review A* **83**, 012318 (2011).
 - [5] R. Lauro, J. Ruggiero, A. Louchet, A. Alexander, T. Chanele?re, I. Lorger?, F. Bretenaker, F. Goldfarb, and J. L. Le Gou?t, *Journal of Luminescence* **129**, 1951 (2009).
 - [6] M. Afzelius, C. Simon, H. de Riedmatten, and N. Gisin, *Physical Review A* **79**, 052329 (2009).
 - [7] E. Saglamyurek, N. Sinclair, J. A. Slater, K. Heshami, D. Oblak, and W. Tittel, *New Journal of Physics* **16**, 065019 (2014).
 - [8] Y. Li, P. Hemmer, C. Kim, H. Zhang, and L. V. Wang, *Opt. Express* **16**, 14862 (2008).
 - [9] J. W. Tay, P. M. Ledingham, and J. J. Longdell, *Appl. Opt.* **49**, 4331 (2010).
 - [10] H. L. L. V. W. Xiao Xu, Sri-Rajasekhar Kothapalli, *Journal of Biomedical Optics* **15**, 15 (2010).
 - [11] P. G. F. R. T. C. J.-L. L. G. Anne Louchet-Chauvet, Romain Lauro, “High-resolution large dynamic range spectral filtering at 800 nm using tm:yag crystals”, (2011).
 - [12] Y. S. T. B. R. M. M. R. L. Cone, C. W. Thiel, “Rare-earth-doped materials with application to optical signal processing, quantum information science, and medical imaging technology”, (2012).
 - [13] C. W. Thiel, R. L. Cone, and T. Bttger, *Journal of Luminescence* **152**, 84 (2014). 18th International Conference on Dynamical Processes in Excited States of Solids.
 - [14] P. B. Sellin, N. M. Strickland, J. L. Carlsten, and R. L. Cone, *Opt. Lett.* **24**, 1038 (1999).
 - [15] P. B. Sellin, N. M. Strickland, T. Böttger, J. L. Carlsten, and R. L. Cone, *Phys. Rev. B* **63**, 155111 (2001).
 - [16] M. J. Thorpe, D. R. Leibrandt, and T. Rosenband, *New Journal of Physics* **15**, 033006 (2013).
 - [17] S. Cook, T. Rosenband, and D. R. Leibrandt, *Phys. Rev. Lett.* **114**, 253902 (2015).
 - [18] .
 - [19] M. Ball, G. Garton, M. J. M. Leask, D. Ryan, and W. P. Wolf, *Journal of Applied Physics* **32**, S267 (1961).
 - [20] V. Amittar, S. Taneja, and S. Puri, *Journal of Physics and Chemistry of Solids* **33**, 813 (1972).
 - [21] K. S. Bagdasarov, V. I. Zhekov, V. A. Lobachev, T. M. Murina, and A. M. Prokhorov, *Soviet Journal of Quantum Electronics* **13**, 262 (1983).
 - [22] S. Payne, L. Chase, L. K. Smith, W. L. Kway, and W. F. Krupke, *Quantum Electronics, IEEE Journal of* **28**, 2619 (1992).
 - [23] C. A. Morrison, D. E. Wortman, and N. Karayianis, *Journal of Physics C: Solid State Physics* **9**, L191 (1976).
 - [24] J. B. Gruber, J. R. Quagliano, M. F. Reid, F. S. Richardson, M. E. Hills, M. D. Seltzer, S. B. Stevens, C. A. Morrison, and T. H. Allik, *Phys. Rev. B* **48**, 15561 (1993).
 - [25] J. A. Koningstein and J. E. Geusic, *Phys. Rev.* **136**, A726 (1964).
 - [26] K. H. Hellwege, S. Hufner, M. Schinkmann, and H. Schmidt, *Physik der kondensierten Materie* **4**, 397 (1966).
 - [27] G. Zverev, G. Y. Kolodnyi, and A. Onischenko, *Sov. Phys. JETP* **30**, 794 (1970).
 - [28] A. R. Devi, C. Jayasankar, and M. Reid, *Journal of Alloys and Compounds* **207-208**, 74 (1994). Proceedings of the 20th Rare Earth Research Conference.
 - [29] G. W. Burdick, J. B. Gruber, K. L. Nash, S. Chandra, and D. K. Sardar, *Spectroscopy Letters* **43**, 406 (2010).
 - [30] N. Ter-Gabrielyan, V. Fromzel, L. D. Merkle, and M. Dubinskii, *Opt. Mater. Express* **1**, 223 (2011).
 - [31] D. Zhou, X. Xu, C. Xia, D. Shen, S. Cheng, D. Li, J. Di, Z. Zhao, F. Wu, and J. Xu, *J. Opt. Soc. Am. B* **28**, 2543 (2011).
 - [32] D. S. Sumida and T. Y. Fan, *Opt. Lett.* **19**, 1343 (1994).
 - [33] T. Böttger, C. W. Thiel, R. L. Cone, Y. Sun, and A. Faraon, *Phys. Rev. B* **94**, 045134 (2016).
 - [34] N. Sinclair, E. Saglamyurek, H. Mallahzadeh, J. A. Slater, M. George, R. Ricken, M. P. Hedges, D. Oblak, C. Simon, W. Sohler, and W. Tittel, *Physical Review Letters* **113**, 053603 (2014).
 - [35] T. Böttger, C. W. Thiel, R. L. Cone, and Y. Sun, *Phys. Rev. B* **77**, 155125 (2008).
 - [36] A. W. A. T. R. W. E. Z. B. C. H. K. M. R. C. W. T. K. D. Merkel, C. R. Stiffler and R. Cone, US Patent 8,829,471 (2014).
 - [37] S. Feofilov, A. Kulinkin, K. Ovanesyan, A. Petrosyan, and C. Dujardin, *Phys. Chem. Chem. Phys.* **16**, 22583 (2014).
 - [38] S. Feofilov, A. Kulinkin, K. Ovanesyan, and A. Petrosyan, *Solid State Communications* **226**, 39 (2016).
 - [39] G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, *Phys. Rev.* **133**, A1029 (1964).
 - [40] J. F. Dillon and L. R. Walker, *Physical Review* **124**, 1401 (1961).
 - [41] Y. Sun, G. M. Wang, R. L. Cone, R. W. Equall, and M. J. M. Leask, *Phys. Rev. B* **62**, 15443 (2000).

- [42] R. Macfarlane and R. Shelby, *Spectroscopy of Crystals Containing Rare Earth Ions* (Elsevier, 1987).
- [43] W. B. Mims, Physical Review **168**, 370 (1968).
- [44] T. Böttger, C. W. Thiel, Y. Sun, and R. L. Cone, Physical Review B **73**, 075101 (2006).
- [45] C. W. Thiel, R. M. Macfarlane, T. Böttger, Y. Sun, R. L. Cone, and W. R. Babbitt, Journal of Luminescence **130**, 1603 (2010).

CHAPTER 9

EFFECTS OF FABRICATION METHODS ON SPIN RELAXATION AND
CRYSTALLITE QUALITY IN Tm-DOPED $\text{Y}_3\text{Al}_5\text{O}_{12}$ POWDERS
STUDIED USING SPECTRAL HOLE BURNING

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Effects of fabrication methods on spin relaxation and crystallite quality in Tm-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ powders studied using spectral hole burning

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ABSTRACT

High-quality rare-earth-ion (REI) doped materials are a prerequisite for many applications such as quantum memories, ultra-high-resolution optical spectrum analyzers and information processing. Compared to bulk materials, REI doped powders offer low-cost fabrication and a greater range of accessible material systems. Here we show that crystal properties, such as nuclear spin lifetime, are strongly affected by mechanical treatment, and that spectral hole burning can serve as a sensitive method to characterize the quality of REI doped powders. We focus on the specific case of thulium doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Tm:YAG). Different methods for obtaining the powders are compared and the influence of annealing on the spectroscopic quality of powders is investigated on a few examples. We conclude that annealing can reverse some detrimental effects of powder fabrication and, in certain cases, the properties of the bulk material can be reached. Our results may be applicable to other impurities and other crystals, including color centers in nano-structured diamond.

ARTICLE HISTORY

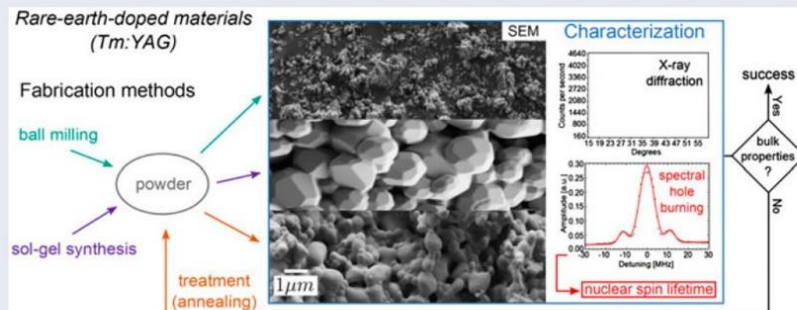
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Rare earth ion doped powders; powder processing; powder synthesis; annealing; spectral hole burning



1. Introduction

Rare-earth-ion (REI) doped bulk crystals cooled to cryogenic temperatures are used for a multitude of applications. Examples are quantum memories [1], quantum information processing [2], and ultra-high-resolution optical spectrum analyzers [3]. In contrast to REI doped bulk materials, powders offer low cost and rapid prototyping. Furthermore, the understanding of powders constitutes a first step towards nanofabrication of devices from these materials [4–7]. However, despite much effort [8–11], producing monodisperse powders with properties comparable to those of bulk materials remains challenging.

Fabrication or manipulation of REI doped powders can induce stress, especially during grinding or milling, that creates strain in the crystal lattice [12,13]. In addition, impurities can contaminate the host matrix during

synthesis. Strain and impurities often significantly impact the performance of the powders in both signal processing and more general luminescence applications. The goal of this work is to study REI doped powders at temperatures near 1.6 K and improve their properties to reach those of bulk materials. Towards that goal, we compared properties of powders that were synthesized chemically or milled down from larger crystals using either high-energy planetary ball mills or low-energy tumbling mills. We used scanning electron microscopy (SEM) to determine the shape and size of the particles, x-ray diffraction (XRD) to analyze the composition and phase of the crystalline structure, and we employed sensitive spectral hole burning (SHB) methods to probe variations in the optical decoherence dynamics, deduced from the spectral hole width, and the ^{169}Tm nuclear spin relaxation dynamics, deduced

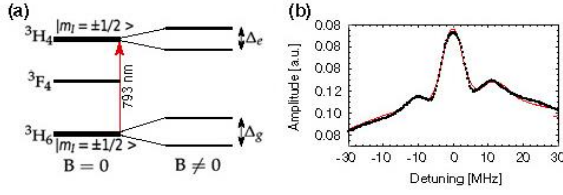


Figure 1. (a) Level structure of Tm:YAG without and with an applied magnetic field. (b) Hole burning spectrum of the 1% Tm:YAG bulk crystal together with a fit (red line).

from the spectral hole lifetime. We find that induced damage and strain in the crystal lattice, which does not affect XRD or SEM measurements, can produce large variations in the measured low-temperature dynamics of the powders that are observed using SHB techniques. Thus, SHB can serve as a quantitative characterization tool, complementing traditional techniques such as XRD, SEM or Raman scattering. Our results also demonstrate that mechanical and thermal treatment of REI doped crystals influences properties, such as the lifetime of nuclear spins, in a surprisingly strong way. Consequently, SHB is a well-suited technique to reveal the presence of residual damage in powders due to fabrication and to evaluate the effectiveness of methods used to reduce strain and improve material quality, such as thermal annealing.

2. Experiment

2.1. Tm:YAG

Our investigations employ crystalline $Y_3Al_5O_{12}$ doped with thulium impurities (Tm:YAG), whose relevant electronic level structure is shown in Figure 1. Under an external magnetic field, both the 3H_6 ground state and the 3H_4 excited state split into two non-degenerate states through the hyperfine interaction with the ^{169}Tm nuclear spin ($I = 1/2$), allowing persistent atomic population storage with lifetimes as long as hours in bulk crystals at liquid helium temperatures through optical pumping of the nuclear spin states.

The 20 GHz wide inhomogeneously broadened line of the $^3H_6 \leftrightarrow ^3H_4$ transition in Tm:YAG is centered at 793.156 nm [14]. The samples were mounted in an Oxford Instruments Spectromag cryostat (Oxford Instruments: Abingdon, UK) and all powders were held in unsealed glass cuvettes. All samples were 0.5 mm thick, and, for the nominal Tm concentration of 1%, featured an optical depth of ≈ 1 . This allowed for direct transmission detection of spectral holes while keeping optical scattering at an acceptable level. To prevent scattered light from reaching the detector, the cuvette was placed inside a copper box with two pinholes to allow light to enter and exit. For all measurements, the samples were cooled in helium vapor to 1.6 K and the applied magnetic field was set to 1 T.

2.2. Spectral hole burning

To assess the quality of different powders, we used persistent spectral holes. We extracted the lifetime of the spin states from the hole decay, and the magnitude of optical decoherence from the width of the hole [15]. As we describe later, we found that both quantities strongly depend on the crystal quality in terms of strain as well as impurities. In this approach, a spectral hole is burnt into the inhomogeneously broadened absorption line by using a laser to optically pump population between the nuclear spin states. After a certain waiting time, the absorption line is scanned using a tunable laser and the area of the spectral hole is measured. From the exponential decay of the hole area with waiting time, the spin lifetime is extracted. Note that the width of the spectral hole ideally corresponds to twice the homogeneous linewidth; however, the measured width is generally larger due to laser frequency jitter, spectral diffusion, and power broadening.

We used a Coherent 899-21 Ti:sapphire laser (Coherent Inc.: Santa Clara, California, USA) emitting at a wavelength of 793.38 nm and with a linewidth of less than 1 MHz. For the bulk single crystal measurement that served as a reference for the best material properties, the laser power was set to $5 \mu\text{W}$. For the powder samples, more power was necessary to overcome loss due to scattering and achieve a sufficiently high signal-to-noise ratio. Otherwise, the experimental conditions were kept the same for all materials. The burn and read pulses were generated from the CW laser beam using two acousto-optic modulators (AOMs) in series. This arrangement gave an extinction ratio of >90 dB, ensuring that no unintentionally leaked light reached the sample. During the reading pulse, the laser sweep was implemented using a double-passed AOM scanned in frequency. A New Focus model 2051 photo-receiver (New Focus: Santa Clara, California, USA) was used to detect the transmitted light.

2.3. Bulk single crystal reference

First, as a reference against which we compare the properties of our Tm:YAG powders (the different methods used to create these powders are described below), we assessed the properties of a 1% doped Tm:YAG crystal from Scientific Materials Corporation (SMC) (Scientific Materials: Bozeman, Montana, United States) (growth number 3-8). The crystal is 0.5 cm thick and features an optical depth of about 0.5. Depending on the crystal orientation, we found spin lifetimes between 5 and 16 h [16]. Furthermore, as shown in Figure 1(b), the observed spectral hole width was limited to 6 MHz – much wider than the intrinsic kHz-wide homogeneous linewidth of Tm:YAG [17] under these conditions – primarily due to power broadening effects. The figure also shows clear side holes, split by 10 MHz T^{-1} .

Table 1. Hole widths (Γ) (bold fonts indicate visible side holes), and lifetimes (T_a) of all measured materials at 1.6 K and $B = 1$ T. *ball milled.

Material	Size [μm]	Γ [MHz]	T_a [min]
SMC bulk		6	300–960
SMC thermal crushing	500	10	60
annealed	500	10	420
SMC low energy BM*	< 0.1	28.6	20
annealed	< 1	17.2	60
Crytur	30–50	10	60
annealed	30–50	10	60
Crytur low energy BM	< 0.1	23	15
annealed	< 1	10	20
Crytur high energy BM	< 2	10	10
Chemical synthesis	< 0.1	26.6	2

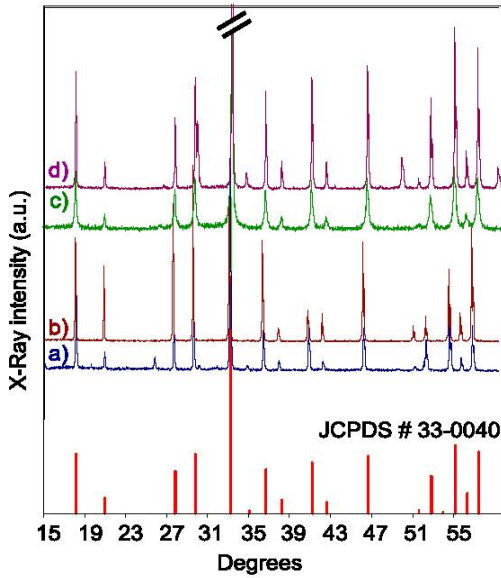


Figure 2. XRD spectra of selected powders together with the reference spectrum (JCPDS # 30-0040) of YAG. (a) Chemical synthesis; (b) Crytur non-annealed; (c) SMC low energy ball milled; (d) SMC low energy ball milled and annealed.

and caused by super-hyperfine coupling between the thulium ions and the nuclear spin of the ^{27}Al present in the host matrix [15,18]. Because powders are composed of randomly oriented crystallites, measurements of powders probe all possible orientations at once and we expect to observe lifetimes that span the range of those observed in the bulk material.

3. Results

In the following, we study the impact of fabrication and annealing methods on nuclear spin lifetimes T_a as well as on hole linewidths Γ . Due to the strong scattering caused by the powders, higher laser power was required for these measurements, leading to additional power broadening. As a consequence, hole linewidths were measurable only down to approximately 10 MHz. A summary of the properties of all investigated materials is shown in Table 1.

In addition, we performed SEM imaging and powder XRD analysis to further characterize each sample. Example powder XRD spectra are shown in Figure 2 for a selected subset of our samples. The spectra were obtained with a Scintag Inc X-1 Advanced Diffraction System (Acintag Inc.: Cupertino, California, USA). We find that all the analyzed samples formed the expected crystalline structure of YAG. Small deviations from the reference spectrum (JCPDS # 30-0040) can be observed for some samples. Differences in peak heights can be assigned mostly to sample preparation issues, while additional peaks correspond to the presence of residual amounts of impurity phases [19].

3.1. Crushing and ball milling

Our first approach to obtain small powders was “top-down” fabrication starting from a 1% doped Tm:YAG bulk single crystal originating from the same growth as the one studied above. To pre-crush the crystal, we heated the bulk crystal to $\approx 500^\circ\text{C}$ and then immersed the hot crystal in water (21°C) to thermally shock the crystal, causing it to crack into millimeter and larger sized pieces. This procedure was repeated on all pieces with sizes greater than ≈ 5 mm until all were in the few millimeter or smaller size range. We then ground the small pieces in a mortar and pestle to produce a powder composed of crystallites with sizes of less than 0.5 mm. With spectral hole burning spectroscopy, we measured a hole width of $\lesssim 10$ MHz, limited by power broadening. Side holes due to superhyperfine coupling with ^{27}Al nuclear spins were still resolvable, as in the bulk material. The spin lifetime was on the order of 1 h – significantly shorter than the values obtained in the bulk material at the same temperature and magnetic field. Since this powder originated from a bulk crystal whose properties were well characterized, and was composed of relatively large particles of ≈ 0.5 mm size that had been ground only for a short time, it is unlikely that any change in chemical composition or interdiffusion of impurities could have occurred (as might be a factor for much smaller particles when processed using high-energy methods). The only explanation for

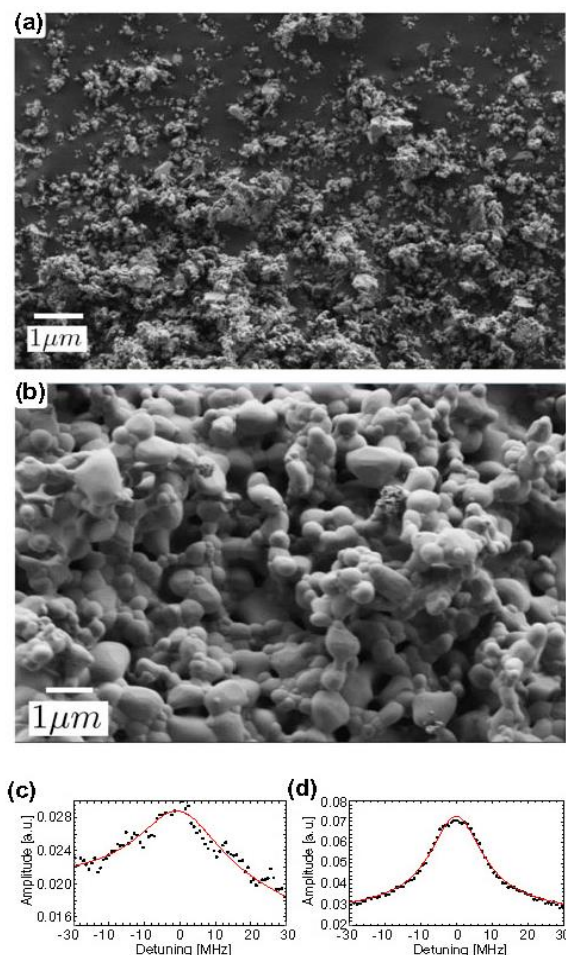


Figure 3. SEM images and typical hole burning spectra of the powder obtained after ball-milling the bulk crystal from SMC for two days. (a), (c) before, and (b), (d) after annealing at 1400°C for 4 h.

the significant reduction in lifetime was residual strain induced in the crystallites due to the thermal shocking and grinding used to produce the powder.

With the < 0.5 mm sized crushed powder as a starting material, we produced a smaller powder using a low-speed tumbling mill. The Tm:YAG powder was dispersed in ethanol and milled for 48 h using a mix of zirconia balls with sizes ranging from 1 mm to 1 cm. Figure 3(a) shows an SEM image of the obtained powder. The average size of the irregular particles was below 100 nm. The XRD spectrum, shown in Figure 2(c) displays the expected YAG structure with no observable peak broadening or amorphous background. A spectral hole burning trace, shown in Figure 3(c), revealed a hole width of 28.6 MHz. The hole was about five times larger than that observed in the bulk, which could not solely be attributed to additional power broadening and reveals a significant difference in the material not detectable from our XRD measurement. No sideholes were visible, which was expected since their splitting (10 MHz at

$B = 1$ T) is less than the spectral hole width. Moreover, we found a further reduction of the spin lifetime to 20 min. Overall, as opposed to the XRD analysis, the SHB results suggest that a significant amount of damage (strain) was induced in the crystallites during the two days of milling.

The surprisingly strong effect of mechanical strain on coherence and spin relaxation dynamics may be understood within the framework of the two-level system (TLS) model first developed to describe dynamic disorder modes in amorphous materials [20,21]. These very low-frequency modes are enabled by the disordered structure and involve groups of atoms tunneling between local configurations with nearly equivalent energies. It has been proposed that low densities of TLS may also be enabled in crystalline materials by large inhomogeneous lattice strains [22], and optical decoherence of rare-earth ions due to interactions with TLS has been observed in both bulk crystals [23,24] and powders [25]. Furthermore, it is known that TLS can also be effective in causing rapid electron and nuclear spin relaxation [26–28]. Here, both the increase in spectral hole widths and the decrease in nuclear spin lifetimes that we observe in powders are likely to result from the creation of TLS from strain induced during the mechanical fabrication process. This interpretation is also consistent with past observations of increased electronic spin-lattice relaxation rates of Nd^{3+} doped into bulk YAG crystals with greater densities of structural defects in the lattice [29].

3.2. Effects of annealing

Next, we investigated to what degree annealing of the powders can repair the induced damage. After we confirmed that low annealing temperatures around 600°C were unable to improve material properties, and since higher temperatures generally lead to better properties [30], we annealed both the 0.5 mm and the 100 nm powders at our highest accessible temperature of 1400°C. The annealing was performed for 4 h in an oxygen atmosphere (using a tube furnace) to minimize the out-diffusion of oxygen from the YAG matrix. The 0.5 mm annealed crystals appeared unchanged under the SEM. The spin-state lifetime improved significantly to 7 h and became comparable to that extracted from measurements on the bulk. This suggests that annealing can mostly repair the damages induced by stress during the grinding via mortar and pestle.

The SEM image of the annealed 100 nm powder, shown in Figure 3(b), reveals that the size of the particles increased to around 1 μm. The particles were almost spherical, with close to uniform size distribution, and appeared to be agglomerated. Compared to the same powder before annealing (panel (a)) this is a major improvement. The XRD spectrum, shown in Figure 2(d), shows no significant change compared to

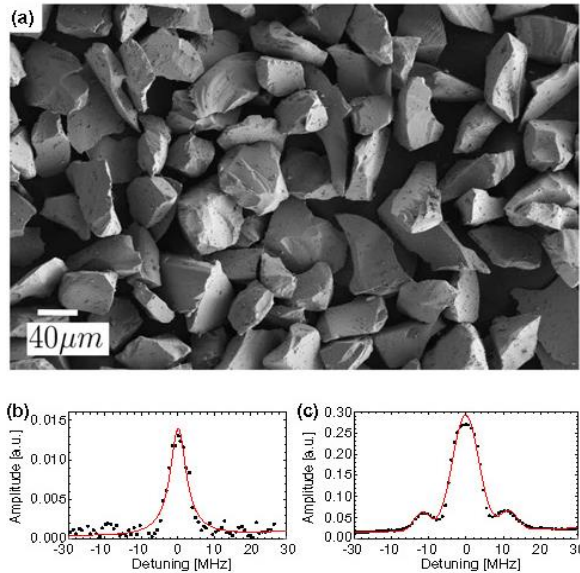


Figure 4. (a) SEM image of the 1% Tm:YAG powder provided by Crytur, and typical hole burning spectrum (b) before and (c) after annealing.

the non-annealed powder. The signal-to-noise ratio in this spectrum is better than the one in the spectrum for the non-annealed powder since more material was available for analysis. This indicates that, in contrary to the SHB measurement, the current XRD analysis is not sensitive enough to detect the changes caused by annealing for this powder. Indeed, the hole burning spectrum in Figure 3(d) shows a hole width of 17.2 MHz, which is 30% smaller than the value measured before annealing. Furthermore, the spin lifetime increased by a factor of three to 1 h. Hence, our method of annealing also improved the properties of the ball-milled powder, but it was not sufficient to completely re-establish the properties of the bulk. We anticipate that optimized annealing procedures, in particular involving temperatures closer to the melting point, will lead to further improvements.

3.3. Comparison of high- and low-energy ball-milling methods

The above results indicated that the grinding methods used here, namely mortar and pestle and ball-milling, caused damage to the host material. To better understand this surprisingly large effect, and to determine the degree to which damage can be repaired through annealing, we continued studying ball-milling methods starting with a powder from a commercial supplier (Crytur). The powder was created from outer fragments of a large crystal, grown from 99.999% pure starting materials using the Czochralski method. Those fragments were then pre-crushed using a mechanical jaw crusher and finally milled down to a size of 30–50 μm

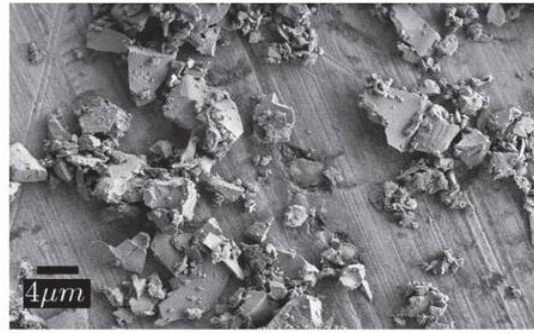


Figure 5. SEM image of the 1% Tm:YAG powder after 4 h of high-energy planetary ball-milling.

in a tumbling mill. The resulting powder was cleaned using mineral acids.

First, we characterized the “as purchased” micro meter-sized Crytur powder using SEM, XRD, and SHB, as shown in Figures 4(a), (b), and 2(b). The SEM image reveals that the powder has sharp edges and few particles with dimensions below 30 μm. The XRD spectrum shows good YAG crystalline structure. From the hole burning trace we extracted a hole width of $\lesssim 10$ MHz; however, the lifetimes were only on the order of one hour and comparable to the thermally crushed bulk crystal. This indicates that the crushing method employed by Crytur also induced a comparable amount or strain that is not detected in the XRD spectrum.

Since our annealing procedure was successful for the 0.5 mm-sized powder made from the SMC bulk crystal, we annealed the Crytur powder using the same method. The SEM image taken after annealing resembles that of the powder before annealing (see Figure 4(a)), and the hole width as well as the spin lifetime also remained comparable to those of the powder before annealing. Hence, in contrast to the powder created from the SMC crystal, besides an improvement in signal strength (see Figure 4(c)), our annealing method did not succeed in improving the properties of the powder. A possible explanation for this observation is the different way of creating the bulk crystal from which the powders were made. While both crystals were grown in a Czochralski process using starting materials of similar purity (99.999% in the case of Crytur, and 99.995% for SMC), the original bulk crystal from SMC has been cut from the center of a boule and annealed before shipping. In contrast, the starting material at Crytur was outer fragments of a large crystal that were not annealed before crushing. These differences in the procedures employed in the growth process and sample preparation may affect the density of intrinsic defects and strain in the initial bulk crystal, potentially explaining the differences between the samples that are observed here.

In addition to jaw crushing and low-energy ball milling, we also used a high-energy planetary ball mill to

obtain small powders. This technique requires shorter milling times compared to the low energy approach, but the energy of the impacts during milling is higher. For a direct comparison between high-energy and low-energy ball milling, we used the same starting material, i.e. the non-annealed, 30–50 μm -size crystals from Crytur, and milled the powder for 4 h using 1 cm-diameter balls in a high-energy ball-mill. The SEM image in Figure 5 showed that the particles were not agglomerated and on average about 2 μm large. This is the smallest average size we could achieve using this mill with balls of that size. Figure 5 also reveals the sharp, irregular surfaces of the particles, suggesting significant strain, as well as a broad size distribution. For this powder, we measured a spectral hole width $\lesssim 10$ MHz (no side holes are visible) and a lifetime of around 10 min – considerably shorter than any other milled material. We conclude that despite the reduced milling time, the crystallites contained an even greater amount of strain and defects due to the high-energy impacts during milling.

Finally, we employed a low-energy tumbling mill for 48 h to reduce the size of the original Crytur powder. The SEM image reveals agglomerated particles on the order of 100 nm. Furthermore, we found a spectral hole width of 23 MHz (no side holes are visible) and spin lifetimes of around 15 min. This new powder was very similar in all its properties to the one obtained from the SMC bulk crystal after the same ball-milling procedure (see Figure 3(a) and (c)).

The same annealing procedure as described before was then applied to the low-energy ball-milled powder. As observed in the case of the powders originating from the SMC bulk crystal, the particles grew from 100 nm to 1 μm , exhibiting clear garnet dodecahedral habit. Improvements in terms of spectral hole burning were more pronounced, with a measurement limited hole width of less than 10 MHz and visible side holes. However, the obtained lifetimes were still only around 20 min (as opposed to 1 h in the case of the SMC powder), which might be explained by a larger number of defects or impurities in the original bulk crystal from which the Crytur powder was obtained.

3.4. Direct chemical synthesis

Apart from milling larger crystals, small-sized powders can also be obtained using “bottom-up” chemical synthesis. In addition to not requiring initial growth of a high-quality crystal – a substantial advantage for fast prototyping – this method does not suffer from potential damage induced during grinding. We therefore examined the performance of a 1% Tm doped YAG powder that was prepared using a co-precipitation method [31–33]. This 1% Tm:YAG powder was synthesized from starting materials with at least 99.9% purity. An aqueous nitrate solution was prepared by dissolving

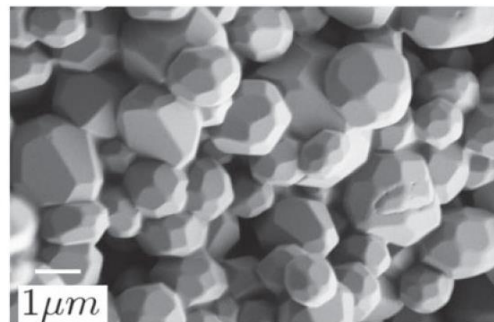


Figure 6. SEM image of the synthesized 1% Tm:YAG powder.

$\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a molar ratio of 0.03:2.97:5 in HPLC-grade water. The precipitant solution was prepared with a 1 M concentration of aqueous ammonium bicarbonate and ≈ 1 mM concentrations of sodium dodecyl sulfate and polyethylene glycol 400 added as anionic and nonionic surfactants, respectively. The solutions were mixed by stirring for 1 h and then the nitrate solution was added drop-wise to an excess of the precipitant solution while stirring at room temperature to form the precipitate. The resulting suspension was aged for several hours while stirring to allow the solutions to fully react, and the resulting gelatinous precipitate was centrifugally separated from the solution. The precipitate was then washed by vortex mixing and sonication using deionized water, ethanol, and finally n-butanol, and it was then allowed to dry overnight in a vacuum desiccator. A YAG precursor powder was obtained by subsequently drying the precipitate at 300°C for 4 h and then grinding in a mortar to obtain a fine powder. The precursor was then mixed with 5% Li_2CO_3 by weight as a flux to promote growth of large crystallites, placed in a covered alumina crucible, and then crystallized in a tube furnace at a temperature of 1300°C for 8 h in air. Analysis of the resulting powder using XRD, shown in Figure 2(a), revealed complete formation of single-phase crystalline YAG. The quality of the XRD spectrum, in terms of signal-to-noise ratio and peak widths, is comparable to the spectrum of the purchased Crytur powder (see Figure 2(b)). An SEM image of the synthesized 1% Tm:YAG powder is shown in Figure 6, revealing that it consisted of uniform, non-agglomerated crystallites with diameters of 500 nm to 2 μm that exhibited the characteristic dodecahedral crystal habit of the garnets.

Although the XRD and SEM results for the synthesized powders appeared promising, spectral hole burning measurements revealed the poor quality of the material. We observed a very broad hole width of 26.6 MHz with no visible side holes. Furthermore, the measured nuclear spin lifetime was limited to values of at most 2 min. Hence, the properties of the synthesized powder were significantly worse than the properties of all of the powders obtained using the top-down

ball-milling approach. We expect that the poor performance of the synthesized crystallites may result from residual chemical impurities that can cause lattice strain from incorporation of the defects as well as the presence of paramagnetic impurities such as iron that can couple to the Tm^{3+} ions and induce nuclear spin relaxation and optical decoherence. Consequently, further studies are required on powders synthesized from higher-purity starting materials to investigate whether the properties show improvement and how they compare to powders of similar purity obtained from top-down fabrication.

4. Discussion of different characterization methods

The three methods used in this work, SEM, XRD and SHB, complement each other as they provide information about different aspects of the nanocrystal properties. We found that SHB was the most sensitive method to detect effects of crushing as well as annealing on the powder quality in our measurements.

SEM images constitute the most convenient method to assess the size of the particles, and also observe their shape, which can be an indication of the crystalline quality, provided one knows the crystal's habit. For instance, the powder obtained by chemical synthesis exhibits the characteristic dodecahedral crystal habit of YAG (see Figure 6). However, the SEM results do not allow one to identify the chemical composition, and thus cannot detect impurities present in the particles.

XRD analysis is the most reliable method to assess the composition and the phase of the nanocrystals. If the concentration of impurities is high enough, they can also be detected by this method. Potential amorphous character of the particles should also be visible as a broad background on the XRD spectrum. However, we were not able to observe the amorphous components or crystal strain that was clearly observed in our SHB measurements. In principle, by analyzing the peak widths in the spectrum, XRD can also give access to the particle size, but this requires a resolution beyond that of our instrument.

The SHB measurement gives access to the population lifetime of the nuclear spin states of Tm^{3+} :YAG, as well as to the homogeneous linewidth of the optical transition if the hole width is not broadened by laser power, which limited our resolution to 10 MHz. Both quantities are very sensitive to the crystal quality in terms of both strain and impurities. This sensitivity originates from the coupling between the ion's nuclear spin and the environment. In some cases, the SHB measurements reveal differences in the materials that are not observed in the SEM or XRD results. For example, the chemically synthesized nanocrystals exhibited very short spin lifetimes despite promising SEM and XRD results. The SHB measurement gives a quantitative,

and sensitive method to determine the overall quality of the nanocrystals, even though it does not directly determine the nature of the limiting factors.

5. Conclusions and outlook

In summary, we studied properties of 1% Tm :YAG powders produced by different methods via SEM imaging, XRD analysis, and spectral hole burning. We found that SHB is a very sensitive and well-suited method to assess the quality of REI doped crystals in a quantitative way.

We found that any grinding or milling technique degraded the performance of the REI doped material in terms of homogeneous linewidth and especially spin-state lifetimes, most likely due to induced stress and deformation to the host matrix. Annealing is crucial and allowed us to recover the bulk spin-state lifetimes in the case of a soft-grinding method. In the case of more severe damage caused by ball-milling, bulk properties were partly recovered in powders originating from high-quality, annealed bulk crystals, whereas it remained poor in the case of powders obtained from non-annealed crystal fragments. This shows the importance of starting with high-quality crystals and the need for annealing. Finally, we found that the performance of the synthesized powder studied here was likely limited by the quality of the starting materials.

We anticipate our findings to be generalizable to other impurities and other hosts, in particular to color centers in nano-structured diamond, and to provide valuable insight towards nano-structuring REI doped crystals. Furthermore, SHB is a way to reveal variations in terms of quality and uniformity of powders that could have consequences for traditional applications where low levels of lattice defects can affect performance, such as luminescence efficiency and thermal quenching of phosphors.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

- [1] de Riedmatten H, Afzelius M. Quantum light storage in solid state atomic ensembles. *ArXiv*. 2015;1502.00307.
- [2] Saglamyurek E, Sinclair N, Slater JA, Heshami K, Oblak D, Tittel W. An integrated processor for photonic quantum states using a broadband light-matter interface. *New J. Phys.* 2014;16:065019.
- [3] Ménager L, Lorgère I, Gouët J-LL, et al. Demonstration of a radio-frequency spectrum analyzer based on spectral hole burning. *Opt. Lett.* 2001;26:1245.
- [4] McAuslan DL, Longdell JJ, Sellars MJ. Strong-coupling cavity QED using rare-earth-metal-ion dopants in monolithic resonators: What you can do with a weak oscillator. *Phys. Rev. A*. 2009;80:062307.
- [5] O'Brien C, Lauk N, Blum S, Morigi G, Fleischhauer M. Interfacing Superconducting Qubits and Telecom Photons via a Rare-Earth-Doped Crystal. *Phys. Rev. Lett.* 2014;113:063603.
- [6] Walther A, Rippe L, Yan Y, Karlsson J, Serrano D, Nilsson AN, Bengtsson S, Kröll S. High fidelity readout scheme for rare-earth solid state quantum computing. *ArXiv*. 2015;1503.08447.
- [7] Lutz T, Veissier L, Thiel CW, Cone RL, Barclay PE, Tittel W. Modification of phonon processes in nano-structured rare-earth-ion-doped crystals. *ArXiv*. 2015;1504.02471.
- [8] Hong K, Meltzer R, Bihari B, et al. Spectral hole burning in crystalline Eu_2O_3 and $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ nanoparticles. Proceedings of the eleventh international conference on dynamical processes in excited states of solids. *J. Lumin.* 1998;7677:234.
- [9] Malyukin YV, Masalov AA, Zhmurin PN. Single-ion fluorescence spectroscopy of a $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocluster. *Phys. Lett. A*. 2003;316:147.
- [10] Macfarlane RM, Dejneka MJ. Spectral hole burning in thulium-doped glass ceramics. *Opt. Lett.* 2001;26:429.
- [11] Perrot A, Goldner P, Giaume D, Lovrić M, Andriamahamanana C, Gonçalves RR, Ferrier A. Narrow Optical Homogeneous Linewidths in Rare Earth Doped Nanocrystals. *Phys. Rev. Lett.* 2013;111:203601.
- [12] Heitjans P, Masoud M, Feldhoff A, Wilkening M. NMR and impedance studies of nanocrystalline and amorphous ion conductors: lithium niobate as a model system. *Faraday Discuss.* 2007;134:67.
- [13] Scholz G, Stösser R, Klein J, Silly G, Buzar JY, Laligant Y, Ziemer B. Local structural orders in nanostructured Al_2O_3 prepared by high-energy ball milling. *J. Phys. Condensed Matter*. 2002;14:2101.
- [14] Sun Y, Wang GM, Cone RL, Equall RW, Leask MJM. *Phys. Rev. B*. 2000;62:15443.
- [15] Macfarlane RM, Shelby RM. Coherent Transient and Holeburning Spectroscopy of Rare Earth Ions in Solids. In: Kaplyanskii AA, RMMacfarlane editors. *Spectroscopy of Solids Containing Rare Earth Ions*. Elsevier; 1987. p. 51–184.
- [16] Veissier L, Thiel CW, Lutz T, Cone RL, Barclay PE, Tittel W. In preparation.
- [17] Liu G, Jacquier B. *Spectroscopic Properties of Rare Earths in Optical Materials*. Berlin, Heidelberg: Springer; 2005.
- [18] Bonarota M, Ruggiero J, Gouët JLL, Chanelière T. Efficiency optimization for atomic frequency comb storage. *Phys. Rev. A*. 2010;81:033803.
- [19] Kareiva A. Aqueous Sol-Gel Synthesis Methods for the Preparation of Garnet Crystal Structure Compounds. *Mater. Sci.* 2011;17:1392–1320.
- [20] Anderson PW, Halperin BI, Varma CM. Anomalous low-temperature thermal properties of glasses and spin glasses. *Philos. Mag.* 1972;25:1.
- [21] Phillips W. Tunneling states in amorphous solids. *J. Low Temp. Phys.* 1972;7:351.
- [22] Watson SK. Tunneling States in Crystals with Large Random Strains. *Phys. Rev. Lett.* 1995;75:1965.
- [23] Flinn GP, Jang KW, Ganem J, Jones ML, Meltzer RS, Macfarlane RM. Sample-dependent optical dephasing in bulk crystalline samples of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. *Phys. Rev. B*. 1994;49:5821.
- [24] Macfarlane RM, Sun Y, Cone RL, Thiel CW, Equall RW. Optical dephasing by disorder modes in yttrium orthosilicate (Y_2SiO_5) doped with Eu^{3+} . Proceedings of the 8th International Meeting on Hole Burning, Single Molecule, and Related Spectroscopies: Science and Applications. *J. Lumin.* 2004;107:310.
- [25] Meltzer R, Jang K, Hong K, Sun Y, Feofilov S. Optical dephasing of rare earth ions in mixed crystalline and size-restricted systems. *J. Alloys Compounds*. 1997;250:279.
- [26] Szeftel J, Alloul H. Nuclear spin lattice relaxation in the amorphous state: Towards an understanding. *J. Non-Crystalline Solids*. 1978;29:253.
- [27] Askew TR, Stapleton HJ, Brower KL. Anomalous electron-spin relaxation in amorphous silicon. *Phys. Rev. B*. 1986;33:4455.
- [28] Balzer-Jöllenbeck G, Kanert O, Steinert J, Jain H. Low-temperature properties of nuclear spin relaxation in inorganic glasses. *Solid State Comm.* 1988;65:303.
- [29] Aminov L, Kurkin I, Lukoyanov D. Some peculiarities of spin-lattice relaxation of impurity rare-earth ions in crystals caused by the structure defects. *Appl. Mag. Reson.* 1998;14:447.
- [30] Georgescu S, Constantinescu S, Chinie A, et al. 2007. Optical and Mossbauer studies on YAG: Eu nanocrystals synthesized by a sol-gel method, ROMOPTO 2006: Eighth Conference on Optics (International Society for Optics and Photonics); p. 67850A–67850A.
- [31] Li X, Liu H, Wang J, Cui H, Zhang X, Han F. Preparation of YAG:Nd nano-sized powder by co-precipitation method. *Mater. Sci. Eng. A*. 2004;379:347.
- [32] Pradhan A, Zhang K, Loutts G. Synthesis of neodymium-doped yttrium aluminum garnet (YAG) nanocrystalline powders leading to transparent ceramics. *Mater. Res. Bull.* 2004;39:1291.
- [33] Xu G, Zhang X, He W, Liu H, Li H, Boughton RI. Preparation of highly dispersed YAG nano-sized powder by co-precipitation method. *Mater. Lett.* 2006;60:962.

CHAPTER 10

EFFECTS OF MECHANICAL PROCESSING AND ANNEALING ON
OPTICAL COHERENCE PROPERTIES OF
 $\text{Er}^{3+}:\text{LiNbO}_3$ POWDERS

Contribution of Authors and Co-Authors

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Effects of mechanical processing and annealing on optical coherence properties of $\text{Er}^{3+}:\text{LiNbO}_3$ powders



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ABSTRACT

Optical coherence lifetimes and decoherence processes in erbium-doped lithium niobate ($\text{Er}^{3+}:\text{LiNbO}_3$) crystalline powders are investigated for materials that underwent different mechanical and thermal treatments. Several complimentary methods are used to assess the coherence lifetimes for these highly scattering media. Direct intensity or heterodyne detection of two-pulse photon echo techniques was employed for samples with longer coherence lifetimes and larger signal strengths, while time-delayed optical free induction decays were found to work well for shorter coherence lifetimes and weaker signal strengths. Spectral hole burning techniques were also used to characterize samples with very rapid dephasing processes. The results on powders are compared to the properties of a bulk crystal, with observed differences explained by the random orientation of the particles in the powders combined with new decoherence mechanisms introduced by the powder fabrication. Modeling of the coherence decay shows that paramagnetic materials such as $\text{Er}^{3+}:\text{LiNbO}_3$ that have highly anisotropic interactions with an applied magnetic field can still exhibit long coherence lifetimes and relatively simple decay shapes even for a powder of randomly oriented particles. We find that coherence properties degrade rapidly from mechanical treatment when grinding powders from bulk samples, leading to the appearance of amorphous-like behavior and a broadening of up to three orders of magnitude for the homogeneous linewidth even when low-energy grinding methods are employed. Annealing at high temperatures can improve the properties in some samples, with homogeneous linewidths reduced to less than 10 kHz, approaching the bulk crystal linewidth of 3 kHz under the same experimental conditions.

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1. Introduction

Rare-earth-ion (REI) doped solid-state materials have received much attention for their properties such as long optical coherence lifetimes, broad inhomogeneous linewidths and long population lifetimes that are appealing for a multitude of applications [1–7]. Erbium-doped lithium niobate ($\text{Er}^{3+}:\text{LiNbO}_3$) features a wide, inhomogeneously broadened transition within the C-band of the current telecommunication infrastructure [8]. This is desirable for high-bandwidth applications such as quantum memories [9] or classical information processing devices, e.g. pulse ordering that would seamlessly integrate with today's technology. Furthermore, lithium niobate is of particular interest due to its strong electro-optic effects [10] that enable amplitude and phase modulation of

light, as well as its high refractive index that can be readily modified to enable optical waveguide applications [11–13]. The optical coherence properties of the 1.5 μm transition of bulk $\text{Er}^{3+}:\text{LiNbO}_3$ crystals have also been studied for optical signal processing and quantum information applications [1,7,14–17], providing a knowledge base for comparing with any changes in the properties of micro- and nano-structured materials.

For many photonic applications, there is a strong trend towards miniaturization of devices with the ultimate goal of on-chip implementation and integration of many optical components. Nanofabrication tools such as chemical etching [18,19] and focused ion beam milling [20] are already available and numerous nano-scale devices have been fabricated specifically from LiNbO_3 . Furthermore, employing LiNbO_3 crystalline films with thicknesses of only a few microns can provide advantages for the design of next generation high-speed, broadband electro-optic modulators [21,22] as well as providing a platform for integration of heterogeneous photonic structures and components [23]. As fabrication techniques are refined further, additional improvements may be

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achieved by employing micron-sized ridge waveguide structures, such as for enhanced optical frequency conversion [24]. Nanos-structured LiNbO_3 is of interest for diverse applications such as nanocrystals for in situ biological imaging [25] or nano-wires for directional optical second-harmonic generation [26] and enhanced pyroelectric sensors [27]. These materials are also promising for nanoscale ferroelectric capacitors that can enable high-density non-volatile data storage [28].

While much progress has been made in recent years on nanofabrication of optical materials [29,30], little is known about how fabrication processes affect the spectroscopic properties of resonant impurities in the host, such as rare-earth ions. Many properties, such as optical coherence lifetimes that are studied here, can be sensitive to the quality of the host crystal and even modest variations can critically affect applications that rely on those properties. Consequently, it is important to find ways to maintain those properties in nanoscale structures.

In the specific area of REI-doped powders and nanocrystals, there have been very few optical coherence studies. The initial work in this field focused on the specific case of Eu^{3+} -doped into sesquioxide host crystals, where fluorescence detection of spectral hole burning revealed rapid decoherence relative to the bulk crystals due to the introduction of glass-like two-level system (TLS) dynamics in the powders [31–34]. Beyond the sesquioxide powders, nano-crystallites in glass ceramics have also suffered from rapid decoherence processes due primarily to interactions with the surrounding amorphous host matrix [35–37]. Following the pioneering demonstrations of photon echo measurements on highly scattering powders [38], optical coherence properties approaching those of bulk crystals have recently been demonstrated in $\text{Eu}:\text{Y}_2\text{O}_3$ nano powders, confirming that there is significant potential to improve these and other nano-materials [39]. In addition, long optical coherence times have been reported for micro-fabricated structures in $\text{Nd}:\text{Y}_2\text{SiO}_5$ crystals, again suggesting that at least some systems and fabrication methods can produce properties suitable for practical applications [40]. Nevertheless, beyond these cases, little is known about optical coherence in nano- and micro-structured crystals or powders.

With this motivation, the focus of the work reported here is to employ high-resolution optical characterization methods, namely two-pulse photon echo (2PE), spectral hole burning (SHB), and free induction decay (FID) techniques, to assess optical coherence lifetimes in micro- and nano-sized powders of Er^{3+} -doped lithium niobate. The greatest challenges in carrying out these studies involve detecting optically coherent signals in highly scattering media and the complexity in behavior introduced by the random orientation of crystallites in the powder relative to both the external magnetic field and light polarization, which crucially influence the spectroscopic properties. In addition, we find that the bulk crystal properties degrade significantly with any mechanical processing used to obtain micro/nanocrystals. Therefore, techniques with a very large measurement dynamic range are necessary.

As a primary goal, our study seeks to probe the thresholds where low-energy mechanical processing methods begin to degrade the optical coherence properties and to what extent the effects might be reversed by high-temperature annealing. Investigating micron-sized crystals allowed us to probe this threshold region and get a better understanding of the mechanisms responsible for degraded properties when the particle size is reduced, down to the nanoscale. In addition to the direct relevance to nano- and micro-fabrication, these results can also reveal insights into potential surface damage introduced by cutting, grinding, and polishing as well as what processing steps may be successful in reducing the resulting surface strain and defects. Another important goal is to demonstrate that powders of highly

anisotropic materials may be quantitatively analyzed within the framework of decoherence models developed for bulk single crystals. Finally, this work demonstrates how combinations of 2PE, SHB, and FID measurement techniques allow optical coherence properties to be studied and compared across a range of samples with very different behaviors as described in the following.

The following section of this paper describes the fabrication of our powder samples. We then discuss and compare the results of the different experimental methods to probe the optical coherence lifetimes. The properties of the fabricated powders are then compared with the ones of a bulk crystal, including quantitative modeling of the effects due to the random orientation of crystallites in the powder. We identify the factors limiting the optical coherence lifetimes in small crystals and show that high-temperature annealing to relieve strain induced by the fabrication process can improve those properties; however, in the majority of samples, the bulk crystal properties could not be preserved or fully recovered.

2. Sample preparation

Mechanical grinding is a very general, simple, rapid, and flexible approach for fabricating nano-powders from bulk crystalline materials. In particular, high-energy planetary ball milling has been extensively used to produce monodisperse nano-powders with crystallite sizes down to less than 10 nm [41,42]. However, it is known that high-energy ball milling can cause significant damage to the crystal structure, with the resulting disorder leading to amorphous-like behavior or even transformations to different crystal phases after extended milling [42,43]. Since very large internal electric fields can be produced through the piezoelectric and pyroelectric effects in LiNbO_3 [10], which are also known to contribute to optical damage processes in the bulk crystals [44], we might expect even greater potential for crystal damage from high-energy milling of this material. High-energy ball milling has been used by a number of groups to produce LiNbO_3 nano-powders, mostly undoped, and the resulting materials have been extensively characterized [45–50]. A range of techniques including nuclear magnetic resonance spectroscopy, extended X-ray absorption fine structure spectroscopy, impedance spectroscopy, X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, thermogravimetric analysis, infrared absorption spectroscopy, and Raman spectroscopy have all indicated a significant increase in amorphous behavior in the LiNbO_3 crystallites when they are reduced to sizes below 100 nm by high-energy ball milling [45–49].

Very little is known regarding how the extent of crystal damage caused by mechanical fabrication or processing relates to the energy, processing time, and specific method used. While it is clear that the extended high-energy milling required to produce nanocrystalline powders produces significant damage, it is unknown if the damage is intrinsically linked to the size reduction or whether lower energy grinding methods might better preserve the properties of the bulk crystal. For LiNbO_3 , some of the same measurements that reveal the large degradation in nanocrystals indicate that microcrystals have nearly the same properties as the bulk crystal [49]. In our previous SHB studies of Tm^{3+} -doped yttrium aluminum garnet powders, we found that high-energy planetary ball milling dramatically affected $^{169}\text{Tm}^{3+}$ nuclear hyperfine state lifetimes; however, we also found that the lifetimes were still significantly reduced in relatively large microcrystals produced by low-energy ball milling [51]. Since we expect crystal defects introduced by grinding to affect optical coherence properties more strongly than nuclear spin lifetimes due to the

stronger coupling of the electronic states to the crystal lattice, optical coherence measurements should provide a uniquely sensitive method for probing even very low levels of crystal damage. For the same reasons, we expect mechanical fabrication methods to be particularly detrimental to material performance in applications that rely on long coherence lifetimes and narrow optical homogeneous linewidths. Consequently, in this work we only used very slow and low-energy grinding methods, resulting in micron-sized powders, in an attempt to minimize the accumulated mechanical strain in the crystallites and also to probe the threshold at which measurable damage is induced to the crystal structure.

As a single crystal reference to compare with powder samples prepared in different ways, we chose a bulk single crystal of 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ with congruent composition, grown by Scientific Materials Corp. (SMC) using the Czochralski method. This crystal has been previously studied by Thiel et al. [16,17] and showed good coherence properties with homogeneous linewidths as narrow as 3 kHz with applied magnetic fields along the crystal's c-axis. The choice of doping concentration is a trade-off between the absorption needed to obtain a reasonable signal-to-noise ratio in powder samples and the additional decoherence created by increased doping due to Er^{3+} - Er^{3+} interactions. Starting from a bulk crystal, we fabricated several powder samples, as detailed below. The procedures used to fabricate each of the samples are outlined in Table 1. In order to analyze the size and shape distribution of the resulting powders, we performed scanning electron microscope (SEM) imaging, as presented in Fig. 1 and 2.

An initial reference powder (powder #1 in Table 1) was first fabricated by relatively gentle mechanical crushing and grinding using an alumina ceramic mortar and pestle. This resulted in monocrystalline particles with a wide distribution of sizes ranging from 1 to 100 μm , as shown in Fig. 1(a). However, we believe that when we later optically probed the samples the signal mainly originated from the largest particles.

To further reduce the crystallite size of the crushed LiNbO_3 powder, we employed two different horizontal tumbling-type low-energy ball mills: a ball mill with a 4-in. diameter HDPE-jar rotating at a relatively slow rate of approximately 5 Hz, and an even slower ball mill rotating at a rate of only approximately 0.5 Hz. Both mills were loaded with a mix of ceramic yttria-stabilized zirconia balls with diameters ranging from 0.3 mm to 1 cm. The reference powder samples were mixed with ethanol to produce a slurry and then ground in a mill under the conditions listed in Table 1. This method was chosen to minimize both the mechanical and thermal energy involved in the grinding. From the powder sample #1, we produced another sample (powder #2) by ball-milling for only 30 min at 0.5 Hz. The corresponding SEM

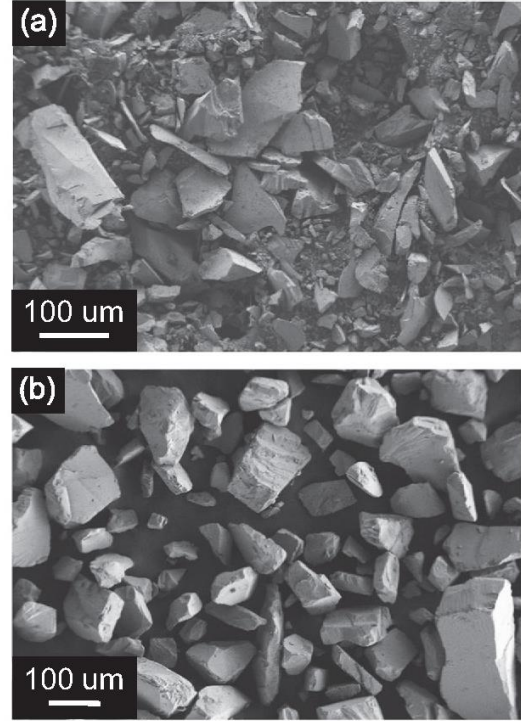


Fig. 1. Scanning electron microscope images of (a) powder #1 made from a 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ bulk crystal (SMC) by grinding with a mortar and pestle, (b) powder #2 ball-milled for only 30 min.

image (Fig. 1(b)), shows very little decrease in particle size demonstrating that our low-energy ball milling method only reduces the particles very slowly by gradual attrition. Nevertheless, even short periods of milling may potentially introduce measurable lattice strain that can be characterized. The next sample fabricated, powder #3, was produced by ball-milling powder #1 for 2 h at 0.5 Hz, resulting in a significant reduction in average particle size. As shown in Fig 2(a), this sample has particle sizes roughly on the order of 1 μm after annealing in the furnace.

To investigate the effect of post fabrication thermal treatment, some powders were annealed in alumina crucibles in a tube furnace using a mullite tube providing peak temperatures of up to 1400C. While thermal annealing can increase defect mobility and relieve crystal strain, LiNbO_3 can also be detrimentally affected by annealing at high temperatures due to the potential for out-diffusion of both lithium and oxygen, affecting the optical and electrical properties of the crystal. Past studies have found that thin crystalline films of LiNbO_3 are particularly sensitive to high annealing temperatures [52,53], suggesting that similar effects might be observed for powders. Furthermore, while bulk crystals generally require reducing atmospheres [54] or vacuum [55] for significant oxygen to diffuse out of the crystal matrix during annealing, we found that in small crystallites the out diffusion occurs even when annealed in an ambient atmosphere, resulting in black powders. To prevent the loss of oxygen from the material, we annealed the powders under a continuous flow of oxygen (ultra-high purity grade), a method that has been shown to inhibit the reduction process for bulk crystals [55], although for thin films there have been some indications that excess oxygen may potentially be absorbed and produce defects [56]. To inhibit the out-diffusion of lithium, we employed the well-known technique used for LiNbO_3 wafer processing of introducing small amounts of water

Table 1
Powders characterized in the manuscript and their fabrication methods.

Sample	Method
bulk	0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ (SMC)
1 (ref)	bulk crushed via mortar and pestle
2	sample 1 re-crushed with mortar and pestle ball milled, 0.5 Hz mill, 30 min
3	sample 1 ball milled, 0.5 Hz mill, 2 h annealed (1 h at 900C and 4 h at 600 C)
4	sample 1 ball milled, 0.5 Hz mill, 2 h annealed (4 h at 1100 C)
5	sample 1 ball milled, 5 Hz mill, 10 h annealed (4 h at 950 C and then 4 h at 1100 C)
6	indiffusion of Er^{3+} into commercial LiNbO_3 powder: $\text{LiNbO}_3 + \text{ErCl}_3$ ball milled, 5 Hz mill, 3 h annealed (4 h at 1100 C)

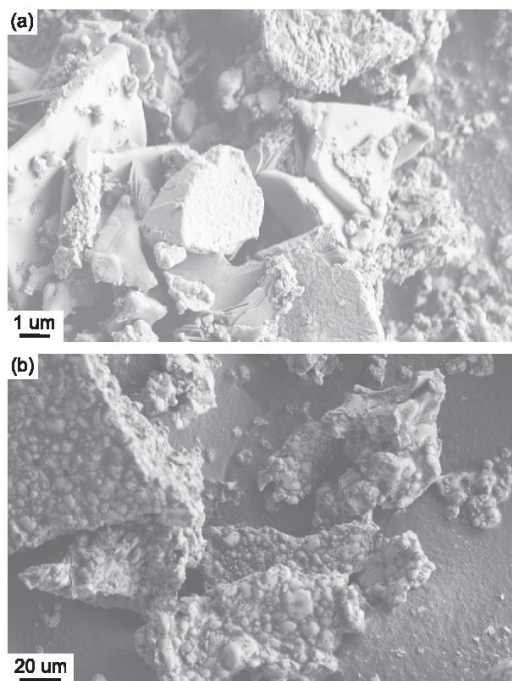


Fig. 2. Scanning electron microscope images (a) powder #3 ball-milled and annealed at 900 C, and (b) powder #6 annealed up to 1100 C.

vapor into the oxygen by bubbling the gas through a column of deionized water [57,58].

The effects of several different annealing procedures were examined. Powder #3 was annealed at a low-temperature of around 900 C, which resulted in a growth in particle size of only a factor of two at most for the micron- and sub-micron-sized particles and only produced weak agglomeration of the powder. The resulting maximum particle size of 2 μm or less constitutes the finest powder examined in this study as shown in Fig. 2(a). We also performed higher temperature annealing at 1100 C that tended to produce significant crystallite growth as well as hard agglomeration and fusing of the particles. Samples #4, #5 and #6 had initial particle sizes of less than 2 μm after ball-milling but fused into much larger masses around 100 μm after annealing at 1000 C, as shown in Fig. 2(b). Powder #5 also underwent an initial pre-annealing step at 950 C. Better crystal quality, and therefore improved coherence properties should in principle come with this increase in size.

Finally, we fabricated an $\text{Er}^{3+}:\text{LiNbO}_3$ powder (sample #6) via in-diffusion of Er^{3+} ions into a commercial congruent LiNbO_3 powder (Sigma Aldrich, 99.9% purity) with initial crystallite sizes of less than 70 μm . The LiNbO_3 powder was mixed with a 5% molar concentration of anhydrous ErCl_3 powder (ProChem Inc., >99.9% purity) and ethanol to produce a slurry, and the mixture was ball milled for 3 h. The powder was then allowed to dry in a desiccator, after which it was heated in the tube furnace for 4 h at 1100 C while under a continuous flow (3 SCFM) of oxygen. The resulting powder was then crushed with a mortar and pestle and washed with deionized water followed by ethanol. Optical spectroscopy of the 1532 nm absorption line verified that significant Er^{3+} had diffused into the LiNbO_3 powder. While the amount of Er^{3+} incorporated into the LiNbO_3 powder is unknown, the magnitude of the optical absorption and the effective homogeneous linewidth were comparable to our other 0.1% Er powders (see Table 3). Not

accounting for possible broadening of the inhomogeneous line, which would have to be very large, this suggests a similar effective doping level in the indiffused powder and our other powders.

3. Optical coherence lifetime measurements

Key requirements for many applications of REI-doped materials in classical and quantum signal processing are long optical and spin coherence lifetimes. To investigate the effect of powder fabrication on the optical coherence lifetime of the 1.5 μm telecom-compatible transition of Er^{3+} , we used several different measurement techniques. One issue that must be overcome for powders is a much weaker signal strength. Powders with particle sizes below 10 μm scatter light very strongly, especially for our samples, since LiNbO_3 has a relatively high refractive index of approximately 2.2 at 1.5 μm wavelengths [59,60] and most of our particles have sizes larger than the wavelength of the probing light. The latter causes light to be scattered at every surface of the micro/nano-crystals, randomizing the direction, path length, and polarization of the light, making the transmitted or emitted light difficult to collect. Therefore, the usual characterization methods employed for REI-doped crystals such as 2PE, SHB, or FID are difficult to perform with powders. Previous measurements on powders have mostly employed detection of fluorescence emission to observe SHB [31,33,61], with direct transmission detection of SHB [51] and 2PE [38,39] only recently being successfully applied to powders. In particular, FID measurements on powders have not been previously reported to our knowledge.

Another consideration is the random orientation of individual crystallites in the powder relative to applied external fields. It is known that Er^{3+} coherence lifetimes strongly depend on the magnetic field orientation due to the anisotropy of the g tensors in both the ground and excited states [62]. As a consequence, the coherence lifetimes measured in a randomly orientated powder sample correspond to an average of the bulk lifetime over all possible orientations, complicating the interpretation of the results.

Finally, the degradation of coherence properties in micro/nano-crystals due to new decoherence mechanisms introduced by the powder fabrication process can limit the range of materials that can be studied using a single technique. In some cases, the optical coherence lifetime is drastically reduced, making a direct measurement via 2PEs difficult with standard techniques.

In the work reported here, we employed a combination of three techniques, SHB, 2PE, and FID, to study optical coherence over the wide range behavior encountered in different powder samples. Also, SHB signals were detected in transmission rather than emission to allow information about absorption depths to be determined. For all of these measurements, unless mentioned otherwise, the powder samples were loaded into a 0.4 mm thick space within an unsealed glass cuvette and then cooled to a temperature of 1.6 K in an Oxford Spectromag cryostat using helium exchange gas. A superconducting solenoid provided magnetic fields of up to 6 T for these measurements. Since most of the incident laser light was diffusely scattered in all directions, it was critical to minimize stray light from reaching the detector and producing a large background signal. For this purpose, the glass cuvette containing the powder was mounted against a mask with a small hole that only allowed light at the center of the cuvette to be transmitted and with extensive light baffles on all sides to direct any scattered light away from the detector.

3.1. Two pulse photon echoes

The most precise method to characterize long coherence lifetimes, as observed in $\text{Er}^{3+}:\text{LiNbO}_3$ bulk crystals, is the 2PE

technique since it is not limited by the linewidth of the excitation laser. For these measurements, a homemade Littman-Metcalf extended-cavity diode laser emitting at 1532 nm was amplified using an erbium-doped fiber amplifier (IPC Photonics Corp EAD-1-C). Two short pulses, separated by a time t_{12} , with duration ranging from 30 to 100 ns, optimized for each sample, were generated using an acousto-optic modulator (Crystal Technology Inc. 3165). The light was then focused on the front face of the sample and the transmitted light was detected using an amplified high-speed InGaAs photodetector (New Focus 1811) with no optical gate used between the photodetector and the powder samples.

In addition to direct detection of the echo intensity, we also performed heterodyne measurements of the echo. For those measurements, after the second excitation pulse, a weak optical local oscillator pulse detuned by 10 MHz was sent through the sample to the detector to ensure it undergoes the same scattering path and to provide better spatial mode matching of the local oscillator and the excitation beam. The envelope of the beat signal between the emitted echo and the local oscillator corresponds to the emitted temporal shape of the photon echo electric field strength. Because of the need to limit the local oscillator pulse intensity to avoid undesired hole burning or heating effects and attenuation due to scattering, the heterodyne signal strength was not significantly larger than the intensity detection. Nevertheless, the factor of two slower echo decay rate of the electric field observed in the heterodyne measurement, compared to the decay rate of the intensity observed in a regular 2PE, allows shorter coherence lifetimes to be characterized with the heterodyne technique.

3.1.1. Echo decays in powders of randomly orientated crystallites

In the simplest 2PE decay measurement, the area of the echo emitted at a time $2t_{12}$ after the first excitation pulse follows an exponential decay determined by the coherence lifetime. In $\text{Er}^{3+}:\text{LiNbO}_3$, as for many other Er^{3+} materials, spectral diffusion broadens the homogeneous linewidth during the measurement timescale [16] leading to a non-exponential echo decay often described by the empirical formula proposed by Mims [63,64].

$$I(t_{12}) = I_0 \exp \left[-2 \left(\frac{2t_{12}}{T_M} \right)^x \right], \quad (1)$$

where the exponent $x \geq 1$ determines the decay shape and T_M is the phase memory lifetime, usually related to the effective homogeneous linewidth as $T_M = 1/\pi\Gamma_{\text{eff}}$ [16]. In heterodyne detection, the electric field of the emitted photon echo is detected rather than the intensity so that the decay of the echo heterodyne envelope area is slower by a factor of two and is given by

$$E(t_{12}) = E_0 \exp \left[- \left(\frac{2t_{12}}{T_M} \right)^x \right]. \quad (2)$$

In general, the effective homogeneous linewidth can strongly depend on the orientation of the applied magnetic field $\mathbf{B}$ as well as the specific ion sites addressed in the crystal by the resonant optical excitation [62]. For amorphous media, there can be a wide range of local environments and a corresponding need to average over a complex distribution of sites and orientations [65]. In contrast, it should be possible to predict the behavior for a powder of randomly oriented crystallites from the measured orientation dependence of the bulk single crystal. In LiNbO_3 , Er^{3+} ions substitute for Li^+ with a local environment that nominally maintains an axial point symmetry with respect to the c -axis described by the C_3 point group [66,67]. Assuming that the sites maintain perfect axial symmetry, the orientation-dependent properties depend only on the angle θ between the magnetic field $\mathbf{B}$ and the c -axis.

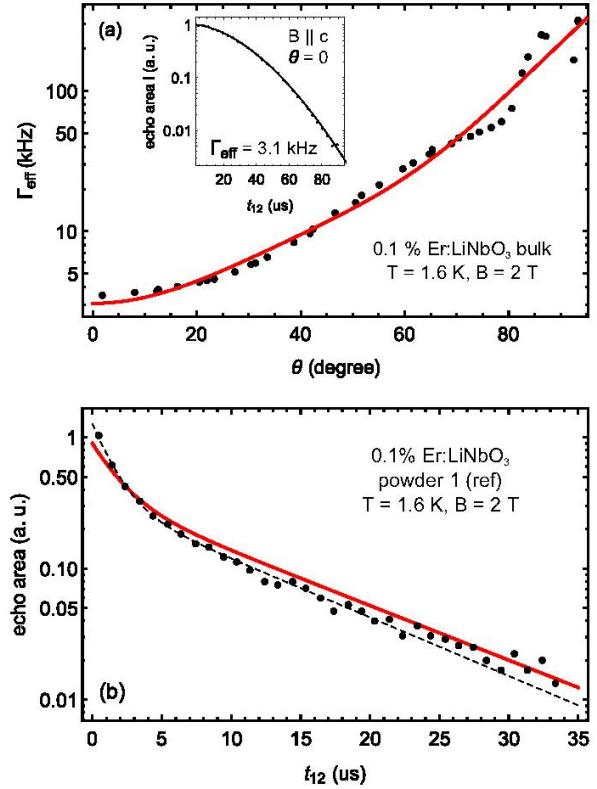


Fig. 3. (a) Orientation dependence of the effective linewidth Γ_{eff} in a 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ bulk crystal measured at $T=1.6$ K and $B=2$ T. The magnetic field orientation is rotated by an angle θ from the c -axis of the crystal. The inset shows an example echo intensity decay at $\theta=0$ i.e. $\mathbf{B}||c$, where the fit of Eq. (1) gives $\Gamma_{\text{eff}} = 1/\pi T_M = 3.1$ kHz. The red solid line is an empirical polynomial fit to the experimental $\Gamma_{\text{eff}}(\theta)$ data. (b) Decay of the echo area for the 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ reference powder. The dashed line corresponds to a fit of a sum of two exponential decays to the experimental data (black dots). The red solid line corresponds to a calculation of the expected decay in the powder due to the orientation dependence of Γ_{eff} in the bulk crystal.

Fig. 3(a) shows the effective linewidth as a function of θ in a 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ bulk crystal at $T=1.6$ K and $B=2$ T. The minimum homogeneous linewidth is observed for $\mathbf{B}$ along the c -axis, i.e. $\theta=0$, with a measured value of 3 kHz, agreeing with the linewidth previously reported for these conditions in a 0.06% $\text{Er}^{3+}:\text{LiNbO}_3$ crystal [16]. The values of Γ_{eff} were extracted from 2PE intensity decays fitted by Eq. (1), as shown in the inset for $\mathbf{B}$ along the c -axis. The measured angular dependence $\Gamma_{\text{eff}}(\theta)$ was fit well using an empirical eighth order polynomial containing only even powers. To simulate the observed echo intensity I_{tot} , we averaged the echo intensities over all possible random crystallite orientations as follows

$$I_{\text{tot}}(t_{12}) = I_0 \int_0^{\pi/2} \exp[-4\pi\Gamma_{\text{eff}}(\theta)t_{12}] \sin\theta d\theta. \quad (3)$$

This model assumes a uniform distribution of particle orientations and that all particles contribute equally to the averaged decay. Fig. 3(b) shows the measured echo intensity as a function of waiting time t_{12} in powder #1 under the same conditions as for the bulk measurements, i.e. $B=2$ T and $T=1.6$ K, as well as the decay simulated using Eq. (3) with the measured bulk crystal parameters. The simulated and measured decays agree very well, indicating that the observed echo signals in this case do represent a simple average over all possible particle orientations. This

conclusion is important for interpreting the later results since it suggests that the probe light interacts uniformly with different particles and that there is no preferential alignment of the crystallites in the powder.

From both the simulations and the measurements, we observed echo decays for the $\text{Er}^{3+}:\text{LiNbO}_3$ powders that could be approximately described by a double-exponential shape. Using simulations to investigate the contributions of different particle orientations to the echo signal, we found that, for the conditions studied in this work, the slow component of the decay corresponds to the subset of crystallites in the powder that have their c -axis oriented almost parallel to the applied magnetic field direction while the fast component of the decay corresponds to all crystallites with other orientations. For example, under the conditions in Fig. 3(a), fitting the powder decay with a double exponential gives effective homogeneous linewidths of 7.6 and 45 kHz for the two components, roughly corresponding to that of the bulk crystal with $\mathbf{B}$ along the c -axis (3.5 kHz), and an average over the behavior for other orientations (up to 300 kHz for $\mathbf{B}$ orthogonal to the c -axis), respectively. Note that the excited state population lifetime in $\text{Er}:\text{LiNbO}_3$ bulk crystals was measured to be 2 ms [16], which leads to an absolute lower limit for the optical homogeneous linewidth of 80 Hz.

Because the slower decay component probes the subset of particles with their c -axis approximately aligned with the external field, as confirmed by the analytical model described by Eq. (3), we can quantitatively analyze the decoherence mechanisms by directly comparing this component of the decay to the bulk crystal behavior for $\mathbf{B}||c$. Consequently, in all of the following analysis, we focus on the slower component of the double exponential decay observed for the powder samples. In the spectral hole burning and free induction decay measurements described later, only single exponential decays are observed since at the timescales of these measurements, additional decoherence effects dominate the decay behavior and are more important than the orientation effect observed in the 2PE measurements.

3.1.2. Magnetic field dependence of coherence lifetimes

In this section we discuss the observed magnetic field dependence of the coherence lifetimes in the different samples and investigate additional decoherence processes resulting from the powder fabrication methods. Fig. 4 shows the magnetic field dependence of the effective linewidth at $T=3$ K for the bulk crystal, powder #1 (the reference), and powder #2. No heterodyne technique was needed here, but we verified that the heterodyne measurement of the decay fitted by Eq. (2) gave the same

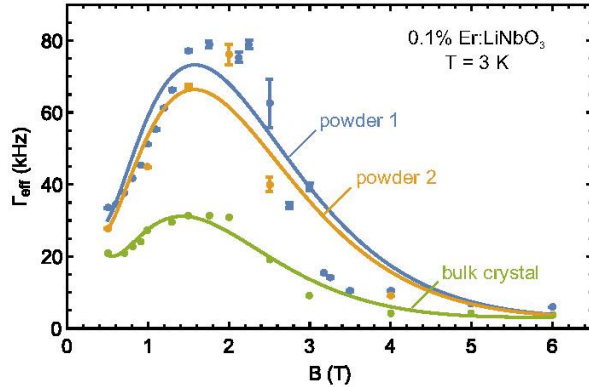


Fig. 4. Magnetic field dependence of the effective homogeneous linewidth in 0.1% $\text{Er}^{3+}:\text{LiNbO}_3$ at $T=3$ K for the bulk crystal (for $\mathbf{B}||c$), the reference powder #1, and a powder ball-milled for 30 min (powder #2).

characteristic lifetime. For all other powder samples listed in Table 1, the signal was either too weak or exhibited a decay too rapid to extract a lifetime corresponding to the slow component with a reasonable uncertainty. The experimental points $\Gamma_{\text{eff}}(B)$ are fitted by the spectral diffusion model from Ref. [16], where the effective linewidth is given by

$$\Gamma_{\text{eff}}(B, T) = \frac{\Gamma_{\text{SD}} R}{-2\Gamma_0 + 2\sqrt{\Gamma_0^2 + \frac{\Gamma_{\text{SD}} R}{\pi}}}, \quad (4)$$

where Γ_0 is the linewidth without spectral diffusion, Γ_{SD} is the broadening caused by interactions between the Er^{3+} electronic spins, and R is the rate of spectral diffusion. The spectral diffusion broadening has a full width at half maximum described by

$$\Gamma_{\text{SD}}(B, T) = \Gamma_{\text{max}} \text{sech}^2\left(\frac{g_{\text{env}} \mu_B B}{2k_B T}\right), \quad (5)$$

where Γ_{max} is the maximum broadening due to magnetic dipole-dipole interactions, $g_{\text{env}} \mu_B B$ is the splitting of the Er^{3+} spin states, and the hyperbolic secant function in Eq. (5) describes the suppression of spectral diffusion at high magnetic fields due to the increased magnetic ordering of the spins. Spectral diffusion occurs at a rate R characterizing the flip rate of the perturbing Er^{3+} spins; that is approximately given by

$$R(B, T) = \alpha_{\text{ff}} \text{sech}^2\left(\frac{g_{\text{env}} \mu_B B}{2k_B T}\right) + \alpha_{\text{D}} g_{\text{env}}^3 B^5 \coth\left(\frac{g_{\text{env}} \mu_B B}{2k_B T}\right). \quad (6)$$

This expression assumes that only the mutual $\text{Er}^{3+}-\text{Er}^{3+}$ spin flip-flop process with coefficient α_{ff} and the direct phonon process with coefficient α_{D} drive Er^{3+} spin flips, as expected for temperatures below 4 K.

Fitting Eq. (4) to the three sets of data (bulk crystal and powders #1 and #2) gives very similar spectral diffusion parameters except for the coefficient α_{D} that is 4 times larger for powder #1 and 3 times larger for powder #2 as compared to the bulk crystal (see Table 2). This suggests that additional spin relaxation processes that increase with magnetic field are introduced through powder fabrication by crushing or ball-milling. Such processes may be understood within the framework of the two-level system (TLS) model developed to describe dynamics in amorphous materials [68,69]. In this model, very low-frequency modes that involve groups of atoms tunneling between local configurations with nearly equivalent energies are enabled by defects and disorder in the crystal structure. It has been proposed that low densities of TLS can be present in some crystalline materials with large inhomogeneous lattice strains [70]. Decoherence attributed to TLS has been previously observed in both bulk crystals [31,61] and powders [32], and it has also been suggested that TLS can cause rapid electron spin relaxation [71]. This interpretation is also consistent with past observations of increased electronic spin-lattice relaxation rates of Nd^{3+} in YAG single crystals with a high

Table 2

Parameters from fitting the experimental data shown in Fig. 4 by Eq. (4). For all samples, the value of Γ_{max} was fixed to 1 MHz and the parameter Γ_0 was constrained to be larger or equal than minimum bulk value ($\Gamma_0 = 3$ kHz at 6 T), which lead to $\Gamma_0 = 3$ kHz.

sample	g	α_{ff} (kHz)	α_{D} (kHz/T ⁵)
bulk	15.7	11	69
1	14	12	240
2	14	9	200

density of structural defects in the lattice [72] as well as increased nuclear spin relaxation rates of $^{169}\text{Yb}^{3+}$ in YAG powders fabricated by ball milling [51]. While it is known that high-energy ball milling of nanocrystals can produce significant disorder in the crystal structure and introduce some amorphous behavior [45–49], our results suggest that even very low-energy grinding methods applied to much larger microcrystals still cause substantial damage that produce TLS. Since the powders examined all have sizes larger than $1\text{ }\mu\text{m}$ we assume that contamination of the crystal surface or surface effects in general do not play a role in this case.

Because 2PE techniques did not allow us to extract the long component of the decay corresponding to the longer coherence lifetime in the bulk, we also used SHB and FID techniques in all of the powder samples to probe the effects of faster decoherence processes. These measurements are described in the following sections.

3.2. Spectral hole burning

We employed spectral hole burning to measure Γ_{eff} as well as the effective absorption depth α_{eff} of our samples. We use the latter to qualitatively estimate the amount of scattering and the quality of the micro/nano-crystals. In this measurement, a $500\text{ }\mu\text{s}$ long burn pulse excited the resonant Er^{3+} ions into the $^4I_{13/2}$ excited state and created a corresponding transparency window in the inhomogeneously broadened absorption line. After a $25\text{ }\mu\text{s}$ delay, a subsequent $50\text{ }\mu\text{s}$ long read pulse with lower power was frequency swept across the spectral hole to measure the absorption spectrum.

A typical hole burning trace is shown in Fig. 5 for powder #1 at a temperature of 1.6 K and a magnetic field of 2 T . In addition to the main hole in the center of the spectrum, we observed additional sideholes originating from the superhyperfine coupling between the Er^{3+} electronic spins and the nuclear spins of the host ions, with ^{93}Nb producing a superhyperfine splitting of 9 MHz/T and ^7Li producing a splitting of 14.8 MHz/T [17].

Spectral hole burning measurements provide information about the optical coherence lifetime via the width of the spectral hole. In the absence of power broadening, the spectral hole width is twice the effective homogeneous linewidth convolved with the laser linewidth [73]. To estimate the effect of power broadening and the laser linewidth, we carried out a series of hole burning measurements on the bulk crystal using different laser powers. This measurement allowed us to extrapolate to the hole width at zero burning power. From a power broadening measurement performed on powder #3, we estimated that our measured hole

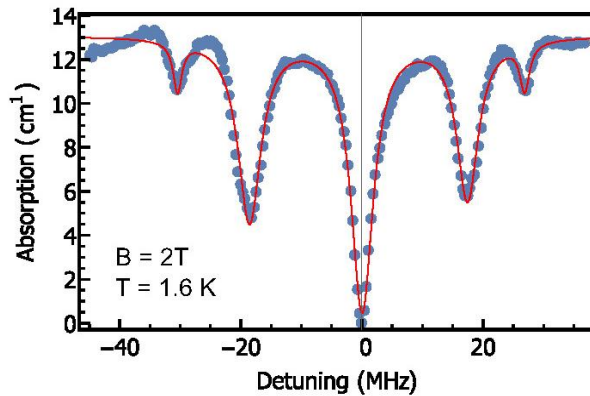


Fig. 5. Hole burning spectrum in $0.1\% \text{ Er}^{3+}:\text{LiNbO}_3$ (powder #1) at $T=1.6\text{ K}$ and $B=2\text{ T}$. Zero detuning corresponds to 1531.882 nm in vacuum.

Table 3

Maximum effective absorption coefficient α_{eff} extracted from SHB measurements, as well as effective linewidths Γ_{eff} extracted from SHB (after a $T_w = 25\text{ }\mu\text{s}$), 2PE (heterodyne measurement for samples #3 to #6) and FID (after a $T_w = 5\text{ }\mu\text{s}$) measurements at $T=1.6\text{ K}$ and $B=2\text{ T}$ for different samples. When a double exponential decay was observed, as described in the main text, both decay values are listed. For the bulk crystal, the magnetic field and light polarization were parallel to the c -axis ($B||E||c$).

sample	α_{eff} (cm^{-1})	$\Gamma_{\text{eff}}^{\text{SHB}}$ (kHz)	$\Gamma_{\text{eff}}^{2\text{PE}}$ (kHz)	$\Gamma_{\text{eff}}^{\text{FID}}$ (kHz)
bulk	3.9	<10	3.2	<10
1 (ref)	13.5	60	4.5/40	32
3	9.4	<10	12/45	38
4	1.4	1050	30	30
5	0.71	990	38	29
6	2.96	150	37	42

widths exhibited 1.93 MHz of power broadening, and we then assumed that the power broadening was the same for each powder under the same excitation conditions. This gives a large uncertainty that we estimated to be 10 kHz on the extracted values of the effective linewidth, but still allows us to compare the effects of the different treatments applied to the powders. A comparison between SHB and 2PE measurements for the bulk crystal resulted in an estimated contribution of the laser linewidth to the hole width of 420 kHz . Using these values, the effective homogeneous linewidths were computed from the hole burning measurements by subtracting the power broadening and laser linewidth contributions, with the outcome summarized in Table 3.

Table 3 contains a summary of effective homogeneous linewidths measured using different techniques. Note that the values obtained using holeburning and FID are influenced by spectral diffusion (on the timescale of $25\text{ }\mu\text{s}$ and $5\text{ }\mu\text{s}$ respectively) and laser jitter. We see that powder #1, which was crushed using only a mortar and pestle, shows broader hole widths than the bulk crystal, meaning that additional spectral diffusion processes occur in this powder. Remarkably, the effective homogeneous linewidth of powder #3, which was ball-milled and then annealed, is narrower, and on the same order of magnitude as that of the bulk crystal. This indicates that crystal damage (strain and defects) caused by mechanical processing, in this case crushing using a mortar and pestle and slow ball milling, could be mostly removed by annealing the powder with the smallest particle sizes studied of roughly $2\text{ }\mu\text{m}$ and lower. On the other hand, powder #4 shows much broader spectral holes with the same mechanical processing as powder #3 but annealing at a higher temperature. To further explore the effect of temperature, powder #5 was ball milled at a higher speed and for a longer time than powders #3 and #4, but was then annealed at the same upper temperature as powder #4, resulting in very large spectral hole widths – nearly the same as for powder #4. These results suggest that the much broader linewidths observed in powders #4 and #5 arise from the higher annealing temperatures. Consequently, it appears that temperatures above 1000 C are detrimental to the material properties rather than beneficial, likely due to additional disorder caused by loss of either lithium or oxygen from the crystal matrix. This hypothesis is consistent with past observations of substantial lithium out-diffusion from the surface of bulk crystals when annealed in a wet oxygen atmosphere at temperatures above approximately 1100 C [58]. Moreover, changes in material properties due to lithium out-diffusion have been observed at temperatures as low as 600 C for LiNbO_3 thin films [52,53], suggesting that even lower annealing temperatures than used here may be optimal for micro/nano-powders.

Finally, we examined powder #6 that was fabricated through in-diffusion of erbium into commercial LiNbO_3 powder. This

powder was processed using similar mechanical and thermal treatments as for powders #4 and #5, although noticeably narrower linewidths than those of powders #4 and #5 were observed. Further study is required to determine whether the difference in linewidth is a result of the different starting materials, the presence of ErCl_3 mixed with the powder, or other factors.

From the hole burning spectra, we also extracted effective absorption depths for each powder sample. Since scattering in the powder increases the optical path length traveled by the light as it passes through the sample, we should observe a larger absorption depth for samples with more scattering, as well as the expected increase in the overall frequency-independent scattering loss. On the other hand, scattering of light between and around loosely packed particles will reduce the absorption compared to a bulk crystal. In particular, any small gap in the 0.4 mm thick loose powder can result in a weakly scattered background signal that does not strongly probe the powder. Furthermore, when the individual crystallites have anisotropic absorption, the transmitted light in general will not follow the usual Beer-Lambert-Bouguer exponential decay law. Nevertheless, if we assume that the incident light polarization is randomized many times during the scattering process, as we observe experimentally from the transmitted light, then we can approximate the propagation through the powder using the absorption coefficient averaged over all polarizations states. Thus, while it is difficult to extract real absorption coefficients or effective path lengths from the measured transmission spectrum, we do expect the observed effective absorption to provide some qualitative information about the relative scattering path lengths in the powder samples.

For the 1532 nm transition of $\text{Er}^{3+}:\text{LiNbO}_3$, the absorption coefficient is dependent on both the polarization and the propagation direction of the light since the transition has comparable electric and magnetic transition dipole strengths [17]. The maximum absorption coefficients are known for light propagating orthogonally to the crystal's c -axis with π polarization, i.e. $\mathbf{E} \parallel c$ (4.1 cm^{-1}), and σ polarization, i.e. $\mathbf{E} \perp c$ (6.8 cm^{-1}), as well as for the light propagating along the crystal's c -axis with the two circular polarization states (11.1 cm^{-1} averaged over left and right handed polarizations). Consequently, averaging over all possible random crystal orientations and polarizations, we would expect an effective absorption coefficient α_{eff} of 7.3 cm^{-1} for a powder in the limit of many scattering events.

To estimate the effective absorption coefficient α_{eff} for each powder sample, we used high-power (resonant) optical excitation to burn a very deep spectral hole for which we assumed complete transparency since further increasing the burning power did not produce any additional increase in the transmission. Using this approach, α_{eff} was calculated from the transmitted intensity I_t at the center of the hole and the intensity I_0 with the laser tuned away from the hole (where it experiences the full absorption) through the relation

$$\alpha_{\text{eff}} = -\ln\left(\frac{I_t}{I_0}\right)/L, \quad (7)$$

where $L=0.4 \text{ mm}$ is the powder thickness. The resulting effective absorption values are listed in Table 3 for each sample.

For powders #1 and #3 we measured absorption coefficients (see Table 3) higher than the bulk average increased by a factor of 1.8 and 1.3 respectively. This is consistent with the transmitted light experiencing a longer path in the powder sample. However, for the other powder samples, the measured absorption coefficient is significantly lower compared to the bulk. We note that all powders with small optical depth (#4 to #6) underwent the same annealing procedure, with maximum temperatures of around 1100C, which might have introduced modifications in the host

matrix that potentially could cause broadening of the inhomogeneous linewidth or other effects responsible for decreased absorption. This explanation would also be consistent with our observation of larger effective homogeneous linewidths in those same samples. Nevertheless, to conclusively identify the cause of the weaker observed spectral hole depths in these samples requires further study.

The experiment described above shows that SHB measurements in direct transmission could be successfully conducted in powder samples and that the effective linewidths were successfully extracted in samples for which 2PE measurements did not allow a good estimation of the coherence lifetime. Overall, we observed that coherence properties degraded in powders that underwent mechanical processing. This suggests the presence of two-level systems in these samples. To further verify these results, we also used FID techniques to probe the coherence properties over an intermediate range that overlaps those accessible through SHB and 2PE measurements.

3.3. Free induction decay and spectral diffusion

SHB measurements may be used to probe powders with broad homogeneous linewidths that cannot be accessed by 2PE techniques. However, in cases where rapid spectral diffusion or complex spectral structure such as spin-flip sidebands are present, optical coherent transient FID measurements can serve as a better method to extract the effective homogeneous linewidth [73]. While FID measurements that probe a single spectral hole are still limited by the laser linewidth, FID may be employed immediately following the hole preparation without the need for laser chirping, allowing the broadening to be probed over shorter timescales than frequency domain SHB measurements. Furthermore, FIDs are more amenable to heterodyne detection techniques, allowing for improved signal discrimination and dynamic range relative to SHB. The shape of the FID curve also reveals the evolution of decoherence processes over the timescale of the measurement in a manner similar to 2PE techniques [16], unlike direct SHB that requires an extensive series of measurements to extract similar information.

Motivated by the ability of FID measurements to probe rapid decoherence processes contributing to the homogeneous linewidth (i.e. processes faster than the shortest timescales observable using 2PEs), we employed FID measurements to study all of our powder samples. Specifically, we applied a variation of the FID technique sometimes referred to as a delayed FID that is analogous to a stimulated photon echo measurement [73]. For this approach, a laser pulse first burnt a hole in the inhomogeneously broadened absorption line of the sample: in our case we used a $50 \mu\text{s}$ long burn pulse to provide an approximately 20 kHz Fourier-limited spectral resolution. After a waiting time T_w , a second brief excitation pulse was applied to induce an optical coherence across the frequency window of the burnt hole. The decay of the coherent emission after the brief pulse provides information about the effective width of the spectral hole resulting from the convolution of the effective homogeneous linewidth and the laser linewidth, as well as any spectral diffusion that occurs over the waiting time T_w . In our case, we employed heterodyne detection to measure the coherence decay by beating it with a third laser pulse shifted in frequency by 10 MHz. The decay of the resulting 10 MHz beat signal is given by

$$E(t) = E_0 \exp\left[-\left(\frac{t}{T_M^{\text{eff}}}\right)^2\right]. \quad (8)$$

By fitting this equation to the experimentally measured decay, we extracted the effective homogeneous linewidth $\Gamma_{\text{eff}} = 1/\pi T_M^{\text{eff}}$ after a waiting time T_w . An exemplary FID decay signal for powder #1

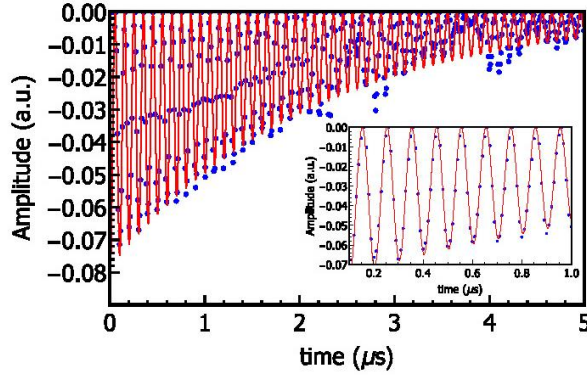


Fig. 6. Typical background-subtracted FID decay of the reference powder #1 at $B=3.9$ T, $T=1.6$ K and waiting time $t_w = 5$ μ s. Solid points are measured values and the solid line is a fit of the FID signal. The inset shows a magnification of the first 1 μ s of the decay.

(reference) at $B=3.9$ T, $T=1.6$ K and waiting time $T_w = 5$ μ s is shown in Fig. 6, where the steady-state transmitted intensity has been subtracted from the signal. The fit of the FID is shown by the solid line, revealing an exponential decay envelope (i.e. $\chi=1$ in Eq. (8)) that corresponds to an effective linewidth of $\Gamma_{\text{eff}} = 147$ kHz.

By changing the waiting time T_w between the burn and excitation pulses, the delayed FID technique was used to determine the effective homogeneous linewidth at different timescales and thus study time-dependent decoherence processes, i.e. spectral diffusion. The effective homogeneous linewidth over a range of waiting times for different powders is shown in Fig. 7. From a comparison of the obtained effective homogeneous linewidths using FID at $T_w = 5$ μ s and the local slope of the two pulse photon echo decay around $t_2 = 5$ μ s for each powder, we estimated the experimental contribution to each FID measurement due to laser linewidth, power broadening and shot-to-shot laser jitter.

As shown in Fig. 7, we observed a rapid time-dependent broadening of the linewidth due to spectral diffusion occurring at timescales of less than 500 μ s, and then a saturation of the broadening at longer timescales, indicating that those waiting times were longer than the inverse of the spectral diffusion rate. Comparing the behaviors at $B=2$ T and $B=3.9$ T (see Fig. 7(a) and (b)) indicates that spectral diffusion is faster at 2 T, whereas the final linewidth at long T_w is similar at both magnetic fields. Overall, the bulk crystal shows the narrowest linewidths, although powder #1 (the reference powder) that underwent minimal grinding using only a mortar and pestle exhibits similar spectral diffusion broadening as the bulk crystal at the longest time delays. All ball-milled powders show significantly larger effective linewidths. For powders #3 and #4 that underwent the same mechanical treatment, the data points at short T_w suggest that the higher annealing temperature of 1100 C for powder #4 was detrimental. Furthermore, we could not observe a clear saturation of the effective homogeneous linewidth with waiting time for powder #4, unlike all of the other powders. Powder #5 that experienced more severe mechanical treatment (fast ball milling for 10 h) but the same annealing process as #4, shows comparable broadening as #4, further suggesting that the high annealing temperature was the limiting factor for these samples. This observation is consistent with the SHB results discussed earlier and again points toward defects and disorder in the crystal caused by out-diffusion of lithium at high temperatures [52,53,58]. Since the dynamic TLS modes enabled by the disorder typically exhibit a broad distribution of relaxation rates, they are expected to cause significant spectral diffusion that often produces a logarithmic increase in the homogeneous linewidth over time [74,75].

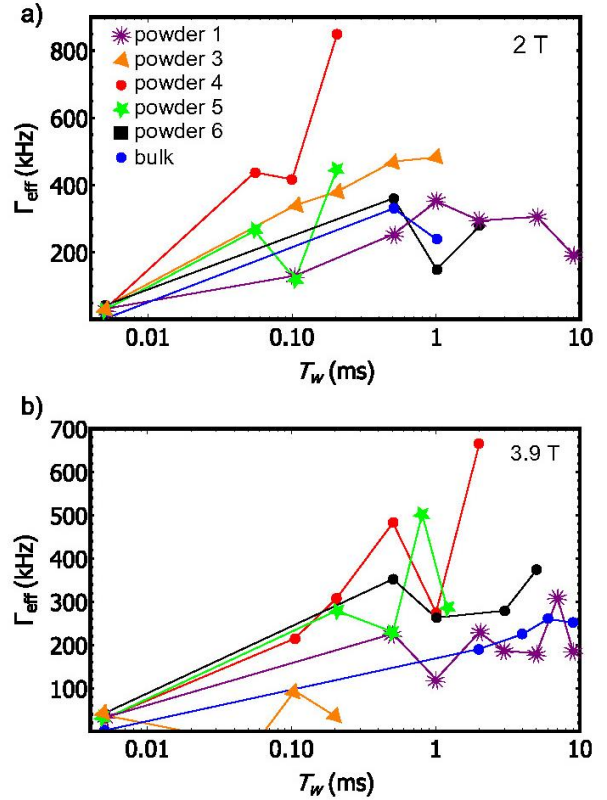


Fig. 7. Effective homogeneous linewidths at (a) $B=2$ T and (b) $B=3.9$ T at $T=1.6$ K as a function of the waiting time T_w measured using the delayed FID technique for powders #1, #3 through #6 and for the bulk crystal. The solid lines are guides to the eye.

The commercial powder with large crystallites that were diffusion-doped with Er^{3+} (powder #6) exhibited better coherence properties at long timescales compared to all of the ball-milled powders, although still significantly worse than the bulk crystal and the crushed reference powder #1. This again suggests that higher processing temperatures are a key factor in producing spectral diffusion, although at a lower level for larger particles as might be expected if lithium out-diffusion is the cause.

4. Conclusion

We demonstrated that spectroscopic properties such as optical coherence lifetimes in $\text{Er}^{3+}:\text{LiNbO}_3$ powders that experienced various mechanical and thermal treatments could be measured despite strong scattering, random orientations, and shorter coherence lifetimes. The 2PE measurements were optimal to access long coherence lifetimes whereas SHB and FID techniques were well suited to quantify fast dephasing processes. Furthermore, we described how the powder properties could be predicted and understood by averaging the orientation dependent properties of the bulk single crystal.

We observed that mechanical grinding of the powders resulted in a broadening of their effective homogeneous linewidths, indicating the presence of dynamic TLS modes characteristic of amorphous phases. This conclusion was also supported by observations of corresponding decreases in the maximum absorption as well as a broader distribution of spectral diffusion rates as

compared to the bulk crystal. Surprisingly, we found that even crushing and grinding with mortar and pestle to produce large microcrystals resulted in significant damage as indicated by an order-of-magnitude increase in the homogeneous linewidth. In the powders that experienced less processing, spectral diffusion broadening at longer timescales approached the values observed in the bulk, suggesting that grinding primarily accelerates existing spectral diffusion mechanisms (such as Er^{3+} electronic spin flips) rather than introducing new sources of broadening. This conclusion is also consistent with the increase in the magnetic-field-dependent spectral diffusion rates extracted from analysis of the 2PE coherence measurements (summarized in Table 2). We found that the broadening could be partially reversed by high-temperature annealing in oxygen atmospheres for some powders; however, treatment at temperatures above 1000°C was detrimental for the coherence properties. The powders annealed at temperatures above 1000°C exhibited a large increase in the magnitude of spectral diffusion, suggesting that additional broadening mechanisms were introduced, possibly due to out-diffusion of lithium and oxygen from the crystallites.

Together, our results demonstrate that even minimal low-energy mechanical processing significantly degrades the material properties of interest for classical and quantum signal-processing applications. Chemical fabrication methods, such as chemical synthesis or etching may minimize the amount of amorphous-like behavior introduced when fabricating micro- and nano-materials and lead to better optical coherence properties. This hypothesis is consistent with past structural and spectroscopic studies of nanocrystalline LiNbO_3 where powders produced by sol-gel methods had significantly better properties than those produced by high-energy ball milling [46,48], although still not reaching the bulk crystal properties [49]. The detrimental effects of high annealing temperatures also suggest that lower temperature bottom-up synthesis may be preferred. The demonstration of long coherence lifetimes in $\text{Eu:Y}_2\text{O}_3$ nanopowders produced using solvothermal methods confirms that at least some materials can be fabricated with optical coherence properties approaching those of the bulk crystal [39]. Based on the recent work on $\text{Nd:Y}_2\text{SiO}_5$ [40], we expect that focused-ion-beam milling may also be successful in preserving the coherence properties of REI-doped LiNbO_3 , potentially providing a suitable tool to fabricate micro- and nano-structures for optical signal-processing applications. Nevertheless, further studies are required to determine whether there are other fundamental limitations of material performance when the crystal size is reduced to the nanoscale.

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References

- [1] Y.C. Sun, in *Spectroscopic Properties of Rare Earths in Optical Materials*, P.R. Hull, P.J. Parisi, P.R.M.O. Jr, P.H. Warlimont, D.G. Liu, and P.B. Jacquier, eds., Springer Berlin Heidelberg, 2005, no. 83 in Springer Series in Materials Science, pp. 379–429.
- [2] L. Ménager, I. Lorgère, J.-L. le Gouët, D. Dolfi, J.-P. Huignard, *Opt. Lett.* **26** (2001) 1245.
- [3] B. Lauritzen, J. Minár, H. de Riedmatten, M. Afzelius, N. Gisin, *Phys. Rev. A* **83** (2011) 012318.
- [4] R. Lauro, J. Ruggiero, A. Louchet, A. Alexander, T. Chanière, I. Lorgère, F. Bretenaker, F. Goldfarb, and J.L. Le Gouët, *Journal of Luminescence* **129**, 195, 1, 2009.
- [5] M. Afzelius, C. Simon, H. de Riedmatten, N. Gisin, *Phys. Rev. A* **79** (2009) 052329.
- [6] E. Saglamyurek, N. Sinclair, J.A. Slater, K. Heshami, D. Oblak, W. Tittel, *New J. Phys.* **16** (2014) 065019.
- [7] C.W. Thiel, T. Böttger, R.L. Cone, *J. Lumin.* **131** (2011) 353.
- [8] J. Amin, B. Dussardier, T. Schweizer, M. Hempstead, *J. Lumin.* **69** (1996) 17.
- [9] E. Saglamyurek, N. Sinclair, J. Jin, J.A. Slater, D. Oblak, F. Bussiès, M. George, R. Ricken, W. Sohler, W. Tittel, *Nature* **469** (2011) 512.
- [10] R.S. Weis, T.K. Gaylord, *Appl. Phys. A* **37** (1985) 191.
- [11] C.E. Rüter, S. Suntsov, D. Kip, G. Stone, V. Dierolf, H. Hu, and W. Sohler (2014), vol. 8982, pp. 89821G–89821G–8.
- [12] M.N. Armenise, *IEEE Proceedings J – Optoelectronics*, **135**, 8, 5, 1988.
- [13] W. Sohler, H. Suche, *Integrated Optical Circuits and Components Design and applications*, Marcel Dekker, 1999.
- [14] Y. Sun, C.W. Thiel, R.L. Cone, R.W. Equall, R.L. Hutcheson, *J. Lumin.* **98** (2002) 281.
- [15] S.R. Hastings-Simon, M.U. Staudt, M. Afzelius, P. Baldi, D. Jaccard, W. Tittel, N. Gisin, *Opt. Commun.* **266** (2006) 716.
- [16] C.W. Thiel, R.M. Macfarlane, T. Böttger, Y. Sun, R.L. Cone, W.R. Babbitt, *J. Lumin.* **130** (2010) 1603.
- [17] C.W. Thiel, Y. Sun, R.M. Macfarlane, T. Böttger, R.L. Cone, *J. Phys. B: At., Mol. Opt. Phys.* **45** (2012) 124013.
- [18] S. Benchabane, L. Robert, J.-Y. Rauch, A. Khelif, V. Laude, *J. Appl. Phys.* **105** (2009) 094109.
- [19] N. Courjal, S. Benchabane, J. Dahdah, G. Ulliac, Y. Gruson, V. Laude, *Appl. Phys. Lett.* **96** (2010) 131103.
- [20] F. Lacour, N. Courjal, M.P. Bernal, A. Sabac, C. Bainier, M. Spajer, *Opt. Mater.* **27** (2005) 1421.
- [21] I.L. Gheorma, P. Savi, R.M. Osgood, *IEEE Photonics Technol. Lett.* **12** (2000) 1618.
- [22] T.A. Ramadan, M. Levy, R.M. Osgood, *Appl. Phys. Lett.* **76** (2000) 1407.
- [23] H. Robinson, C.W. Pitt, R.A. Gibson, *Appl. Opt.* **32** (1993) 3981.
- [24] H. Hu, R. Ricken, W. Sohler, R.B. Wehrspohn, *IEEE Photonics Technol. Lett.* **19** (2007) 417.
- [25] B. Knabe, K. Buse, W. Assenmacher, W. Mader, *Phys. Rev. B* **86** (2012) 195428.
- [26] R. Grange, J.-W. Choi, C.-L. Hsieh, Y. Pu, A. Magrez, R. Smajda, L. Forró, D. Psaltis, *Appl. Phys. Lett.* **95** (2009) 143105.
- [27] A.N. Morozovska, E.A. Eliseev, G.S. Svechnikov, S.V. Kalinin, *J. Appl. Phys.* **108** (2010) 042009.
- [28] A. Rüdiger, T. Schneller, A. Roelofs, S. Tiedke, T. Schmitz, R. Waser, *Appl. Phys. A* **80** (2005) 1247.
- [29] N. Kunkel, J. Bartholomew, S. Welinski, A. Ferrier, A. Ikesue, P. Goldner, *Phys. Rev. B* **94** (2016) 184301.
- [30] J.G. Bartholomew, K. de Oliveira Lima, A. Ferrier, P. Goldner, *Nano Lett.* **17** (2017) 778.
- [31] G.P. Flinn, K.W. Jang, J. Ganem, M.L. Jones, R.S. Meltzer, R.M. Macfarlane, *Phys. Rev. B* **49** (1994) 5821.
- [32] R. Meltzer, K. Jang, K. Hong, Y. Sun, S. Feofilov, *J. Alloy. Compd.* **250** (1997) 279.
- [33] K.S. Hong, R.S. Meltzer, B. Bihari, D.K. Williams, B.M. Tissue, *J. Lumin.* **76** (1998) 234.
- [34] S.P. Feofilov, *Phys. Solid State* **44** (2002) 1407.
- [35] R.M. Macfarlane, M.J. Dejneka, *Opt. Lett.* **26** (2001) 429.
- [36] H. Zheng, X.-j. Wang, S.-X. Qu, M.J. Dejneka, R.S. Meltzer, *J. Lumin.* **(119)**, 2006) 153.
- [37] R.S. Meltzer, H. Zheng, M.J. Dejneka, *J. Lumin.* **107** (2004) 166.
- [38] F. Beaudoux, A. Ferrier, O. Guillot-Noël, T. Chanière, J.-L. le Gouët, P. Goldner, *Opt. Express* **19** (2011) 15236.
- [39] A. Perrot, P. Goldner, D. Gaume, M. Lovrić, C. Andriamadanana, R.R. Gonçalves, A. Ferrier, *Phys. Rev. Lett.* **111** (2013) 203601.
- [40] T. Zhong, J.M. Kindem, E. Miyazono, A. Faraon, *Nature Commun.* **6** (2015) 8206.
- [41] C.C. Koch, *Nanostruct. Mater.* **2** (1993) 109.
- [42] V. Šepelák, S. Bégin-Colin, G.L. Caër, *Dalton Trans.* **41** (2012) 11927.
- [43] D. Michel, L. Mazerolles, P. Berthet, E. Gaffet, *Eur. J. Solid State Inorg. Chem.* **32** (1995) 673.
- [44] S.L. Bravina, A.N. Morozovska, N.V. Morozovsky, Y.A. Skryshevsky, *Ferroelectrics* **298** (2004) 31.
- [45] D. Bork, P. Heitjans, *J. Phys. Chem. B* **102** (1998) 7303.
- [46] M.J. Pooley, A.V. Chadwick, *Radiat. Eff. Defects Solids* **158** (2003) 197.
- [47] P. Heitjans, S. Indris, *J. Mater. Sci.* **39** (2004) 5091.
- [48] A.V. Chadwick, M.J. Pooley, S.L.P. Savin, *Phys. Status Solidi (C)* **2** (2005) 302.
- [49] P. Heitjans, M. Masoud, A. Feldhoff, and M. Wilkening, *NMR and Impedance Studies of Nanocrystalline and Amorphous Ion Conductors: Lithium Niobate as a Model System*, vol. 134, 2007.
- [50] S. Kar, S. Logad, O.P. Choudhary, C. Debnath, S. Verma, K.S. Bartwal, *Univers. J. Mater. Sci.* **1** (2013) 18.
- [51] T. Lutz, L. Veissier, C.W. Thiel, P.J.T. Woodburn, R.L. Cone, P.E. Barclay, W. Tittel, *Sci. Technol. Adv. Mater.* **17** (2016) 63.
- [52] X. Wang, Z. Ye, G. Li, B. Zhao, *J. Cryst. Growth* **306** (2007) 62.
- [53] G.C. Budakoti, R.S. Rawat, *J. Cryst. Growth* **310** (2008) 4205.
- [54] H. Jhans, J.M. Honig, C.N.R. Rao, *J. Phys. C: Solid State Phys.* **19** (1986) 3649.
- [55] A. Dhar, A. Mansingh, *J. Appl. Phys.* **68** (1990) 5804.
- [56] A.Z. Simões, M.A. Zaghe, B.D. Stojanovic, A.H. Gonzalez, C.S. Riccardi, M. Cantoni, J.A. Varela, *J. Eur. Ceram. Soc.* **24** (2004) 1607.

- [57] J.L. Jackel, V. Ramaswamy, S.P. Lyman, *Appl. Phys. Lett.* 38 (1981) 509.
- [58] S. Forouhar, G.E. Betts, W.S.C. Chang, *Appl. Phys. Lett.* 45 (1984) 207.
- [59] U. Schlarb, K. Betzler, *Phys. Rev. B* 48 (1993) 15613.
- [60] D.E. Zelmon, D.L. Small, D. Jundt, *JOSA B* 14 (1997) 3319.
- [61] R. Macfarlane, Y. Sun, R. Cone, C. Thiel, and R. Equall, *Journal of Luminescence* 107, 31, 0, 2004, in: *Proceedings of the 8th International Meeting on Hole Burning, Single Molecule, and Related Spectroscopies: Science and Applications*.
- [62] T. Böttger, C.W. Thiel, R.L. Cone, Y. Sun, *Phys. Rev. B* 79 (2009) 115104.
- [63] W.B. Mims, *Phys. Rev.* 168 (1968) 370.
- [64] T. Böttger, C.W. Thiel, Y. Sun, R.L. Cone, *Phys. Rev. B* 73 (2006) 075101.
- [65] L. Veissier, M. Falamarzi, T. Lutz, E. Saglamyurek, C.W. Thiel, R.L. Cone, W. Tittel, *Phys. Rev. B* 94 (2016) 195138.
- [66] T. Gog, M. Griebenow, G. Materlik, *Phys. Lett. A* 181 (1993) 417.
- [67] J. Garcia Solé, L.E. Bausá, D. Jaque, E. Montoya, H. Murrieta, F. Jaque, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 54 (1998) 1571.
- [68] P.W. Anderson, B.I. Halperin, c.M. Varma, *Philos. Mag.* 25 (1972) 1.
- [69] W. Phillips, *J. Low. Temp. Phys.* 7 (1972) 351.
- [70] S.K. Watson, *Phys. Rev. Lett.* 75 (1995) 1965.
- [71] T.R. Askew, H.J. Stapleton, K.L. Brower, *Phys. Rev. B* 33 (1986) 4455.
- [72] L. Aminov, I. Kurkin, D. Lukoyanov, *Appl. Magn. Reson.* 14 (1998) 447.
- [73] R.M. Macfarlane, *Coherent transient and holeburning spectroscopy of rare earth ions in solids*, in: *Spectroscopy of Solids Containing Rare Earth Ions*, North-Holland, 1987.
- [74] J.L. Black, B.I. Halperin, *Phys. Rev. B* 16 (1977) 2879.
- [75] R.J. Silbey, J.M.A. Koedijk, S. Völker, *J. Chem. Phys.* 105 (1996) 901.

CHAPTER 11

MODIFICATION OF RELAXATION DYNAMICS IN

 $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ NANOPOWDERSContribution of Authors and Co-Authors

Manuscript in Chapter 11

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Contributions: Prepared and synthesized material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

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Modification of relaxation dynamics in $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ nanopowders

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Nanostructured rare-earth-ion-doped materials are increasingly being investigated for on-chip implementations of quantum information processing protocols as well as commercial applications such as fluorescent lighting. However, achieving high-quality and optimized materials at the nanoscale is still challenging. Here we present a detailed study into the restriction of phonon processes in the transition from bulk crystals to small (≤ 40 -nm) nanocrystals by observing the relaxation dynamics between crystal-field levels of $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$. We find that the population relaxation dynamics are modified as the particle size is reduced, consistent with our simulations of inhibited relaxation through a modified vibrational density of states and hence modified phonon emission. However, our experiments also indicate that nonradiative processes not driven by phonons are also present in the smaller particles, causing transitions and rapid thermalization between the levels on a time scale of < 100 ns.

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I. INTRODUCTION

Crystalline materials doped with impurities, such as rare-earth ions or diamond silicon-vacancy and nitrogen-vacancy centers, have found many applications in fields as diverse as quantum information processing [1–4], quantum memories [5–7], sensing [8], lasers [9], and phosphors [10,11]. Nanometer-sized structures fabricated from these materials have begun to be investigated for on-chip implementations of these applications. In addition, small nanophosphors are desired for high-quality window materials used in lamps as well as for state-of-the-art displays [12,13]. Finally, nanopowders have also been proposed for optical refrigeration applications where their modified phonon spectrum and particle morphology could enhance the cooling efficiency [14].

Nanomaterials can be obtained through different routes: nanostructures can be milled or etched from high-quality bulk materials, and nanocrystals can be obtained through chemical synthesis, mechanical crushing, or ablation techniques. The transition to nanosized structures generally introduces detrimental effects such as poor crystal quality, surface effects, and amorphous behavior that can severely restrict practical applications [15,16]. While some of these effects, such as the increasing surface-to-volume ratio, are fundamental, others can be minimized by optimizing the fabrication process [15]. Indeed, in some cases, both chemical synthesis and fabrication methods starting with bulk materials produced high-quality

materials [17,18]. However, none of these structures have allowed study of the effects of decreasing dimensions on phonon-mediated population dynamics. Furthermore, a general procedure for achieving consistently high-quality nanomaterials is still unknown and many open questions remain regarding the transition to smaller sizes, requiring further systematic studies.

During the transition from a bulk material to nanostructures, many material properties change. One interesting effect is the predicted modification of the vibrational density of states (VDOS) in small structures. Whereas a bulk crystal has a Debye VDOS (a continuous function that increases with the square of the vibrational frequency), the distribution becomes discrete in small crystallites, exhibiting gaps and even a cutoff below which no phonons are supported. Furthermore, phononic crystals—nanomachined, periodic structures—can feature engineered frequency band gaps where vibrations are forbidden [19]. These approaches to phonon engineering could potentially benefit applications in the field of quantum information, in particular, quantum memories, since the absence of phonons could enhance spin-population lifetimes as well as optical coherence times. Modifications of population dynamics in rare-earth-ion-doped nanocrystals have been previously reported by Meltzer *et al.* [20,21], Liu *et al.* [22], and Mercier *et al.* [23], and it was suggested that the changes were due to phonon suppression in the nanocrystals. However, the particles employed in some of those studies were not sufficiently small to suppress phonons at the desired frequencies, and locally elevated temperatures caused by the optical excitation of the powder materials might explain some of the observed effects. Thus, unambiguous confirmation of the suppression of phonon-mediated relaxation in optical centers through VDOS engineering remains an open challenge.

In this paper we examine the effect of the transition from bulk crystals to ≤ 40 -nm particles (see Fig. 1) on the population dynamics between excited-state crystal-field levels in

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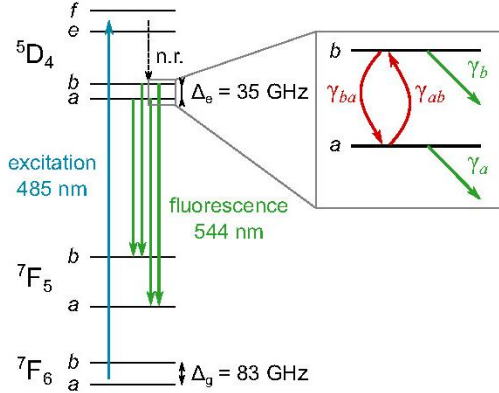


FIG. 1. Relevant energy levels of $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (vertical axis not to scale) for measurement of the population relaxation between the first two crystal-field levels within the $^5\text{D}_4$ excited-state manifold. A pulsed laser excited the ions from the $^7\text{F}_6a$ ground state to the $^5\text{D}_4f$ excited state, from where they decay rapidly into $^5\text{D}_4a$ and b . The resulting fluorescence due to the four $^5\text{D}_4a/b \rightarrow ^7\text{F}_5a/b$ transitions was collected, spectrally resolved, and then analyzed. Inset: Relaxation processes (nonradiative, red; radiative, green) for populations on the two excited levels $^5\text{D}_4a/b$ (see definitions in the text).

Tb^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG). Specifically, we study the influence of size restriction on the relaxation dynamics and equilibrium population distribution between the crystal-field levels, i.e., thermalization. We observe that the population dynamics are strongly modified for smaller particles, which can be explained by a modified density of states. However, we also find that the thermal population distribution exhibited by the nanopowders is the same as in the bulk material. As described in detail in later sections, the observation of rapid thermalization suggests that, in addition to possible phonon suppression, other nonphononic processes—e.g., related to surface defects or energy transfer [24]—are introduced, enabling rapid thermalization of populations between the closely spaced energy levels.

II. EXPERIMENTAL DETAILS

We chose Tb^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) since the combination of its energy level structure and its high acoustic velocity is well suited to investigation of the effects of size on the direct phonon process. More precisely, the small excited-state splitting $\Delta_e = 35$ GHz (denoted Δ in the following) between the Tb^{3+} crystal-field levels $^5\text{D}_4a/b$ (see Fig. 1), together with the acoustic velocity of 6400 m/s [25], results in an expected suppression of the direct phonon process for relatively large particles, ~ 100 nm in diameter. In addition, in the bulk crystal, the inhomogeneous broadening of about 20 GHz allows one to selectively address each of the $^5\text{D}_4a/b$ crystal-field levels. Furthermore, the ground-state splitting $\Delta_g = 83$ GHz is large enough that resonant phonons are not expected to be inhibited in the >40 -nm-diameter nanocrystals, and we could therefore directly measure the internal sample temperature through the ratio of population in the two levels $^7\text{F}_6a/b$.

We created our powders using a sol-gel synthesis (method 1 [26]) and a modified sol-gel synthesis with a freeze-drying step under vacuum and at temperatures below -20°C to restrict agglomeration (method 2 [27]). Each method leads to slightly different particle morphologies and size distributions. Additional size control can be achieved by changing the annealing duration and temperature. In this way we were able to vary the nanocrystal diameter d between 40 and 500 nm and between 40 and 70 nm using methods 1 and 2, respectively. We evaluated the crystal quality of our powders using a scanning electron microscope (SEM), a transmission electron microscope (TEM), x-ray diffraction (XRD), and optical spectroscopy methods (Appendixes A and B). From these measurements we conclude that the bulk crystal quality can be maintained for crystallites with diameters down to ~ 80 nm. For smaller sizes, we observe a slight decrease in crystal quality that manifests itself in an increase in the inhomogeneous broadening. Measurements of the radiative lifetime as a function of the particle size (Appendix A) confirm that we can approximately treat the powders as individual particles rather than large agglomerates, with method 2 producing less agglomeration than method 1.

All powders were mounted in an unsealed glass cuvette within an Oxford Instruments cryostat. The samples were held at temperatures from ~ 1 up to 10 K; for temperatures below 2.17 K, the samples were immersed in superfluid liquid helium, whereas for higher temperatures, the samples were cooled with a continuous flow of helium vapor. A pulsed Hänsch-style nitrogen-laser-pumped dye laser [28] with peak powers of up to 10 kW, a pulse duration of 6 ns, and a repetition rate of 6 Hz was used with Coumarin 481 dye to provide excitation light at 485 nm. As shown in Fig. 1, we resonantly excited Tb^{3+} ions from the ground state $^7\text{F}_6a$ to the $^5\text{D}_4f$ level, a transition that provides strong absorption. From the $^5\text{D}_4f$ level, the population rapidly decays in less than 1 ns nonradiatively by emission of high-frequency acoustic phonons into the two levels $^5\text{D}_4a$ and b . Using a SPEX 1401 monochromator (<3 -GHz resolution), we selectively collected fluorescence from each of the four $^5\text{D}_4a/b \rightarrow ^7\text{F}_5a/b$ transitions. The collection was at an angle of 90° relative to the excitation laser, and the fluorescence was measured using a photomultiplier tube (Hamamatsu R928) terminated with a variable resistance that allowed for time resolutions as fast as 100 ns.

For all powders and experimental configurations described below, we directly measured the local temperature through the relative population in the two levels $^7\text{F}_6a$ and b , as detailed in Appendix C. We find no local heating, thus confirming that observed changes in relaxation dynamics were not due to elevated sample temperatures.

III. TIME-RESOLVED FLUORESCENCE MEASUREMENTS

Before studying the population dynamics of the $^5\text{D}_4a/b$ levels, we ensured that we could selectively collect fluorescence from the two excited levels $^5\text{D}_4a/b$ for each of our samples. We recorded fluorescence spectra by scanning the monochromator over the four lines connecting $^5\text{D}_4a/b \rightarrow ^7\text{F}_5a/b$, with typical fluorescence spectra shown in Fig. 2. We observed that the smallest nanocrystals feature an increased inhomogeneous broadening compared to the bulk (for details see

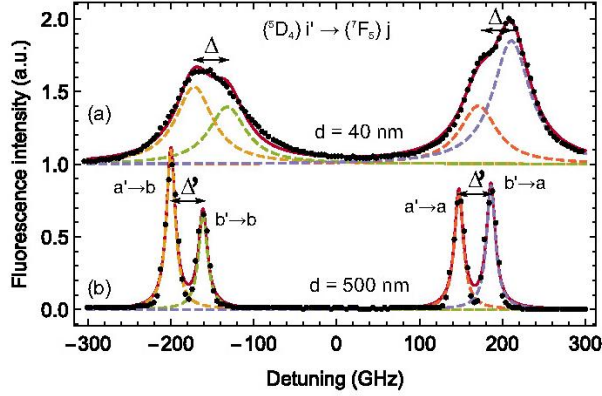


FIG. 2. Fluorescence spectra at 5 K of (a) a 40-nm-diameter powder and (b) a 500-nm-diameter powder (synthesized via method 1). Each spectrum (black circles) was fitted by the sum of four identical Lorentzian lines with the same pairwise energy splitting Δ (Δ'). For $d = 40$ nm the width is 53 GHz and Δ is 40 GHz, and for $d = 500$ nm the width is 13 GHz and Δ' is 39 GHz.

Appendix B). As a consequence, some fraction of the detected emission originates from the neighboring transition. Since this can lead to observations that could wrongfully be interpreted as modifications in relaxation dynamics, it must be considered in the analysis of any obtained data as described later.

Following this initial characterization, we recorded fluorescence decays from the two crystal-field levels $^5D_4 a/b$ at a temperature of 1.5 K. The individual decays were collected by sequentially tuning the monochromator on resonance with each of the four transitions $^5D_4 a/b \rightarrow ^7F_5 a/b$. The specific frequencies of these transitions were obtained from the fluorescence spectra measured for each sample as described above. After excitation of the $^5D_4 f$ level, 2 THz above $^5D_4 a$, the population decays rapidly first into both $^5D_4 a/b$ levels and from there into $^7F_5 a/b$. In a sufficiently large crystal, fluorescence decays originating from the four transitions (see Fig. 3) are composed of two components. The first component

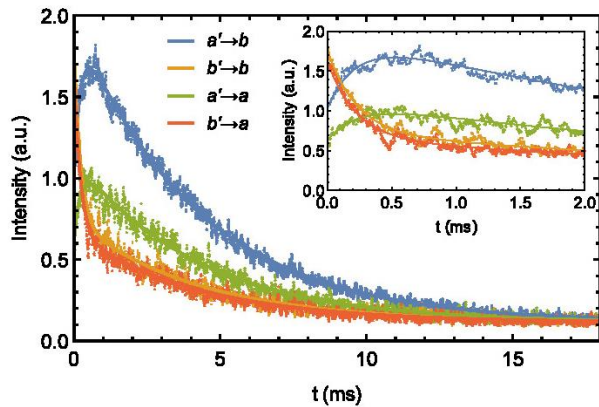


FIG. 3. Fluorescence decays $^5D_4 a/b \rightarrow ^7F_5 a/b$ at 1.5 K in large crystallites ($d = 500$ nm). The experimental points were fitted by Eq. (9) (solid lines), resulting in $\gamma_a = 237 \pm 0.5$ Hz and $\gamma_{ba} = 3.36 \pm 0.03$ kHz. Inset: Magnification of the first 2 ms of the decay.

corresponds to the nonradiative decay of population from $^5D_4 b$ to $^5D_4 a$ and manifests itself in the fluorescence decays from $^5D_4 a$ to $^7F_5 a/b$ as a fill-in, i.e., an increase in the fluorescence intensity with time, and in the fluorescence from $^5D_4 b$ to $^7F_5 a/b$ as an initial, fast decay, both with the same characteristic time of about 0.2 ms. The second, long component corresponds to the radiative decay, with a characteristic time of about 4 ms.

The dynamics are captured by the rate equations

$$\begin{aligned} \dot{n}_a^{\text{bulk}}(t) &= -(\gamma_a + \gamma_{ab})n_a^{\text{bulk}}(t) + \gamma_{ba}n_b^{\text{bulk}}(t), \\ \dot{n}_b^{\text{bulk}}(t) &= +\gamma_{ab}n_a^{\text{bulk}}(t) - (\gamma_b + \gamma_{ba})n_b^{\text{bulk}}(t), \end{aligned} \quad (1)$$

where $n_{a/b}^{\text{bulk}}(t)$ denote the populations in the levels $^5D_4 a/b$ at a time t after excitation (see inset in Fig. 1). The rates $\gamma_{a/b}$ correspond to the radiative decay from each level into the 7F_5 multiplet, and we assume that $\gamma_a = \gamma_b$. The latter assumption is justified by the good quality of our fits. The rates $\gamma_{ab/ba}$ characterize the nonradiative processes coupling the levels $^5D_4 a$ and b (absorption/emission of a phonon with energy $\hbar\Delta$). At high temperatures, they are equal, but γ_{ab} depends on the number of phonons available. Therefore, they differ at low temperatures; in fact, we can write

$$\gamma_{ab} = e^{-\hbar\Delta/kT} \gamma_{ba}, \quad (2)$$

where $\hbar\Delta$ is the energy difference between the a and the b levels, k the Boltzmann constant, and T the temperature. Note that relaxation into the ground-state multiplet 7F_6 is ignored [experimentally and in Eq. (1), due to the transitions' comparably low rates]. The solutions of Eq. (1) are

$$\begin{aligned} n_a^{\text{bulk}}(t, T) &= \frac{1}{1 + e^{-\hbar\Delta/kT}} [(n_{a0} e^{-\hbar\Delta/kT} - n_{b0}) \\ &\quad \times e^{-(\gamma_a + \gamma_{ba}(1 + e^{-\hbar\Delta/kT}))t} + (n_{a0} + n_{b0})e^{-\gamma_a t}], \\ n_b^{\text{bulk}}(t, T) &= \frac{1}{1 + e^{-\hbar\Delta/kT}} [-(n_{a0} e^{-\hbar\Delta/kT} - n_{b0}) \\ &\quad \times e^{-(\gamma_a + \gamma_{ba}(1 + e^{-\hbar\Delta/kT}))t} + (n_{a0} + n_{b0}) \\ &\quad \times e^{-\hbar\Delta/kT} e^{-\gamma_a t}], \end{aligned} \quad (3)$$

where n_{a0} and n_{b0} are the initial populations in the $^5D_4 a/b$ levels.

The fluorescence that we measured is proportional to the populations but must be weighted by the transition strengths, which manifest themselves in the corresponding fluorescence spectrum. The spectra (see Fig. 2) can be modeled by four Lorentzian functions with amplitude $d_{i \rightarrow j}$, center frequency $f_{0, i \rightarrow j}$ (separated by Δ for the a and b transitions), and width γ :

$$I_{i \rightarrow j}(f) = \frac{d_{i \rightarrow j}}{1 + \left(\frac{f - f_{0, i \rightarrow j}}{\gamma}\right)^2}. \quad (4)$$

Therefore, the fluorescence intensity detected at frequency f is

$$\begin{aligned} i_{\text{bulk}}(t, T, f) &= \sum_{j=a,b} I_{a \rightarrow j}(f) n_a^{\text{bulk}}(t, T) \\ &\quad + \sum_{j=a,b} I_{b \rightarrow j}(f) n_b^{\text{bulk}}(t, T). \end{aligned} \quad (5)$$

The parameters $d_{i \rightarrow j}$, $f_{0,i \rightarrow j}$, Δ , and γ were obtained for each powder by fitting the fluorescence spectra. Then we could fit all four fluorescence decays at once by taking the above expression at the frequencies we picked for the measurements (f_{aa} , f_{ba} , f_{ab} , f_{bb}). This enabled us to obtain one set of parameters for each powder sample, and at the same time takes into account fluorescence that originates from neighboring transitions. The only free parameters were the rates γ_a and γ_{ba} , as well as parameters accounting for experimental imperfections: a background fluorescence and four independent scaling factors for the four fluorescence intensities (i.e., we allowed the collection efficiency to vary). The initial population n_{a0} ($n_{b0} = 1 - n_{a0}$) was left free for the large samples ($d > 100$ nm); the fit gave values around 0.5. This is in agreement with random relaxation from $^5D_4 f$ via many paths to $^5D_4 a/b$. Therefore, we fixed $n_{a0} = n_{b0} = 0.5$ for the small samples where the fits tended to give larger uncertainties. The fit reproduced the experimental data very well and resulted in $\gamma_a = 237 \pm 0.5$ Hz and $\gamma_{ba} = 3.36 \pm 0.03$ kHz for the largest powder sample ($d = 500$ nm) (see Fig. 3).

By reducing the size of the particles, we expect to introduce a frequency cutoff in the VDOS below which phonons are not allowed. Consequently, we expect to observe a change in the nonradiative relaxation between the two closely spaced crystal-field levels $^5D_4 a$ and b , represented by the terms with the rate γ_{ba} in Eq. (3). The cutoff frequency is given by

$$\nu_{\min} = \eta \frac{c}{\pi d}, \quad (6)$$

where c is the sound velocity, d is the diameter of the crystal, and η is a numerical constant that equals 2.05 for one spherical particle and phonon modes with negligible broadening [29]. According to this formula, YAG particles (where $c = 6400$ m/s [25]) with diameters below $d_0 = 100$ nm should not be able to support phonons at $\Delta = 35$ GHz, corresponding to the splitting between the two crystal-field levels $^5D_4 a/b$.

If the phonons are completely forbidden, the population decays simply become

$$\begin{aligned} n_a^{\text{np}}(t) &= n_{a0} e^{-\gamma_a t}, \\ n_b^{\text{np}}(t) &= n_{b0} e^{-\gamma_a t}, \end{aligned} \quad (7)$$

with $n_{a/b}^{\text{np}}$ the population in the levels $^5D_4 a/b$ for the case where phonons are not allowed. Here, the first, fast component completely disappeared, and the populations are independent of the temperature. If we assume $n_{a0} = n_{b0} = 0.5$, we can write the fluorescence intensity as

$$i_{\text{np}}(t, f) = \sum_{i,j} I_{i \rightarrow j}(f) e^{-\gamma_a t}. \quad (8)$$

Because our powder samples inevitably exhibit some distribution of particle sizes (the horizontal error bars in Fig. 4 correspond to one standard deviation in the respective size distribution), the nonradiative relaxation should be suppressed in more and more particles as the mean of the size distribution is reduced below ~ 100 nm. This should lead to a gradual decrease in the amplitude of the fast component of the fluorescence decays. For a distribution of particle sizes, the fluorescence intensity can be written as

$$i_{\text{tot}}(t, T, f) = (1 - \beta) i_{\text{bulk}}(t, T, f) + \beta i_{\text{np}}(t, f), \quad (9)$$

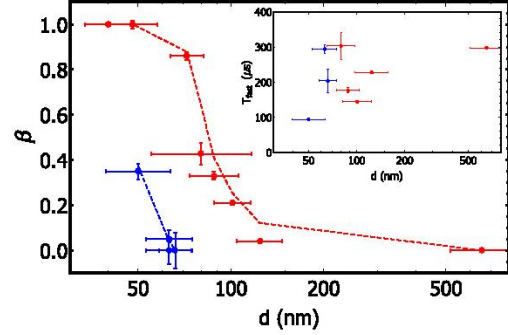


FIG. 4. Fraction of particles suppressing phonons β obtained from an average of the fits of Eq. (9) to the four decays $^5D_4 a, b \rightarrow ^7F_5 a, b$ as a function of the average nanocrystal diameter d for powder 1 (red) and powder 2 (blue) at 1.5 K. Simulations are depicted using dashed lines. Inset: Characteristic time of the fast decay component as a function of the nanocrystal diameter d .

where β is the fraction of particles for which we get a cutoff of the VDOS at Δ . Therefore we fitted the experimental decays by Eq. (9) and obtained the parameter β for each sample. As shown in Fig. 4, we find that for particles created using method 1, the parameter β begins to increase at diameters of around 130 nm, whereas the onset for particles created via method 2 occurs at sizes of ~ 70 nm.

We modeled this effect by calculating the VDOS [19], assuming that each mode contributes a Lorentzian with a width $\Delta\nu$, for 10^5 particles with different particle diameters following a Gaussian distribution. We obtained the mean diameter and the standard deviation of this distribution from the SEM images of our samples. We assumed that ions in a nanocrystal with diameter d have a fast decay only if the VDOS of the nanocrystal at $\Delta = 35$ GHz is greater than 0. For each of the 10^5 particles, we simulated the fluorescence decay, either the sum of two exponential functions, in cases where fast decay is allowed, or only a single-exponential decay with radiative decay time in cases where fast decay is forbidden. We then averaged the individual decays to obtain the overall fluorescence decay for the ensemble of 10^5 particles. Finally, we fitted the resulting decay with Eq. (9), which returned the fraction of particles that suppress phonons β . The only free parameter in the simulations was the width $\Delta\nu$ of the individual vibrational modes, which we obtained through a fit to the experimental data. Note that the mode width was forced to be the same for all powders fabricated using a specific method. The results of the simulations are presented in Fig. 4.

For large crystal diameters d , the simulated values of β (for crystals created via either method) are around 0, which corresponds to the bulk value at 1.5 K. When we reduce d , the fraction of particles that suppress phonons starts to increase at two distinct diameters (130 nm for method 1 and 70 nm for method 2 crystals). This can be explained by different mode widths ($\Delta\nu = 1.2$ and 11 GHz for powders from methods 1 and 2, respectively) obtained from the simulations. If phonon modes are broad, as in powders from method 2, it is more likely that they overlap with the transition between the $^5D_4 a/b$ levels, even for small crystals. However, for sharp modes

(powders from method 1), overlap becomes significant only for larger particles in which more modes exist. Note that the width of the phonon modes is related to the powder quality. In particular, crystallites with reduced surface roughness should feature narrower phonon modes. This leads us to conclude that powder 1 should be of higher quality, which, however, cannot be verified given the insufficient resolution of our SEM pictures. Note that the optical inhomogeneous line widths suggest that method 2 produces powders with less internal strain; however, it is not known whether there is a relationship between particle surface morphology and internal strain.

Overall, the simulated values are in good agreement with the experimental data for powders produced by either method, consistent with suppression of phonon-induced relaxation in sufficiently small powders. In particular, we observed the complete transition from large particles, where the relevant phonon processes are fully allowed, to the smallest particles, where we could not measure any contribution of the phonon-induced component to population relaxation.

In addition to a change in the amplitude of the fast nonradiative decay, we also expect a change in its characteristic decay time $T_{nr} = 1/\gamma_{ba}$. For the fraction of particles with $v_{min} \simeq \Delta_e$, the phonon density of states at Δ_e should deviate from the bulk value. With small enough particles we expect a decrease in the VDOS as the lowest phonon mode moves towards higher frequencies. Thus, because the rate of nonradiative relaxation is proportional to the VDOS, the phonon-induced decay rate for these nanocrystals should be slower than the one for the bulk, i.e., T_{nr} should increase with decreasing particle size. Note that in some cases, an enhanced VDOS can occur due to phonon confinement, which would lead to faster decay rates. Experimentally (see inset in Fig. 4), we observed a decrease in T_{nr} for some particles but we did not observe the expected increase due to a reduced density of states for the smallest particles. This is consistent with the conjecture of having sharp phonon modes (resulting from the fit of the decay ratios in Fig. 4), in which case the phonon cutoff occurs abruptly as the size is reduced so that the particles experience either a phonon rate equal to or larger than that in the bulk or no phonon decay. At this stage, the scatter of our experimental data unfortunately does not allow for a more in-depth analysis and interpretation.

IV. MEASUREMENT OF TEMPERATURE-DEPENDENT POPULATION RE-DISTRIBUTION

Another indication of the restriction of any nonradiative transition processes, including phonon modes, is the inhibition of thermalization (population re-distribution) between the two crystal-field levels $^5D_4 a/b$ after their initial population through decay from $^5D_4 f$. In the case of the bulk crystal, for $t > 1/\gamma_{ba}$, Eq. (3) gives the expected equilibrium population ratio, i.e., the Boltzmann distribution: $n_b^{\text{bulk}}(t, T)/n_a^{\text{bulk}}(t, T) = e^{\hbar\Delta/kT}$. In the extreme opposite case of total suppression of any nonradiative relaxation, the population ratio is constant and $n_b^{\text{np}}(t)/n_a^{\text{np}}(t) = 1$ if the initial populations are equal. In the case of our powder samples, where the suppression of phonons occurs only in a fraction of particles, we expect partial thermalization. From the expression of the total fluorescence intensity [see Eq. (9)], we can calculate the

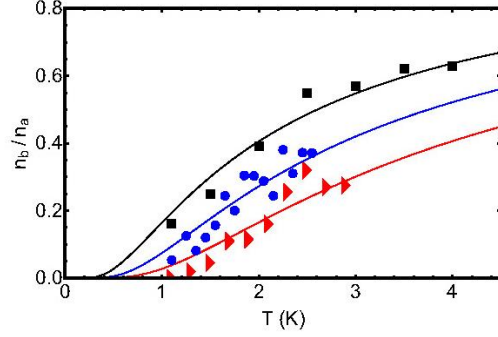


FIG. 5. Ratio of population n_b/n_a as a function of temperature in the bulk crystal (black squares) and in nanocrystals from method 1 of average diameter $d = 72$ nm (red triangles) and $d = 40$ nm (blue circles). Solid lines are best fits using Eq. (3), and shaded areas represent uncertainties.

population ratio

$$\frac{n_b(t, T)}{n_a(t, T)} = \frac{(1 - \beta)n_b^{\text{bulk}}(t, T) + \beta n_{np}^b(T)}{(1 - \beta)n_a^{\text{bulk}}(t, T) + \beta n_{np}^a(T)}, \quad (10)$$

where α is a coefficient accounting for an eventual difference in transition strength between the bulk and the powder samples, and β is the fraction of particles in which no thermalization (i.e., no fast nonradiative relaxation) occurs.

Experimentally, the population ratio $n_b(t, T)/n_a(t, T)$ can be extracted from the fluorescence decays for times $t > 1/\gamma_{ba}$. When there was no overlap between the transitions, i.e., in the case of the bulk crystal, we directly computed the ratio between the fluorescence intensities $i(t, T, f_{bj})/i(t, T, f_{aj})$ after background subtraction and averaged over all $t > 1/\gamma_{ba}$. We repeated this for $j = a, b$ and took the mean value. In the case of overlaps between neighboring transitions, i.e., in the case of small particles, we used Eqs. (5) and (8) and computed the population ratio for $t > 1/\gamma_{ba}$ as follows:

$$\frac{n_b(t, T)}{n_a(t, T)} = \frac{I_{a \rightarrow j}(f_{aj})i(t, T, f_{bj}) - I_{a \rightarrow j}(f_{bj})i(t, T, f_{aj})}{I_{b \rightarrow j}(f_{bj})i(t, T, f_{aj}) - I_{b \rightarrow j}(f_{aj})i(t, T, f_{bj})}. \quad (11)$$

Figure 5 shows the measured temperature dependence of n_b/n_a in the bulk crystal (black squares) and in nanocrystals from method 1 with an average diameter $d = 72$ nm (red triangles) and 40 nm (blue circles). We fitted the experimental points for each sample by Eq. (10). The only free parameters were the energy splitting Δ between the $^5D_4 a$ and b levels since the splitting might slightly change from powder to powder and the fraction β of particles in which no thermalization occurs between the levels $^5D_4 a/b$. We obtained $\Delta = 36 \pm 13$ GHz for the bulk, 72 ± 12 GHz for the 72-nm powder, and $\Delta = 42 \pm 11$ GHz for the 40-nm powder. In all cases the fits resulted in $\beta = 0$ with an uncertainty of ± 0.3 for the bulk, ± 0.1 for the 72-nm powder, and ± 0.14 for the 40-nm powder. Therefore, we observe no deviation from normal thermalization in the samples where the particles are small enough to inhibit phonon relaxation even though those samples did show a reduction of the nonradiative component in the fluorescence decays. This observation indicates that other processes, happening on time

scales shorter than the 100-ns resolution of the detector used in our time-resolved fluorescence measurements, are responsible for the population re-distribution in our smallest nanocrystals. Such fast relaxation could be caused by coupling of the Tb^{3+} ions to tunneling modes characteristic of amorphous materials [30,31] (note that the increase in amorphous character as the particle size is reduced is supported by the observation of larger inhomogeneous broadening). Other explanations are relaxation driven by energy transfer [24] and interactions between ions and surface states.

V. CONCLUSION

In conclusion, we observed modifications in relaxation dynamics between crystal-field levels of $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ crystals as the particle size was varied from bulk to 40 nm and confirmed via absorption measurements that this effect is not due to local heating. One possible explanation is a modification of the VDOS in the nanocrystals, which restricts phonon processes between the first two crystal-field levels in the $^5\text{D}_4$ excited state manifold, which are separated by 35 GHz.

However, other measurements suggest a different explanation: population redistribution is still observed within the two closely spaced levels, meaning that other fast and nonradiative processes must enable this transition. These processes may arise from the partially amorphous character of the nanocrystals, even though significant effort was dedicated to achieving good crystal quality by exploring two synthesis methods and modifying different important parameters in each of them, such as the addition of surfactants or the annealing temperature. We note that the case of YAG is particularly difficult because of the high annealing temperature—which favors particle growth—required to crystallize the particles.

Improving the nanocrystal quality by optimizing fabrication methods, as well as switching to a different material with a lower annealing temperature, such as fluoride crystals, may enable one to observe the full phonon restriction. However, there may exist a fundamental limit to how small a particle can become while still preserving the spectroscopic properties of a large crystal; this limit is frequently estimated to be around 10 nm [32]. Our results suggest that, for YAG, it may be around 100 nm. Measurements of crystal structure may shine more light on this important question.

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APPENDIX A: POWDER CHARACTERIZATION

For all investigations of population dynamics presented in the text, information about the morphology and size distribution of the various powders is needed to interpret the results. We obtained this information for powders from methods 1 and 2 using an SEM, with example images shown in Fig. 6. The images indicate that method 2 produces slightly less agglomerated powder compared to method 1. In addition, we confirmed that we obtained good single-phase crystalline YAG particles using powder XRD analysis. Figures 6(e) and 6(f) show the perfect overlap between the XRD spectrum of the $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powders produced by methods 1 and 2 and the reference spectrum for YAG (JCPDS No. 30-0040). For selected powder samples, we also directly probed the quality of the crystal structure using a TEM, as shown in Fig. 6(d). The TEM analysis revealed that the crystallite orientations in agglomerated nanocrystals can remain nearly aligned throughout multiple grains when they are fused together. Since it is possible that phonon modes extend across several crystallites in these cases, we considered the effective particle size in agglomerated samples to be equal to the larger size of the approximately aligned agglomerations rather than the individual grain size. The effect of agglomeration on phonon propagation dynamics cannot be quantified at this stage.

In addition to using the TEM measurements, we investigated the degree to which the crystallites within the powder act as isolated particles versus being part of a larger agglomerated

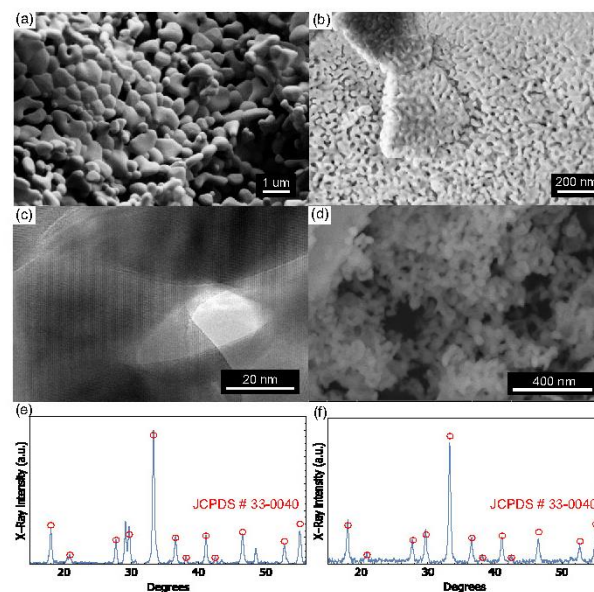


FIG. 6. Microscope images of 1% $\text{Tb}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ created using method 1 and annealing at 1400 °C (a) or 900 °C (b, c) and using method 2 and annealing at 900 °C (d). (a, b, d) SEM images, showing the size distribution of the nanocrystals. (e, f) XRD spectra of powders produced by methods 1 and 2, respectively (solid blue lines), and the corresponding reference spectrum (JCPDS No. 30-0040; red circles) for YAG. (c) High-resolution TEM image showing the crystalline structure (narrow white lines), which can extend over several particles if they are agglomerated.

mass by observing the increase in radiative lifetime as the particle sizes are reduced. As known from relations such as the Strickler-Berg equation [33], the radiative lifetime T_{rad} of an electric dipole transition depends on the average index of refraction, n , of the material. Because of this, when the size of a fluorescing particle becomes comparable to the wavelength of the emitted light, the index of the medium surrounding the particle can have a significant effect on the radiative lifetime [20,34,35]. Consequently, we expect to observe an increase in the fluorescence lifetime as the average particle size in our powders is reduced. Note that strongly agglomerated particles would effectively act as a single, larger particle in this case.

We employ a simple analytical model to estimate the size dependence of the fluorescence lifetime for perfectly isolated particles. More precisely, we used the form of the Lorentz local field, sometimes referred to as the virtual cavity model [36], where the radiative lifetime in the medium T_{rad} is related to the lifetime in vacuum T_0 according to $1/T_{\text{rad}} = (1/T_0) n_{\text{eff}}^2 (n_{\text{eff}}^2 + 2)^2/9$, with n_{eff} being an effective index of refraction averaged over the surrounding medium within a distance of the order of the wavelength of light from the ion.

For particles smaller than the wavelength of light, the electric field extends beyond the particle. To evaluate n_{eff} for such particles, we assumed that the electric field of the emitted light experiences the bulk crystal dielectric constant within the particle and the vacuum dielectric constant outside the particle. We, furthermore, assumed that the electric field outside the particle decays as $E(r) = E_0 e^{-r/l}$ over the decay length l , which is equal to the evanescent field decay length outside of a bulk dielectric given by $l = \lambda_0/2\pi\sqrt{n^2 - 1}$ [37]. Here n is the refractive index of the bulk material and λ_0 the wavelength of the transition. The value of n_{eff} experienced by the emitting ion, and the resulting change in radiative lifetime, was then estimated by calculating the field-strength-weighted average dielectric constant over the area of nonzero electric field.

By using this simple model, we estimated the change in lifetime with particle size using only the known bulk crystal index, transition wavelength, and lifetime with no free parameters, resulting in the solid line in Fig. 7. We find that

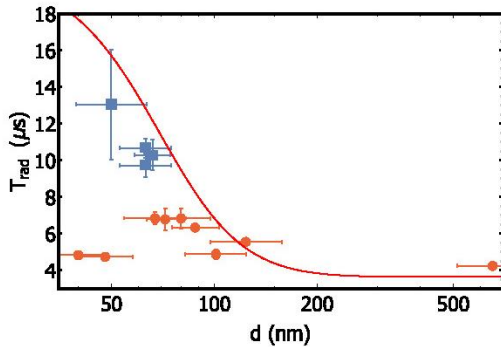


FIG. 7. Particle-size (d) dependence of the radiative lifetime of the $^5\text{D}_4 a$ level for powders from method 1 (red circles) and powders from method 2 (blue squares). The solid line shows the expected dependence.

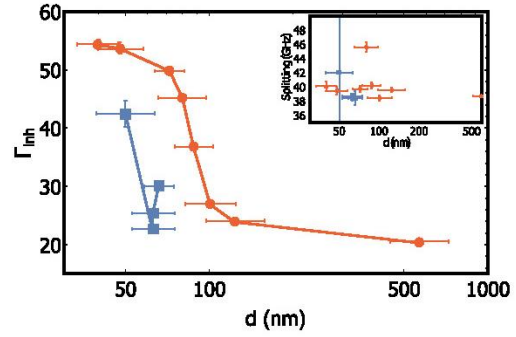


FIG. 8. Particle-size dependence of the inhomogeneous line width for powders from method 1 (red circles) and powders from method 2 (blue squares). Inset: Splitting Δ between the $^5\text{D}_4 a/b$ levels versus particle size. Solid lines are guides for the eye.

the measured lifetimes in our samples agree reasonably well with the calculated dependence (Fig. 7). With method 1, the radiative lifetime increases up to 7 ms, as the crystallite size decreases, but powders smaller than 50 nm show lifetimes similar to that of the bulk crystal, indicating that some degree of agglomeration is present. With method 2, the radiative lifetime increases up to 13 ms, indicating that the particles in powders synthesized with this method indeed behave as individual particles with sizes approximately equal to the values estimated from the SEM and TEM analysis.

APPENDIX B: SPECTROSCOPIC INVESTIGATIONS OF POWDER QUALITY

To ensure that we can selectively collect fluorescence from the two excited levels $^5\text{D}_4 a/b$ for each of our samples, we recorded fluorescence spectra by scanning the monochromator over the four lines connecting $^5\text{D}_4 a/b \rightarrow ^7\text{F}_5 a/b$. As shown in Fig. 8, we observed that with both fabrication methods, the smallest nanocrystals feature an increased inhomogeneous broadening compared to the bulk. This increase, which was expected due to the increased amount of strain, was not observable in the XRD spectra due to the limited resolution of our XRD diffractometer (Rigaku Multiflex). The observation of increased inhomogeneous broadening is consistent with the emergence of relaxation that is facilitated by amorphous phases and surface defects (see the text). However, as shown in the inset in Fig. 8, the splitting Δ between the $^5\text{D}_4 a/b$ levels does not change with particle size, which indicates that the ions' crystal-field splittings and local lattice symmetry are not measurably different in the small powders.

APPENDIX C: LOCAL TEMPERATURE MEASUREMENT

In past measurements, the thermal conductivity of small powders in a gas environment was observed to decrease with particle size due to two effects. First, the phonon scattering length is reduced in small powders, and second, heat flow is hindered by the surface resistance of the small particles contained in the powder [38–40]. These effects could lead to a locally elevated powder temperature, especially when the powder is probed using a high-power laser. An elevated sample

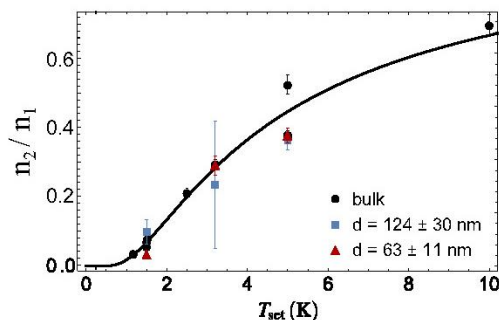


FIG. 9. Ratio n_2/n_1 of populations in the ground manifold 7F_6 b/a levels as a function of the temperature T_{set} read by the cryostat sensor for a bulk crystal (black circles) and nanocrystalline powder samples with diameters $d = 124 \pm 30$ nm, produced by method 1 (blue squares), and $d = 63 \pm 11$ nm, produced by method 2 (red triangles). The solid line is the fit to a Boltzmann distribution with $\Delta_g = 83.5$ GHz. Note that the large error bar for 3.2 K and $d = 124$ nm is caused by the large uncertainty of the fit to that particular absorption spectrum.

temperature in turn would produce significant changes in population relaxation and thermalization that could potentially be misinterpreted as arising from other effects. To ensure that the laser excitation did not induce localized heating, a

direct temperature measurement that enables the true internal temperature of the particles to be monitored is required.

We measured the internal temperature for each sample by recording the absorption spectrum 7F_6 $a, b \rightarrow {}^5D_4$ f and comparing the populations n_1 and n_2 on the first and second crystal-field levels 7F_6 a and b of the ground-state multiplet, which are separated by $\Delta_g = 83$ GHz. This allowed us to determine the effective internal sample temperature T via the Boltzmann law $n_2/n_1 = A \exp(-\Delta_g/k_B T)$, with k_B the Boltzmann constant. We obtained the coefficient A , which depends on the relative oscillator strengths of the transitions, from a calibration measurement using a 1% Tb:YAG bulk crystal, which we assumed to thermalize quickly to the temperature T_{set} that was measured by the cryostat sensor. The temperature-dependent population ratio n_2/n_1 is shown in Fig. 9 for a selected set of nanocrystals. The close overlap between the bulk and the powder results confirms that all powders thermalize as well as the bulk when immersed in liquid helium or vapor and that the laser is not measurably heating the nanocrystals, even for the smallest sizes. Since these measurements are conducted using the same laser power and focusing parameters as those used for all other measurements described in the text, they confirm that the changes in dynamics that we observe in the powders are not caused by local heating. Also, with this method, we ensure that the ions that are studied in the relaxation dynamics measurements (as in the text) are also the same ions that are used to measure the temperature.

- [1] H. de Riedmatten and M. Afzelius, *Quantum Light Storage in Solid State Atomic Ensembles* (Springer International, Cham, Switzerland, 2015), pp. 241–273.
- [2] K. Heshami, D. G. England, P. C. Humphreys, P. J. Bustard, V. M. Acosta, J. Nunn, and B. J. Sussman, *J. Mod. Opt.* **63**, 2005 (2016).
- [3] A. Sipahigil, R. E. Evans, D. D. Sukachev, M. J. Burek, J. Borregaard, M. K. Bhaskar, C. T. Nguyen, J. L. Pacheco, H. A. Atikian, C. Meuwly, R. M. Camacho, F. Jelezko, E. Bielejec, H. Park, M. Lončar, and M. D. Lukin, *Science* **354**, 847 (2016).
- [4] B. Hensen, H. Bernien, A. E. Dreau, A. Reiserer, N. Kalb, M. S. Blok, J. Ruitenberg, R. F. L. Vermeulen, R. N. Schouten, C. Abellan, W. Amaya, V. Pruneri, M. W. Mitchell, M. Markham, D. J. Twitchen, D. Elkouss, S. Wehner, T. H. Taminiau, and R. Hanson, *Nature* **526**, 682 (2015).
- [5] M. P. Hedges, J. J. Longdell, Y. Li, and M. J. Sellars, *Nature* **465**, 1052 (2010).
- [6] E. Saglamyurek, N. Sinclair, J. Jin, J. A. Slater, D. Oblak, F. Bussi eres, M. George, R. Ricken, W. Sohler, and W. Tittel, *Nature* **469**, 512 (2011).
- [7] P. C. Maurer, G. Kucsko, C. Latta, L. Jiang, N. Y. Yao, S. D. Bennett, F. Pastawski, D. Hunger, N. Chisholm, M. Markham, D. J. Twitchen, J. I. Cirac, and M. D. Lukin, *Science* **336**, 1283 (2012).
- [8] S. Hong, M. S. Grinolds, L. M. Pham, D. Le Sage, L. Luan, R. L. Walsworth, and A. Yacoby, *MRS Bull.* **38**, 155 (2013).
- [9] R. C. Powell, *Physics of Solid-State Laser Materials* (Springer-Verlag, New York, 1998).
- [10] A. J. Kenyon, *Prog. Quantum Electron.* **26**, 225 (2002).
- [11] T. J ustel, H. Nikol, and C. Ronda, *Angew. Chem. Int. Ed.* **37**, 3084 (1998).
- [12] F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu, *Nature* **463**, 1061 (2010).
- [13] E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, *Science* **273**, 1185 (1996).
- [14] X. L. Ruan and M. Kaviani, *Phys. Rev. B* **73**, 155422 (2006).
- [15] T. Lutz, L. Veissier, C. W. Thiel, P. J. T. Woodburn, R. L. Cone, P. E. Barclay, and W. Tittel, *Sci. Technol. Adv. Mater.* **17**, 63 (2016).
- [16] T. Lutz, L. Veissier, C. W. Thiel, P. J. Woodburn, R. L. Cone, P. E. Barclay, and W. Tittel, *J. Lumines.* **191**, 2 (2017).
- [17] T. Zhong, J. M. Kindem, E. Miyazono, and A. Faraon, *Nat. Commun.* **6**, 8206 (2015).
- [18] A. Ferrier, C. W. Thiel, B. Tumino, M. O. Ramirez, L. E. Baus , R. L. Cone, A. Ikesue, and P. Goldner, *Phys. Rev. B* **87**, 041102 (2013).
- [19] T. Lutz, L. Veissier, C. W. Thiel, R. L. Cone, P. E. Barclay, and W. Tittel, *Phys. Rev. A* **94**, 013801 (2016).
- [20] H.-S. Yang, S. P. Feofilov, D. K. Williams, J. C. Milora, B. M. Tissue, R. S. Meltzer, and W. M. Dennis, *Physica B: Condens. Matter* **263**, 476 (1999).
- [21] H.-S. Yang, K. Hong, S. Feofilov, B. M. Tissue, R. Meltzer, and W. Dennis, *J. Lumines.* **83**, 139 (1999).
- [22] G. K. Liu, H. Z. Zhuang, and X. Y. Chen, *Nano Lett.* **2**, 535 (2002).
- [23] B. Mercier, C. Dujardin, G. Ledoux, C. Louis, O. Tillement, and P. Perriat, *J. Lumines.* **119**, 224 (2006).

- [24] T. Förster, *Ann. Phys.* **437**, 55 (1948).
- [25] L. Mezeix and D. J. Green, *Int. J. Appl. Ceram. Technol.* **3**, 166 (2006).
- [26] N. Kaithwas, M. Dave, S. Kar, S. Verma, and K. S. Bartwal, *Cryst. Res. Technol.* **45**, 1179 (2010).
- [27] H. Gong, D.-Y. Tang, H. Huang, and J. Ma, *J. Am. Ceram. Soc.* **92**, 812 (2009).
- [28] T. W. Hänsch, *Appl. Opt.* **11**, 895 (1972).
- [29] H. Lamb, *Proc. Lond. Math. Soc.* **s1-13**, 189 (1881).
- [30] P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).
- [31] W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).
- [32] X. C. G. Liu, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier Science & Technology, Amsterdam, 2007).
- [33] S. J. Strickler and R. A. Berg, *J. Chem. Phys.* **37**, 814 (1962).
- [34] H. Schniepp and V. Sandoghdar, *Phys. Rev. Lett.* **89**, 257403 (2002).
- [35] A. Aubret, A. Pillonnet, J. Houel, C. Dujardin, and F. Kulzer, *Nanoscale* **8**, 2317 (2016).
- [36] S. Scheel, L. Knöll, and D.-G. Welsch, *Phys. Rev. A* **60**, 4094 (1999).
- [37] F. de Fornel, *Evanescent Waves* (Springer-Verlag, Berlin, 2001).
- [38] K. W. Garrett and H. M. Rosenberg, *J. Phys. D* **7**, 1247 (1974).
- [39] T. Rettelbach, J. Säuberlich, S. Korder, and J. Fricke, *J. Non-Cryst. Solids* **186**, 278 (1995).
- [40] D. E. Brodie and C. F. Mate, *Can. J. Phys.* **43**, 2344 (1965).

CHAPTER 12

SOLID-STATE LASER COOLING OF OPTICALLY LEVITATED PARTICLES

Contribution of Authors and Co-Authors

Manuscript in Chapter 12

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Contributions: Prepared material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

Co-Author: Philip J. T. Woodburn:

Contributions: Prepared material samples, designed and set up experimental apparatus, performed the measurements to acquire data, analyzed and interpreted results, generated figures, wrote and edited the manuscript.

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Solid-state laser cooling of optically levitated particles

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ABSTRACT

Ultra-high sensitivity sensors can be achieved with optically levitated particles in ultra-high vacuum (UHV). Trapped particles act as high-Q harmonic oscillators, whose amplitude, position, and frequency can be monitored to provide high sensitivity measurements of the particle's acceleration. Larger particles (10-30 microns in diameter) provide higher sensitivity, but they are difficult to trap in UHV without particle loss. To overcome the radiometric forces that lead to particle loss, rare earth (RE) ion dopants can be incorporated into the particles to enable solid-state laser cooling of the particle's internal temperature. The laser used for optical trapping can be tuned to a wavelength on the lower energy side of the ion absorption band, and thus also serve as the pump laser for solid-state laser cooling. Internal cooling occurs when the average energy of the photons emitted is larger than the average energy of the photons absorbed. Ions will rapidly thermalize while in the ground and the excited states to create the energy difference. Solid-state laser cooling has been realized in bulk host materials and is well understood. This technique of internal cooling for reducing loss pressure is currently being tested.

Keywords: Optical Trapping, Particle Levitation, Anti-Stokes Cooling

1. INTRODUCTION

Optical levitation has been used since 1970 when Arthur Ashkin trapped the first particles at Bell Laboratories using a focused continuous wave laser beam.¹ Before Ashkin's groundbreaking work, it was unknown that a 3-dimensional optical trap could be used to study particles with only radiation forces. Now commonly known as optical tweezers, these traps are used to study atoms, molecules, variously sized dielectric particles, and even biological cells. Levitated particles could also serve as ultra-high sensitivity sensors, with industry applications such as inertial navigation systems (accelerometers and gyroscopes) and time-keeping (PNT) technology. To achieve high levels of sensitivity, large particles must be levitated in ultra-high vacuum. However, the current technique for levitated particles is to first trap them at atmospheric pressures. Levitated large particles become unstable during the pump down to vacuum due the absorption of the trap laser causing internal heating of the particle and producing strong radiometric forces that kick the particles out of the trap. Therefore, finding a way to counteract this heating is essential to maintaining a stable trap during pump down to high vacuum.

2. RADIATION FORCES

Radiation pressure is simply the pressure exerted upon any surface due to the exchange of momentum between the object and the electromagnetic field. When a flat laser beam strikes a mirror normal to its surface, the momentum of each incident photon, $h\nu/c$, where c is the speed of light in vacuum and ν is the frequency of the light is reversed. Collectively, a flux of photons $P/h\nu$ photons per second on a surface, where P is the incident power creates, due to reflection from the mirror, a total change in momentum per unit time of $2P/c$. By conservation of momentum, this produces a force of $2P/c$ on the mirror. In Ashkin's seminal paper on this subject,¹ he describes the radiation pressure on particles due to a focused light beam. Ashkin showed that in addition to the longitudinal radiation forces exerted on the particles in the direction of the laser beam as described above, there was an additional transverse radiation force on the particles in the direction of the center of the focused laser beam. These transverse restoring forces produce a two dimensional potential well about the center of the laser beam. By using two counter propagating focused laser beams, Ashkin showed that the longitudinal forces could roughly cancel and produce a potential well in the longitudinal direction and thus produce a three dimensional well for trapping particles. This phenomenon is most easily described in

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the ray optics regime, which holds then the radius of the particle is much larger than the wavelength of the pump laser, which is the regime of interest when trapping large particles. For particles with radii less than or on the order of the wavelength of the trapping beam, optical levitation is also possible, though better described using Rayleigh and Mie scattering theories.

In the geometric optics regime, where the particle radius, R , is much larger than the wavelength of light, λ , we can utilize ray optics to help in our descriptions of the radiation pressure force. We consider a sphere that is entirely refractive with no reflective properties at this time. Figure 1 shows the sphere in the presence of a laser beam with two individual rays striking the sphere, a and b , equally displaced from the equator of the sphere. The rays can be thought of as momentum vectors. If we track single photon momentums along these two paths, we see that on the output, the “ a ” photon is deflected down, and the “ b ” photon is deflected up. To get the change in momentum imparted on sphere by each photon, we subtract the output momentum vector of the photon from the input momentum vector. The two photons impart a change in momentum, Δp_L , onto the sphere in the positive longitudinal direction. The change in momentum imparted per photon in the transverse direction, Δp_T , are equal and opposite. However, if we consider the intensity of the laser beam, the photons per second with ray a is much higher than the photons per second with ray b . Thus, net transverse force, F_G , due to the transverse gradient of the laser beam is towards the axis of the laser beam. The net force on a particle can be calculated by considering all possible rays with their respected photon fluxes due to the intensity gradient of the beam. This is done in a computer code (called OTGO) developed by Agnese Callegari, et. Al.²

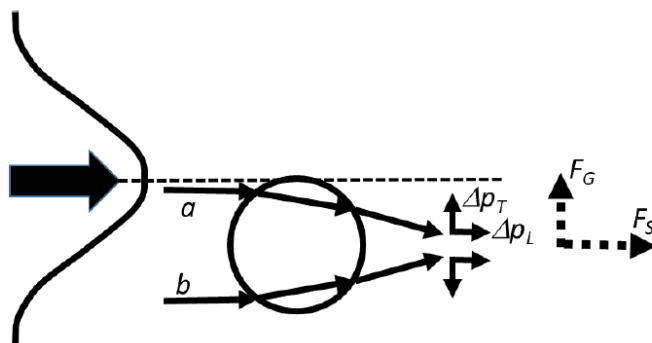


Figure 1. The ray tracing and momentum changes due to propagation of a laser beam with a strong intensity gradient of radius smaller than the particle diameter. The figure is similar that of Ashkin's original paper [REF]. The combination of the change in momentum per photon and the transverse gradient of the laser beam results in two net forces: a gradient force towards the beam axis and a scattering force in the direction of the laser beam's propagation.

Only when the sphere is centered on the laser beam's axis are the net transverse gradient forces zero. In all positions there is still a net longitudinal scattering force, F_S , in the direction of the laser beam. Thus, for a single laser beam passing through a particle, these combined forces will push the particle not only in the direction of the laser beam, but also towards the axis of the laser beam. This transverse gradient force acts as a restoring force to trap the particle along the axis of the laser beam.

If a focused laser beam was pointed upward in a gravitational field (pointing downward), and the optical power level and focused beam waist are appropriately chosen, a stable point can be found above the focal point of the beam where the gravitational force and the scattering force balance. Above and below this point, either the gravitational force or the scattering force dominates, resulting in a restoring force back to the balance point. Thus, a three dimensional gravitational vertical optical trap can be achieved.³

If two counter-propagating focused beams are used, the longitudinal forces of the two beams are in opposite directions. If the two beams have the same foci, the scattering forces would cancel at all positions. However, if a separation is introduced between the foci, as shown in Figure 2, the scattering forces don't cancel. For the right propagating beam, the scattering forces are strongest as the beam's focus. At the right propagating beams focus, the scattering force of the right propagating beam is greater the opposite scattering forces of the left propagating beam at this point, since it is away from its focus. The result is that a particle at the focus of the right propagating beam's focus would have a net force to the

right. Likewise, particles at the focus of the left propagating beam would have a net force to the left. At the center point between the two foci, the forces cancel. This results in a stable longitudinal trap of the particle.

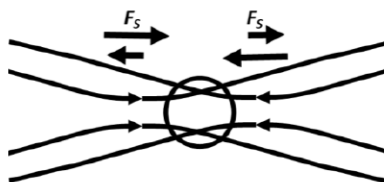


Figure 2. Two counter-propagating focused laser beams for an optical trap.

The Rayleigh regime ($R \ll \lambda$) and Mie regime ($R \sim \lambda$), the ray optics description breaks down. In the Rayleigh regime, the small spheres are treated as dipoles and the dipole forces that result in trapping can be calculated analytically.⁴ In the Mie regime, Lorentz-Mie theory is used. The necessary mathematical calculations can be quite detailed to represent. We utilize MATLAB code from Christian Mätzler to model this regime,⁵ but further discussion is omitted at this point since we are focused on large particles.

2.1 Radiometric forces and importance of cooling

A trapped particle will always have a finite optical absorption. As such, the strong trapping laser intensity inside the particle will induce heating of the particle. At atmospheric pressures, the air or buffer gas surrounding the optically trapped particle conducts the heat away and the particles temperature is on the order of the surrounding gas temperature. As the pressure is lowered, the conductive cooling of the gases decreases and the temperature of the particle increases. Gas molecules colliding with the particle carry away more kinetic energy than they had before the collision. Radiometric forces arise from temperature gradients on the surface of the sphere. Differential surface temperature result in differential force acting on the particle, which create instabilities that can result in the particle being kicked out of the trap. At ultra-high vacuum these forces diminish, but to get from trapping at atmosphere to ultra-high vacuum, the particle must go through the transition of strong radiometric forces. The main result is losing the particle from the trap at a certain gas pressure, which depend on the particle size, shape, and composition and on the laser intensity, as well as the other trapping parameters. Figure 3 shows this effect. Loss pressure is defined as the pressure at which a particle is lost of the optical trap while evacuating the trapping chamber. The loss pressure increases rapidly with increasing laser intensities.

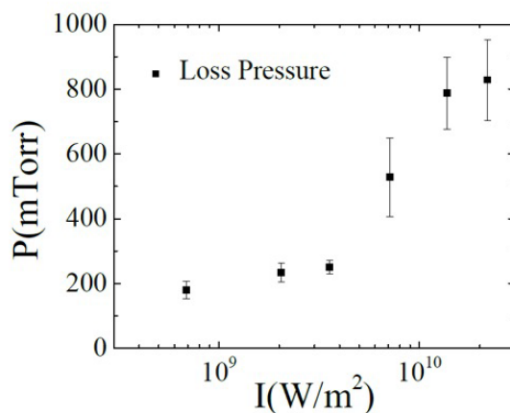


Figure 3. The average chamber pressure when 3 micron spherical particles are lost as a function of laser intensity. Each point represents the average loss pressure for 5 trapped particles at a given intensity. (from David Atherton's PhD dissertation⁶)

To combat these instabilities, common solutions include reducing the trap intensity and trapping small particles. Our interest is in increased sensitivity of precision sensors for accelerometry or gyroscopes, which improve with large particles. Our solution to combat radiometric forces and the issues of loss pressure is to introduce rare-earth dopants into the fabrication of our particles and implement solid-state laser cooling. Solid-state laser cooling is well known and will

be discussed in detail in Section 3. The first demonstration of cooling of trapped particles by solid-state laser cooling was from Barker's group Yb^{3+} -YLF nanocrystals.⁷ By keeping the particles relatively cool as the particle is transitioned from atmosphere to high-vacuum, the radiometric forces will be greatly reduced, hopefully to a level that particle loss on vacuum pump down will not be an issue.

3. MATERIAL SCIENCE & COOLING DEMOS

3.1 Bulk cooling theory

Solid state laser cooling of rare earth doped host materials (crystals and glasses) has previously been realized by several researchers in bulk host materials.⁸ The cooling results from pumping the rare earth doped materials with photons that have less energy than the photons that are emitted due by fluorescence. This process is possible due to vibrational modes of the host material, which populate higher energy levels of the ground and excited state manifolds. The net release of energy reduces the internal temperature of the particles. The appropriate wavelength must be chosen within the absorption bands of the Rare Earth dopant. Figure 4 shows a simplified model of solid-state laser cooling. A laser is used to excite ions from the thermally excited levels of the ground state to the lowest level of the excited state. Rapid thermalization of the excited state populates thermally excited upper state levels, which can then decay to the ground state, on average to levels below the initial level that was excited by the laser. Therefore, the photon emitted contains more energy than the excitation photon, which results in a net removal of energy. Rare earth ions that are good for laser cooling have a large energy gap between the ground state and the first electronic excited state and have long-lived excited states that decay optically with small quantum defect, such as thulium, erbium, and ytterbium.

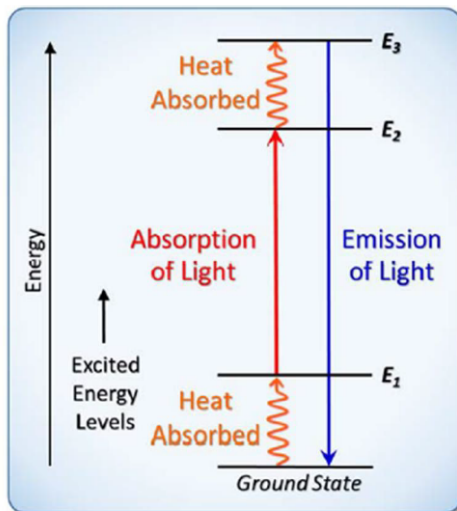


Figure 4. Basic concept of solid-state (anti-Stokes) laser cooling. The absorbed light from a thermally excited ground state level to the lowest excited state level and subsequent emission from a thermally excited state level to a lower ground state level results in a net loss in energy from the material.

3.2 Bulk cooling demonstration of Yb:YAG

We have chosen to focus efforts on ytterbium doped yttrium aluminum garnet (Yb:YAG) particles. To demonstrate the potential for anti-Stokes cooling in Yb:YAG particles, we first demonstrated in a bulk 1mm diameter crystal rod. A standard silicon CCD camera with interference filters was used to create a two-color hyperspectral imaging system to observe the laser excitation at 1030 nm and material fluorescence at 950 nm. Figure 5 shows these efforts along with a thermal image of the rod when a 200 mW laser was tuned to resonantly excite the Yb^{3+} ions. The ambient temperature in the room was 74°F and as shown in the far right panel, no significant observable heating was observed.

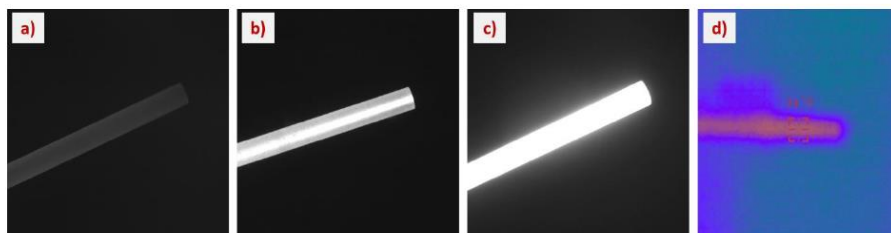


Figure 5. Imaging of Yb³⁺-doped YAG crystals under laser excitation traveling down the center of the rod. a) Yb³⁺-YAG single crystal rod (1 mm diameter) under laser excitation by 200 mW of non-resonant laser light at 1040 nm as seen through a ~950nm filter. Minimal fluorescence is observed. b) Observation of ~950 nm anti-Stokes fluorescence from Yb³⁺ ions as laser is tuned near resonance at 1030 nm. c) Strong anti-Stokes emission observed when laser is tuned to peak of resonance at 1030 nm. d) Thermal image of crystal with 200 mW of on-resonance 1030 nm laser light, demonstrating no significant heating of crystal relative to ambient temperature (74°F) even when laser light is strongly absorbed.

3.3 Fabrication of doped particles

We have developed fabrication methods to produce Yb:YAG particles that are large in size (5-30 microns). Figure 6 shows SEM images of Yb:YAG particles that have been fabricated. In addition, we are exploring fabrication methods for other materials that could be utilized for optical traps. Figure 7 shows birefringent vaterite crystals (CaCO₃) with sizes ranging from 1-30 microns. These microspheres have been successfully doped with rare-earth ion Eu³⁺. The right panel in the figure shows the visible fluorescence marker.

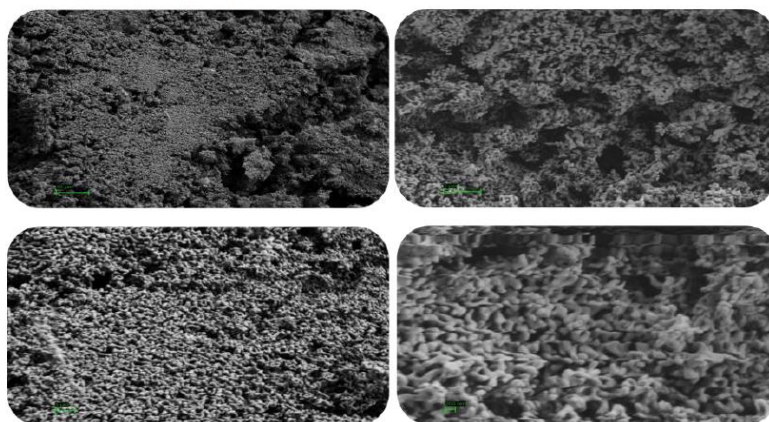


Figure 6. Top Left: 3240x Magnification Yb:YAG, Scale 10um. Top Right: 18560x Magnification Yb:YAG, Scale 2um. Bottom Left: 21560x Magnification Yb:YAG, Scale 1um. Bottom Right: 49310x Magnification Yb:YAG #1, Scale 200nm.

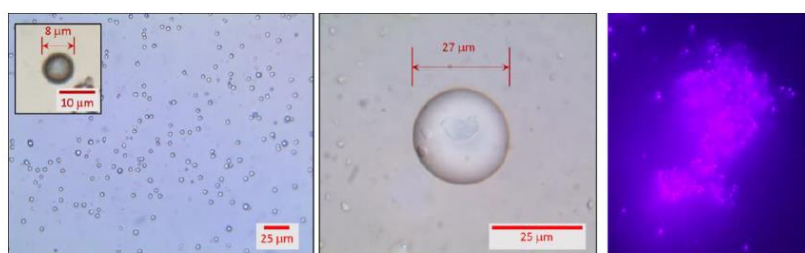


Figure 7. Examples of spherical particles of birefringent vaterite crystals (CaCO₃) fabricated at MSU. Left: Typical microspheres produced with sizes in the 1 to 10 micron size range. Middle: Example of larger ~30 micron diameter vaterite microsphere produced by increasing growth time. Right: Example fluorescence image of rare-earth-doped vaterite particles produced with Eu³⁺ ions used as the fluorescence marker, demonstrating the ability to dope the vaterite microspheres with rare-earth ions.

3.4 Thermometry demonstration

To observe the anti-Stokes cooling in trapped particles a simple setup was first created to test the ability to measure the temperature of a bulk crystal through fluorescence thermometry. The fluorescence of each transition depends on relative level populations determined by Boltzmann's distribution. The ratio of Yb^{3+} fluorescence for two different transitions was measured while pumping at the 1030 nm cooling transition. Two 10 nm band-pass filters centered at 940 nm and 970 nm were used. Figure 8 shows the experimental setup in the left two images along with results on the right-hand side. With a simple setup and calibration in the bulk materials, the temperature of trapped particles can be measured using this technique to within a few degrees.

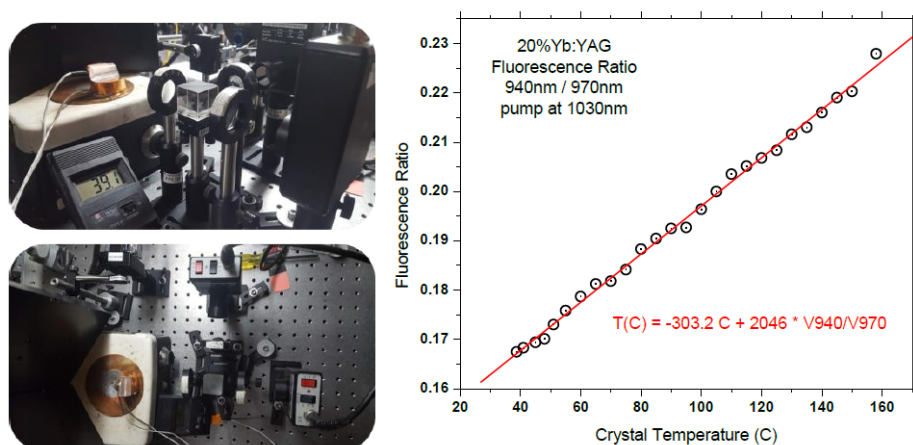


Figure 8. Left: Optical thermometry setup Right: Results from fluorescence thermometry experiment showing a linear relationship of the fluorescence ratio at high temperature.

4. OPTICAL TRAPPING EXPERIMENTAL SETUP

Optical trapping involves multiple intricate processes that must fit together to conduct a single experiment. This section will describe our launching mechanisms of microspheres, our optical trap design and implementation. Trapped microspheres will be shown in Section 5.

4.1 Launching microspheres

We implemented two launching methods during the experiments. The first method utilized a microscope slide mounted to a piezoelectric ring placed between an aluminum base and aluminum top that is secured with four plastic 8/32" screws. The piezoelectric ring is connected to a function generator, which produces a sine wave. It was determined that a resonance of ~33 kHz to accelerate micro-spheres off the microscope slide. The aluminum base is secured to a tip/tilt stage with a 1" base which allowed for adjustment of the angle of the slide. The problem with this method was the broad area over which particles were launched, which was inefficient in its use of particles. Given the potential for a limited quantity of fabricated particles, two other designs were explored in order to get more efficient launching of particles into our trap region.

The second method utilized an aluminum bar as the launching arm instead of the microscope slide. We went through two iterations on this design. The first iteration used a milled reservoir to hold the particles with a small drop hole in the center, as shown at left in Figure 9. The problem with this design was that imperfections in fabrication led to the particles either congregating around the outside of reservoir or all at the center, even with fine tip-tilt adjustment. The second iteration kept the reservoir for the particles, but to create a trenched channel, out of which the particles could flow, as shown in the middle and right pictures in Figure 9. The narrow 0.4mm channel allows for efficient dispersing of the launched particles into the trap region. A small piezoelectric transducer (5mm x 5mm x 2.4 mm) vibrated the launcher. An Arduino controlled chirped drive circuit enabled computer controlled (Matlab code triggered) pulsing of the particle launching. The amplitude of the driver and the tip-tilt control of the launcher allows for fine control of the

quantity of particles launched with each pulse. The result was a very efficient launcher. This will be more important when the loss pressure measurements are undertaken, as multiple load cycles are needed. Efficient loading means far less refills of the launcher are required. The computer control of the launcher circuit and efficient loading combine to allow for the loading process to be automated (see SPIE paper by Alec Dinerstein in this same conference).

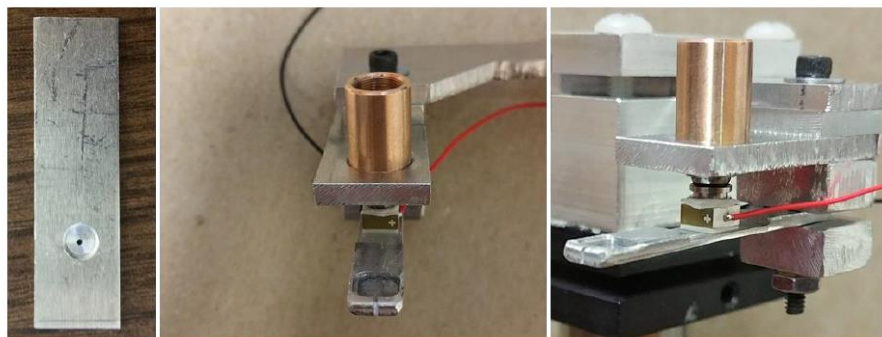


Figure 9. Left: Launcher with reservoir and small drop hole. Middle and right: Launcher with reservoir and trenched channel.

4.2 Horizontal dual-beam optical trap

The horizontal dual-beam trap configuration utilizes the gradient and scattering forces of the two laser beams to create a stable three dimensional trap, as described above in section 1. If the two beams are not aligned correctly (i.e. focused aligned on same axis and separated by an appropriate distance) the configuration will not form a stable trap, thus position control of the optical beams is critical.

Figure 10 shows a schematic of the horizontal dual-beam optical trap in air. A 1030 nm laser diode is expanded through a telescope and passed through a Babinet-compensator (BC) to balance the powers of the two counter-propagating beams that are created from the polarizing beam splitter (PBS). Two identical 8 mm aspheric lenses are placed inside the vacuum chamber to focus each laser beam. One lens is placed into a stationary mount and another is placed into a mount attached to an XYZ-translation stage. The two beams are aligned using a 5-micron pinhole attached to an XYZ-translation stage that could be inserted between the lenses for alignment and removed for trapping. Our launching mechanism described above is placed between the two lenses.

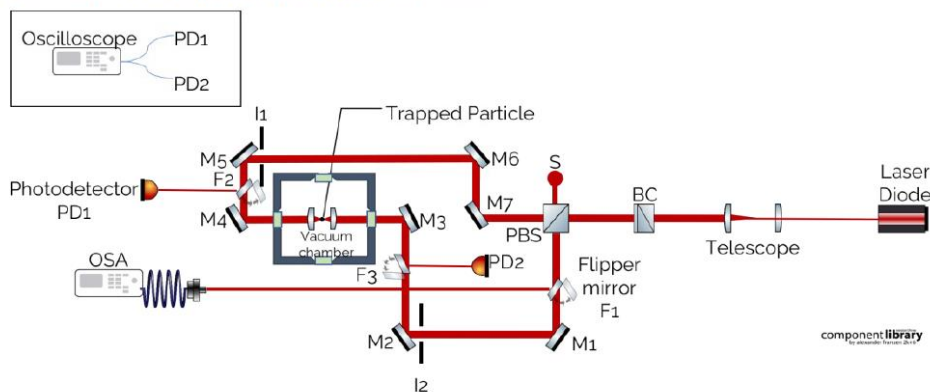


Figure 10. A schematic of our horizontal dual-beam optical trap for trapping microspheres in air and vacuum. A single 1030 nm laser beam is split into two counter-propagating beams (B1 and B2) with a polarizing beam splitter (PBS) and balanced in power with a Babinet-compensator (BC). The beams enter the vacuum chamber and each pass through an 8 mm aspheric lens. The component library from gwoptics was used to create this diagram.

5. CONCLUSIONS/FUTURE WORK

Figure 11 shows a successfully trapped particle in our horizontal optical trap. Our new launching system allows for efficient, computer controlled loading of particles, with fine control of where the particles drop into our trap region. We have fabricated a wide range of particles for demonstration of anti-Stokes laser cooling of levitated particles and developed a simple calibrated method for measuring particle temperatures.

As work continues, the next steps are to tune the lasers as we measure the temperature of large trapped particles. This will enable us to show anti-Stokes laser cooling of our particles. Once we have demonstrated cooling, we plan to show a reduction or elimination of the loss pressure that inhibits the pumping down of the vacuum chamber to high vacuum.

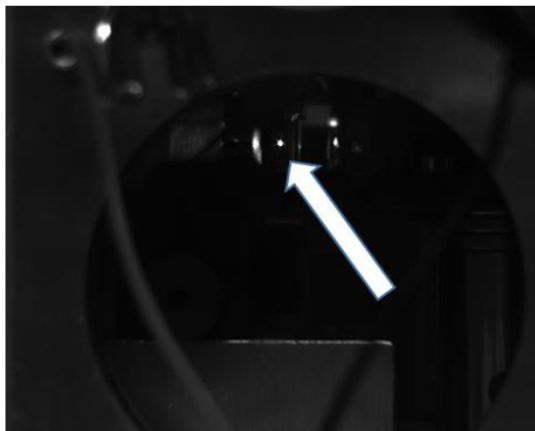


Figure 11. Trapped soda lime glass microsphere (5-25 micron diameters) in horizontal dual-beam optical trap.

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REFERENCES

- [1] Ashkin, A., "Acceleration and trapping of particles by radiation pressure," *Phys. Rev. Lett.*, 24, 156–159 (1970).
- [2] Callegari, A., Mijalkov, M., Burak Gököz, A., and Volpe, G., "Computational toolbox for optical tweezers in geometrical optics," *J. Opt. Soc. Am. B* 32, 11-19 (2015).
- [3] Ashkin, A. and Dziedzic, J. M., "Optical Levitation by Radiation Pressure," *Appl. Phys. Lett.*, 19 (8), 283-285 (1971).
- [4] Harada, Y., and Asakura, T., "Radiation forces on a dielectric sphere in the rayleigh scattering regime," *Optics Comm.*, 529, 529-541 (1996).
- [5] Matzler, C., "MATLAB Functions for Mie Scattering and Absorption," Research Report No. 2002-11, http://www.atmo.arizona.edu/students/courselinks/spring09/atmo656b/maetzler_mie_v2.pdf (June 2002).
- [6] Atherton, D. P., "Sensitive Force Measurements with Optically Trapped Micro-Spheres in High Vacuum," PhD. Thesis, University of Nevada, Reno (2015).
- [7] Rahman, A. T. M. A. and Barker, P. F., "Laser refrigeration, alignment and rotation of levitated Yb³⁺:YLF nanocrystals," *Nature Photonics*, 11 (10), 634–638 (2017).
- [8] Seletskiy, D. V., Epstein, R., and Sheik-Bahae, M. "Laser cooling in solids: advances and prospects," *Rep. Prog. Phys.* 79, 096401 (2016) and references therein.

CHAPTER 13

SUMMARY

Studying rare earth ions in solid state crystal structures for fundamental discoveries and industrial application is an interesting and complex science. They can be studied to probe the quality of a crystal's synthesis and fabrication process or used to store coherent information on the electron spins for quantum transduction. The REIs are used commercially for worldwide optical communication and the production of extreme wideband radio frequency sensors and signal processors.

In this work the optical properties of REI doped insulators are the focus. Several characterization methods were used to determine critical aspects of REI doped powders and single crystals. High resolution spectroscopy was the main tool used to characterize the materials, using an array of coherent and conventional techniques. The spectral properties of triply ionized erbium, thulium, terbium and ytterbium were characterized at liquid helium temperatures. Linear and coherent techniques were used as sensitive methods to assess the effects of the mechanical, thermal, and chemical processes used to synthesize the materials. The optical spectral features of REIs dopants gave an insight into how the host material's atomic structure holds the REIs. Static and dynamic defects are characterized using spectral properties, allowing a deeper understanding of the fundamental aspects of the REI and the host materials. The optical characterization is also used as a method to provide feedback to the synthesis and processing of the material, to improve the next crystal or powder growth.

Material crystallinity and phase were determined using x-ray diffraction. Scanning electron microscopes were used to image the powder particle's size, shape and growth structure.

Birefringence was used to quickly orient lower symmetry crystals by viewing the optical axes of the indicatrix. And birefringence images were also used to view strain and defects in single crystals. Chemical analysis was determined by glow discharge mass spectroscopy and laser ablation inductively coupled plasma mass spectrometry.

To engineer a material, one can introduce similar ions into the lattice of a known or similar host. This can be done by gradually changing the chemistry in the case of $\text{Y}_y\text{Lu}_x\text{Al}_5\text{O}_{12}$ or 1%Eu, 0.01%Er: Y_2SiO_5 or by completely replacing an ion as Ga replaces Al in $\text{Y}_3\text{Ga}_5\text{O}_{12}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ shown in Chapter 6 and Chapter 8.

The synthesis and fabrication of the material was shown to be as important as the choice of material itself. Even single crystals such as Tm:YGG used in Chapter 6 can have significant differences depending on the parameters used in the Czochralski growth method, as discussed in Chapter 2. Materials that have industrial applications often have the production optimized enabling very high-quality material such as the single crystals of Er:YSO used in Chapter 5 as material for optical to radio frequency quantum transducer or the Yb:YVO₄ characterized in Chapter 7 for next generation quantum memories built into a chip size device.

High-quality material can also be produced in the lab with good technique and care. This was found to be especially true for the powders materials such as Tm:YAG, Er:LN and Tb:YAG presented in chapters 9, 10, and 11. We found that low levels of strain and defects in the crystal lattice that are not measurably detected by XRD or SEM analysis can still produce large variations in the observed low-temperature dynamics of the powders observed using SHB techniques, significantly impacting the performance of the powders in applications. Thus, SHB can serve as a quantitative characterization tool, complementing traditional techniques such as

XRD, SEM, or Raman scattering. Our results also demonstrate that mechanical and thermal treatment of REI doped crystals can reverse some detrimental effects of powder fabrication, such as minimizing the reduction in lifetime of nuclear spin states, in a surprisingly strong way, and in certain cases, the properties of the bulk material can be reached.

Choosing the best host material is not simple. The number of available host materials are almost uncountable, but they can be put into a few very general classifications; crystals, glass, ceramics, and organics. For long coherence properties crystals are the usual choice. Surveying the REI doped materials, we find that high resolution optical spectroscopy such as spectral hole burning, and other coherent methods are well-suited to reveal the quality in REI doped powders and crystals. The optical techniques combined with external fields also allow the materials to be fully characterized for their practicality in classical and quantum information systems.

REFERENCES CITED

- [1] Dieke, G. H., & Crosswhite, H. M. (1963). The spectra of the doubly and triply ionized rare earths. *Applied optics*, 2(7), 675-686.
- [2] Morrison, C. A., & Leavitt, R. P. (1982). Spectroscopic properties of triply ionized. *Handbook on the physics and chemistry of rare earths*, 5, 461-692.
- [3] Macfarlane, R. M. (2002). High-resolution laser spectroscopy of rare-earth doped insulators: a personal perspective. *Journal of luminescence*, 100(1-4), 1-20.
- [4] Macfarlane, R. M., & Shelby, R. M. (1987). Coherent transient and holeburning spectroscopy of rare earth ions in solids. *Modern Problems in Condensed Matter Sciences* (Vol. 21, pp. 51-184). Elsevier.
- [5] Sun, Y., Thiel, C. W., Cone, R. L., Equall, R. W., & Hutcheson, R. L. (2002). Recent progress in developing new rare earth materials for hole burning and coherent transient applications. *Journal of luminescence*, 98(1-4), 281-287.
- [6] Cone, R. L., Thiel, C. W., Sun, Y., Böttger, T., & Macfarlane, R. M. (2012, February). Rare-earth-doped materials with application to optical signal processing, quantum information science, and medical imaging technology. *Advances in Photonics of Quantum Computing, Memory, and Communication V* (Vol. 8272, p. 82720E). International Society for Optics and Photonics.
- [7] Bjorklund, G.C., Haarer, D., Hayes, J.M., Jankowiak, R., Lenth, W., Macfarlane, R.M., Moerner, W.E., Rebane, K.K., Rebane, L.A., Shelby, R.M. & Sievers, A.J., (2012). *Persistent spectral hole-burning: science and applications* (Vol. 44). Springer Science & Business Media.
- [8] Sousa Filho, P. C. D., Lima, J. F., & Serra, O. A. (2015). From lighting to photoprotection: fundamentals and applications of rare earth materials. *Journal of the Brazilian Chemical Society*, 26(12), 2471-2495.
- [9] Rebane, A. K., Thiel, C. W., Mohan, R. K., & Cone, R. L. (2010). Slow decoherence and the radiative decay limit in rare-earth-doped crystals for coherent optical storage. *Bulletin of the Russian Academy of Sciences: Physics*, 74(7), 891-900.
- [10] Liu, G., & Jacquier, B. (Eds.). (2006). *Spectroscopic properties of rare earths in optical materials* (Vol. 83). Springer Science & Business Media.
- [11] Cone, R. L., Thiel, C. W., Sun, Y., Böttger, T., & Macfarlane, R. M. (2013). Quantum information, laser frequency stabilization, and optical signal processing with rare-earth doped materials. *Laser Science*, LTu1G-3.
- [12] Thiel, C. W., Cone, R. L., & Böttger, T. (2014). Laser linewidth narrowing using transient spectral hole burning. *Journal of luminescence*, 152, 84-87.

- [13] Böttger, T., Pryde, G. J., Thiel, C. W., & Cone, R. L. (2007). Laser frequency stabilization at 1.5 microns using ultranarrow inhomogeneous absorption profiles in Er^{3+} : LiYF_4 . *Journal of luminescence*, 127(1), 83-88.
- [14] Böttger, T., Sun, Y., Pryde, G. J., Reinemer, G., & Cone, R. L. (2001). Diode laser frequency stabilization to transient spectral holes and spectral diffusion in Er^{3+} : Y_2SiO_5 at 1536 nm. *Journal of luminescence*, 94, 565-568.
- [15] Sellin, P. B., Strickland, N. M., Böttger, T., Carlsten, J. L., & Cone, R. L. (2001). Laser stabilization at 1536 nm using regenerative spectral hole burning. *Physical Review B*, 63(15), 155111.
- [16] Strickland, N. M., Sellin, P. B., Sun, Y., Carlsten, J. L., & Cone, R. L. (2000). Laser frequency stabilization using regenerative spectral hole burning. *Physical Review B*, 62(3), 1473.
- [17] Merkel, K. D., Mohan, R. K., Cole, Z., Chang, T., Olson, A., & Babbitt, W. R. (2004). Multi-Gigahertz radar range processing of baseband and RF carrier modulated signals in Tm^{3+} : YAG. *Journal of luminescence*, 107(1-4), 62-74.
- [18] Harris, T. L., Merkel, K. D., Mohan, R. K., Chang, T., Cole, Z., Olson, A., & Babbitt, W. R. (2006). Multigigahertz range-Doppler correlative signal processing in optical memory crystals. *Applied Optics*, 45(2), 343-352.
- [19] Mohan, R. K., Chang, T., Tian, M., Bekker, S., Olson, A., Ostrander, C., Khallaayoun, A., Dollinger, C., Babbitt, W. R., Cole, Z., & Wagner, K. H. (2007). Ultra-wideband spectral analysis using S2 technology. *Journal of luminescence*, 127(1), 116-128.
- [20] Babbitt, W. R., Neifeld, M. A., & Merkel, K. D. (2007). Broadband analog to digital conversion with spatial-spectral holography. *Journal of luminescence*, 127(1), 152-157.
- [21] Li, Y., Hemmer, P., Kim, C., Zhang, H., & Wang, L. V. (2008). Detection of ultrasound-modulated diffuse photons using spectral-hole burning. *Optics express*, 16(19), 14862-14874.
- [22] Gunther, J. E., Walther, A., Rippe, L., Kröll, S., & Andersson-Engels, S. (2018). Deep tissue imaging with acousto-optical tomography and spectral hole burning with slow light effect: a theoretical study. *Journal of biomedical optics*, 23(7), 071209.
- [23] Kinoshita, A., Li, Q., Rippe, L., & Kröll, S. (2016). Development and characterization of high suppression and high étendue narrowband spectral filters. *Applied optics*, 55(36), 10442-10448.
- [24] Thiel, C. W., Böttger, T., & Cone, R. L. (2011). Rare-earth-doped materials for applications in quantum information storage and signal processing. *Journal of luminescence*, 131(3), 353-361.
- [25] Sun, Y. C. (2005). Rare earth materials in optical storage and data processing applications. *Spectroscopic properties of rare earths in optical materials*, 379-429.

- [26] Tittel, W., Afzelius, M., Chaneliere, T., Cone, R. L., Kröll, S., Moiseev, S. A., & Sellars, M. (2010). Photon-echo quantum memory in solid state systems. *Laser & Photonics Reviews*, 4(2), 244-267.
- [27] Thiel, C. W., Sinclair, N., Tittel, W., & Cone, R. L. (2014). Tm 3+: Y 3 Ga 5 O 12 Materials for Spectrally Multiplexed Quantum Memories. *Physical review letters*, 113(16), 160501.
- [28] Böttger, T., Sun, Y., Thiel, C. W., & Cone, R. L. (2003, July). Material optimization of Er3+: Y2SiO5 at 1.5 μ m for optical processing, memory, and laser frequency stabilization applications. In *Advanced Optical Data Storage* (Vol. 4988, pp. 51-61). International Society for Optics and Photonics.
- [29] Bussi eres, F., Sangouard, N., Afzelius, M., De Riedmatten, H., Simon, C., & Tittel, W. (2013). Prospective applications of optical quantum memories. *Journal of Modern Optics*, 60(18), 1519-1537.
- [30] Chaneli ere, T., Bonarota, M., Damon, V., Lauro, R., Ruggiero, J., Lorger e, I., & Le Gou et, J. L. (2010). Light storage protocols in Tm: YAG. *Journal of luminescence*, 130(9), 1572-1578.
- [31] Miyazono, E., Zhong, T., Craiciu, I., Kindem, J. M., & Faraon, A. (2016). Coupling of erbium dopants to yttrium orthosilicate photonic crystal cavities for on-chip optical quantum memories. *Applied Physics Letters*, 108(1), 011111.
- [32] Zhong, T., & Goldner, P. (2019). Emerging rare-earth doped material platforms for quantum nanophotonics. *Nanophotonics*, 8(11), 2003-2015.
- [33] Welinski, S., Woodburn, P. J., Lauk, N., Cone, R. L., Simon, C., Goldner, P., & Thiel, C. W. (2019). Electron spin coherence in optically excited states of rare-earth ions for microwave to optical quantum transducers. *Physical review letters*, 122(24), 247401.
- [34] Stoneham, A. M. (1969). Shapes of inhomogeneously broadened resonance lines in solids. *Reviews of Modern Physics*, 41(1), 82.
- [35] Kindem, J. M., Bartholomew, J. G., Woodburn, P. J., Zhong, T., Craiciu, I., Cone, R. L., ... & Faraon, A. (2018). Characterization of Yb 3+ 171: YVO 4 for photonic quantum technologies. *Physical Review B*, 98(2), 024404.
- [36] Lutz, T., Veissier, L., Thiel, C. W., Woodburn, P. J., Cone, R. L., Barclay, P. E., & Tittel, W. (2016). Effects of fabrication methods on spin relaxation and crystallite quality in Tm-doped Y3Al5O12 powders studied using spectral hole burning. *Science and technology of advanced materials*, 17(1), 63-70.
- [37] Lutz, T., Veissier, L., Thiel, C. W., Woodburn, P. J., Cone, R. L., Barclay, P. E., & Tittel, W. (2017). Effects of mechanical processing and annealing on optical coherence properties of Er3+: LiNbO3 powders. *Journal of Luminescence*, 191, 2-12.

- [38] Lutz, T., Veissier, L., Woodburn, P. J., Cone, R. L., Barclay, P. E., Tittel, W., & Thiel, C. W. (2018). Modification of relaxation dynamics in Tb $3+$: Y 3 Al 5 O 12 nanopowders. *Physical Review B*, 98(5), 054308.
- [39] Kaminskii, A. A. (2003). Modern developments in the physics of crystalline laser materials. *physica status solidi (a)*, 200(2), 215-296.
- [40] Kaminskii, A. A. (2013). *Laser crystals: their physics and properties* (Vol. 14). Springer.
- [41] [Cone1998] Cone, R. L. (1998). *Persistent Spectral Hole Burning Materials for Time-and-Frequency-Domain Optical Memories and Signal Processing*. AFOSR-DEPSCoR Contract Number F49620-94-1-0465.
- [42] Dhanaraj, G., Byrappa, K., Prasad, V., & Dudley, M. (Eds.). (2010). *Springer Handbook of Crystal Growth*. Springer Science & Business Media
- [43] Caprez, A., Meyer, P., Mikhail, P., & Hulliger, J. (1997). New host-lattices for hyperfine optical hole burning: Materials of low nuclear spin moment. *Materials research bulletin*, 32(8), 1045-1054.
- [44] Teal, G. K., Sparks, M., & Buehler, E. (1951). Growth of germanium single crystals containing p– n junctions. *Physical Review*, 81(4), 637.
- [45] Macfarlane, R. M., Harris, T. L., Sun, Y., Cone, R. L., & Equall, R. W. (1997). Measurement of photon echoes in Er: Y 2 SiO 5 at 1.5 μ m with a diode laser and an amplifier. *Optics letters*, 22(12), 871-873.
- [46] Harris, T. L., Sun, Y., Cone, R. L., Macfarlane, R. M., & Equall, R. W. (1998). Demonstration of real-time address header decoding for optical data routing at 1536 nm. *Optics letters*, 23(8), 636-638.
- [47] Becerro, A. I., & Escudero, A. (2004). Revision of the crystallographic data of polymorphic Y 2 Si 2 O 7 and Y 2 SiO 5 compounds. *Phase Transitions*, 77(12), 1093-1102.
- [48] Brandle, C. D., Valentino, A. J., & Berkstresser, G. W. (1986). Czochralski growth of rare-earth orthosilicates (Ln 2 SiO 5). *Journal of Crystal Growth*, 79(1-3), 308-315.
- [49] Thiel, C. W., Sinclair, N., Tittel, W., & Cone, R. L. (2014). Optical decoherence studies of Tm $3+$: Y 3 Ga 5 O 12 . *Physical Review B*, 90(21), 214301.
- [50] Kränkel, C., Fagundes-Peters, D., Fredrich, S. T., Johannsen, J., Mond, M., Huber, G., ... & Uecker, R. (2004). Continuous wave laser operation of Yb $3+$: YVO 4 . *Applied Physics B*, 79(5), 543-546.
- [51] Pestryakov, E. V., Petrov, V. V., Trunov, V. I., Kirpichnikov, A. V., Merzliakov, M. A., Laptev, A. V., & Matrosov, V. N. (2006, June). Availability of new Yb: YVO 4 and Yb: Gd x Y $1-x$ VO 4 laser crystals for femtosecond laser systems at low temperature. In International

Conference on Lasers, Applications, and Technologies 2005: Advanced Lasers and Systems (Vol. 6054, p. 60540I). International Society for Optics and Photonics.

[52] Zhong, T., Kindem, J. M., Miyazono, E., & Faraon, A. (2015). Nanophotonic coherent light-matter interfaces based on rare-earth-doped crystals. *Nature Communications*, 6(1), 1-6.

[53] Ryba-Romanowski, W., Lisiecki, R., Jelinková, H., & Šulc, J. (2011). Thulium-doped vanadate crystals: Growth, spectroscopy and laser performance. *Progress in Quantum Electronics*, 35(5), 109-157.

[54] Veissier, L., Thiel, C. W., Lutz, T., Barclay, P. E., Tittel, W., & Cone, R. L. (2016). Quadratic Zeeman effect and spin-lattice relaxation of Tm $3+$: YAG at high magnetic fields. *Physical Review B*, 94(20), 205133.

[55] Ahlefeldt, R. L., Pascual-Winter, M. F., Louchet-Chauvet, A., Chaneliere, T., & Le Gouët, J. L. (2015). Optical measurement of heteronuclear cross-relaxation interactions in Tm: YAG. *Physical Review B*, 92(9), 094305.

[56] Sun, Y., Wang, G. M., Cone, R. L., Equall, R. W., & Leask, M. J. M. (2000). Symmetry considerations regarding light propagation and light polarization for coherent interactions with ions in crystals. *Physical Review B*, 62(23), 15443.

[57] Guillot-Noël, O., Goldner, P., Antic-Fidancev, E., & Le Gouët, J. L. (2005). Analysis of magnetic interactions in rare-earth-doped crystals for quantum manipulation. *Physical Review B*, 71(17), 174409.

[58] Louchet, A., Habib, J. S., Crozatier, V., Lorgeré, I., Goldfarb, F., Bretenaker, F., Guillot-Noël, O. & Goldner, P. (2007). Branching ratio measurement of a Λ system in Tm $3+$: YAG under a magnetic field. *Physical Review B*, 75(3), 035131.

[59] De Seze, F., Louchet, A., Crozatier, V., Lorgeré, I., Bretenaker, F., Le Gouët, J. L. F., Guillot-Noël, O., & Goldner, P. (2006). Experimental tailoring of a three-level Λ system in Tm $3+$: YAG. *Physical Review B*, 73(8), 085112.

[60] Goldner, P., Guillot-Noël, O., Louchet, A., de Sèze, F., Crozatier, V., Lorgeré, I., Bretenaker, F. & Le Gouët, J. L. (2006). Hyperfine structure of Tm $3+$ in YAG for quantum storage applications. *Optical Materials*, 28(6-7), 649-654.

[61] Macfarlane, R. M. (1993). Spectral hole burning in the trivalent thulium ion. *Optics letters*, 18(10), 829-831.

[62] Macfarlane, R. M. (1993). Photon-echo measurements on the trivalent thulium ion. *Optics letters*, 18(22), 1958-1960.

[63] Cone, R. L., Wang, G., Sun, Y., & Equall, R. W. (2002). *Coherent interaction of optical radiation beams with optical-electronic materials of generalized crystal symmetry*. U.S. Patent No. 6,407,831. Washington, DC: U.S. Patent and Trademark Office.

- [64] Merkel, K. D., Stiffler, C. R., Woidtke, A., Traxinger, A., Equall, R. W., Barber, Z., Harrington, C., Rupavatharam, K.M., Thiel, C.W. & Cone, R. (2014). *Techniques for spatial spectral holography*. U.S. Patent No. 8,829,471. Washington, DC: U.S. Patent and Trademark Office.
- [65] Li, X., Liu, H., Wang, J., Cui, H., Zhang, X., & Han, F. (2004). Preparation of YAG: Nd nano-sized powder by co-precipitation method. *Materials Science and Engineering: A*, 379(1-2), 347-350.
- [66] Nassau, K. (1984). Early history of lithium niobate: personal reminiscences. *Processing of Guided Wave Optoelectronic Materials I* (Vol. 460, pp. 2-5). International Society for Optics and Photonics.
- [67] Wong, K. K. (Ed.). (2002). *Properties of lithium niobate* (No. 28). IET.
- [68] Malovichko, G., Grachev, V., & Schirmer, O. (1999). Interrelation of intrinsic and extrinsic defects—congruent, stoichiometric, and regularly ordered lithium niobate. *Applied Physics B*, 68(5), 785-793.
- [69] Kis, Z., Mandula, G., Lengyel, K., Hajdara, I., Kovacs, L., & Imlau, M. (2014). Homogeneous linewidth measurements of Yb³⁺ ions in congruent and stoichiometric lithium niobate crystals. *Optical Materials*, 37, 845-853.
- [70] Burrows, L. (2017). Now entering, lithium niobate valley. Researchers demonstrate high-quality optical microstructures using lithium niobate. *Harvard School of Engineering and Applied Sciences*.
- [71] Cone, R. L., & Liu, G. K. (1988). Power-dependent photon echo decay due to ‘instantaneous diffusion’ in Tb³⁺: LiYF₄. *Bull. Am. Phys. Soc*, 33, 676.
- [72] Liu, G. K., Cone, R. L., Joubert, M. F., Jacquier, B., & Skinner, J. L. (1990). Energy transfer and instantaneous spectral diffusion processes in Tb³⁺ compounds as probed in photon echo experiments. *Journal of luminescence*, 45(1-6), 387-391.
- [73] Thiel, C. W., Macfarlane, R. M., Sun, Y., Böttger, T., Sinclair, N., Tittel, W., & Cone, R. L. (2014). Measuring and analyzing excitation-induced decoherence in rare-earth-doped optical materials. *Laser Physics*, 24(10), 106002.
- [74] Gerber, M., & Graf, T. (2001). Optimum parameters to etch Nd: YAG crystals with orthophosphoric acid H₃PO₄. *Optics & Laser Technology*, 33(7), 449-453.
- [75] Zhang, W., Yu, H., Wu, H., & Halasyamani, P. S. (2017). Phase-matching in nonlinear optical compounds: a materials perspective. *Chemistry of Materials*, 29(7), 2655-2668.
- [76] Carvalho, N. C., Le Floch, J. M., Krupka, J., & Tobar, M. E. (2015). Multi-mode technique for the determination of the biaxial Y₂SiO₅ permittivity tensor from 300 to 6 K. *Applied Physics Letters*, 106(19), 192904.

- [77] Sun, Z., Li, M., & Zhou, Y. (2009). Thermal properties of single-phase Y_2SiO_5 . *Journal of the European Ceramic Society*, 29(4), 551-557.
- [78] Höfer, S., Uecker, R., Kwasniewski, A., Popp, J., & Mayerhöfer, T. G. (2016). Complete dispersion analysis of single crystal yttrium orthosilicate. *Vibrational Spectroscopy*, 83, 151-158.
- [79] T. Böttger, C. Thiel, R. Cone, & Y. Sun. (2009). Effects of magnetic field orientation on optical decoherence in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, *Physical Review B*, 79, 115104.
- [80] Y. Sun, T. Böttger, C. Thiel, & R. Cone. (2008), Magnetic g tensors for the $I_{15/2,4}$ and $I_{13/2,4}$ states of $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, *Physical Review B*, 77, 085124.
- [81] Petit, Y., Joly, S., Ségonde, P., & Boulanger, B. (2013). Recent advances in monoclinic crystal optics. *Laser & Photonics Reviews*, 7(6), 920-937.
- [82] New, G. H. C. (2013). Biaxial media revisited. *European Journal of Physics*, 34(5), 1263.
- [83] Roberts, D. A. (1992). Simplified characterization of uniaxial and biaxial nonlinear optical crystals: a plea for standardization of nomenclature and conventions. *IEEE Journal of Quantum Electronics*, 28(10), 2057-2074.
- [84] Maksimov, B., V. Ilyukhin, Y. Kharitonov and N. Belov. (1971). Sov. Phys.- Cryst. 15, 806. Crystal Structure of yttrium orthosilicate $\text{Y}_2\text{O}_3 \cdot \text{SiO}_2$ Y_2SiO_5 dual function of yttrium
Translated from *Kristallografiya* 15, 926, 2.
- [85] IEEE Standard for Relaxor-Based Single Crystals for Transducer and Actuator Applications, in IEEE Std 1859-2017 , vol., no., pp.1-25, 22 Dec. 2017, doi: 10.1109/IEEESTD.2017.8241013.
- [86] Beach, R., Shinn, M. D., Davis, L., Solarz, R. W., & Krupke, W. F. (1990). Optical absorption and stimulated emission of neodymium in yttrium orthosilicate. *IEEE journal of quantum electronics*, 26(8), 1405-1412.
- [87] Bloss, F. D. (1978). The spindle stage; a turning point for optical crystallography. *American Mineralogist*, 63(5-6), 433-447.
- [88] Gunter, M. E., & Twamley, B. (2001, May). A Rapid Method to Determine the Optical Orientation of Biaxial Minerals. In *Eleventh Annual VM Goldschmidt Conference* (p. 3188).
- [89] Thomas, T., Rossman, G. R., & Sandstrom, M. (2014). Device and method of optically orienting biaxial crystals for sample preparation. *Review of Scientific Instruments*, 85(9), 093105.
- [90] Inácio, P. L., Traum, C., Félix, C., Segonds, P., Boulanger, B., Debray, J., ... & Ferrier, A. (2014, November). Direct measurement of the dielectric frame rotation of potential monoclinic crystals as a function of the wavelength. In *Advanced Solid State Lasers* (pp. ATh2A-13). Optical Society of America.

- [91] Traum, C., Inácio, P. L., Felix, C., Segonds, P., Pena, A., Debray, J., ... & Ferrier, A. (2014). Direct measurement of the dielectric frame rotation of monoclinic crystals as a function of the wavelength. *Optical Materials Express*, 4(1), 57-62.
- [92] Jen, S. J. S., & Hartmann, C. S. (1994, November). Conoscope: an apparatus for determining crystal orientation of saw wafers. In *1994 Proceedings of IEEE Ultrasonics Symposium* (Vol. 1, pp. 397-401). IEEE.
- [93] Bond, W.L. . (1976). *Crystal technology*, John Wiley & Sons, 1976.
- [94] Bloss, F. D. (1961). *An introduction to the methods of optical crystallography* (No. 548 BLO).
- [95] Dyar, M. D., Gunter, M. E., & Tasa, D. (2008). *Mineralogy and optical mineralogy* (p. 708). Chantilly, VA: Mineralogical Society of America.
- [96] Wood, E. A. (1977). *Crystals and light: an introduction to optical crystallography*. Courier Corporation.
- [97] Wahlstrom, E.E. (1969). *Optical crystallography*, Wiley.
- [98] Goldner, P., Ferrier, A., & Guillot-Noël, O. (2015). Rare earth-doped crystals for quantum information processing. In *Handbook on the Physics and Chemistry of Rare Earths* (Vol. 46, pp. 1-78). Elsevier.
- [99] Zhong, M., Hedges, M. P., Ahlefeldt, R. L., Bartholomew, J. G., Beavan, S. E., Wittig, S. M., Wittig, S.M., Longdell, J.J., & Sellars, M. J. (2015). Optically addressable nuclear spins in a solid with a six-hour coherence time. *Nature*, 517(7533), 177-180.
- [100] Laplane, C., Jobez, P., Etesse, J., Gisin, N., & Afzelius, M. (2017). Multimode and long-lived quantum correlations between photons and spins in a crystal. *Physical review letters*, 118(21), 210501.
- [101] Clausen, C., Usmani, I., Bussières, F., Sangouard, N., Afzelius, M., de Riedmatten, H., & Gisin, N. (2011). Quantum storage of photonic entanglement in a crystal. *Nature*, 469(7331), 508-511.
- [102] Bussi eres, F., Clausen, C., Tiranov, A., Korzh, B., Verma, V.B., Nam, S.W., Marsili, F., Ferrier, A., Goldner, P., Herrmann, H. & Silberhorn, C., (2014). Quantum teleportation from a telecom-wavelength photon to a solid-state quantum memory. *Nature Photonics*, 8(10), pp.775-778.
- [103] Maring, N., Farrera, P., Kutluer, K., Mazzera, M., Heinze, G., & de Riedmatten, H. (2017). Photonic quantum state transfer between a cold atomic gas and a crystal. *Nature*, 551(7681), 485-488.

- [104] Bonarota, M., Le Gouët, J. L., & Chaneliere, T. (2011). Highly multimode storage in a crystal. *New Journal of Physics*, 13(1), 013013.
- [105] Sinclair, N., Saglamyurek, E., Mallahzadeh, H., Slater, J.A., George, M., Ricken, R., Hedges, M.P., Oblak, D., Simon, C., Sohler, W. & Tittel, W., (2014). Spectral multiplexing for scalable quantum photonics using an atomic frequency comb quantum memory and feed-forward control. *Physical review letters*, 113(5), p.053603.
- [106] Hedges, M. P., Longdell, J. J., Li, Y., & Sellars, M. J. (2010). Efficient quantum memory for light. *Nature*, 465(7301), 1052-1056.
- [107] Sabooni, M., Li, Q., Kröll, S., & Rippe, L. (2013). Efficient quantum memory using a weakly absorbing sample. *Physical review letters*, 110(13), 133604.
- [108] Saglamyurek, E., Sinclair, N., Slater, J. A., Heshami, K., Oblak, D., & Tittel, W. (2014). An integrated processor for photonic quantum states using a broadband light–matter interface. *New Journal of Physics*, 16(6), 065019.
- [109] Bartholomew, J. G., de Oliveira Lima, K., Ferrier, A., & Goldner, P. (2017). Optical line width broadening mechanisms at the 10 kHz level in Eu³⁺: Y₂O₃ nanoparticles. *Nano letters*, 17(2), 778-787.
- [110] Zhong, T., Kindem, J.M., Bartholomew, J.G., Rochman, J., Craiciu, I., Miyazono, E., Bettinelli, M., Cavalli, E., Verma, V., Nam, S.W. and Marsili, F., 2017. Nanophotonic rare-earth quantum memory with optically controlled retrieval. *Science*, 357(6358), pp.1392-1395.
- [111] Williamson, L. A., Chen, Y. H., & Longdell, J. J. (2014). Magneto-optic modulator with unit quantum efficiency. *Physical review letters*, 113(20), 203601.
- [112] O’Brien, C., Lauk, N., Blum, S., Morigi, G., & Fleischhauer, M. (2014). Interfacing superconducting qubits and telecom photons via a rare-earth-doped crystal. *Physical review letters*, 113(6), 063603.
- [113] Fernandez-Gonzalvo, X., Chen, Y. H., Yin, C., Rogge, S., & Longdell, J. J. (2015). Coherent frequency up-conversion of microwaves to the optical telecommunications band in an Er: YSO crystal. *Physical Review A*, 92(6), 062313.
- [114] Chen, Y. H., Fernandez-Gonzalvo, X., & Longdell, J. J. (2016). Coupling erbium spins to a three-dimensional superconducting cavity at zero magnetic field. *Physical Review B*, 94(7), 075117.
- [115] Probst, S., Rotzinger, H., Ustinov, A. V., & Bushev, P. A. (2015). Microwave multimode memory with an erbium spin ensemble. *Physical Review B*, 92(1), 014421.
- [116] Probst, S., Rotzinger, H., Wünsch, S., Jung, P., Jerger, M., Siegel, M., ... & Bushev, P. A. (2013). Anisotropic rare-earth spin ensemble strongly coupled to a superconducting resonator. *Physical Review Letters*, 110(15), 157001.

- [117] Böttger, T., Thiel, C. W., Sun, Y., & Cone, R. L. (2006). Optical decoherence and spectral diffusion at 1.5 μ m in Er³⁺: Y₂SiO₅ versus magnetic field, temperature, and Er³⁺ concentration. *Physical Review B*, 73(7), 075101.
- [118] Cruzeiro, E. Z., Tiranov, A., Usmani, I., Laplane, C., Lavoie, J., Ferrier, A., ... & Afzelius, M. (2017). Spectral hole lifetimes and spin population relaxation dynamics in neodymium-doped yttrium orthosilicate. *Physical Review B*, 95(20), 205119.
- [119] Herzog, B., & Hahn, E. L. (1956). Transient nuclear induction and double nuclear resonance in solids. *Physical Review*, 103(1), 148.
- [120] Cruzeiro, E. Z., Tiranov, A., Lavoie, J., Ferrier, A., Goldner, P., Gisin, N., & Afzelius, M. (2018). Efficient optical pumping using hyperfine levels in 145Nd³⁺: Y₂SiO₅ and its application to optical storage. *New Journal of Physics*, 20(5), 053013.
- [121] Böttger, T., Sun, Y., Thiel, C. W., & Cone, R. L. (2006). Spectroscopy and dynamics of Er³⁺: Y₂SiO₅ at 1.5 μ m. *Physical Review B*, 74(7), 075107.
- [122] Saglamyurek, E., Jin, J., Verma, V.B., Shaw, M.D., Marsili, F., Nam, S.W., Oblak, D. & Tittel, W., (2015). Quantum storage of entangled telecom-wavelength photons in an erbium-doped optical fibre. *Nature Photonics*, 9(2), pp.83-87.
- [123] Mlynek, J., Wong, N. C., DeVoe, R. G., Kintzer, E. S., & Brewer, R. G. (1983). Raman heterodyne detection of nuclear magnetic resonance. *Physical Review Letters*, 50(13), 993.
- [124] Li, C., Wyon, C., & Moncorge, R. (1992). Spectroscopic properties and fluorescence dynamics of Er³⁺ and Yb³⁺ in Y₂SiO₅. *IEEE journal of quantum electronics*, 28(4), 1209-1221.
- [125] Hilborn, R. C. (1982). Einstein coefficients, cross sections, f values, dipole moments, and all that. *American Journal of Physics*, 50(11), 982-986.
- [126] Young, B. A., & Stapleton, H. J. (1966). Apparent lowering of energy levels as measured by Orbach relaxation rates. *Physics Letters*, 21(5), 498-501.
- [127] Wolfowicz, G., Maier-Flaig, H., Marino, R., Ferrier, A., Vezin, H., Morton, J. J., & Goldner, P. (2015). Coherent storage of microwave excitations in rare-earth nuclear spins. *Physical review letters*, 114(17), 170503.
- [128] Böttger, T., Thiel, C. W., Cone, R. L., Sun, Y., & Faraon, A. (2016). Optical spectroscopy and decoherence studies of Yb³⁺: YAG at 968 nm. *Physical Review B*, 94(4), 045134.
- [129] Lim, H. J., Welinski, S., Ferrier, A., Goldner, P., & Morton, J. J. L. (2018). Coherent spin dynamics of ytterbium ions in yttrium orthosilicate. *Physical Review B*, 97(6), 064409.
- [130] Macfarlane, R. M., Wannemacher, R., Boye, D., Wang, Y. P., & Meltzer, R. S. (1991). Nonexponential photon echo decay of Er³⁺ in fluorides. *Journal of luminescence*, 48, 313-317.

- [131] Guillot-Noël, O., Goldner, P., Le Du, Y., Baldit, E., Monnier, P., & Bencheikh, K. (2006). Hyperfine interaction of Er $3+$ ions in Y 2SiO_5 : An electron paramagnetic resonance spectroscopy study. *Physical Review B*, 74(21), 214409.
- [132] Mims, W. B. (1968). Phase memory in electron spin echoes, lattice relaxation effects in CaWO $_4$: Er, Ce, Mn. *Physical Review*, 168(2), 370.
- [133] Thiel, C. W., Babbitt, W. R., & Cone, R. L. (2012). Optical decoherence studies of yttrium oxyorthosilicate Y 2SiO_5 codoped with Er $3+$ and Eu $3+$ for optical signal processing and quantum information applications at 1.5 microns. *Physical Review B*, 85(17), 174302.
- [134] Kraus, B., Tittel, W., Gisin, N., Nilsson, M., Kröll, S., & Cirac, J. I. (2006). Quantum memory for nonstationary light fields based on controlled reversible inhomogeneous broadening. *Physical Review A*, 73(2), 020302.
- [135] Sangouard, N., Simon, C., Afzelius, M., & Gisin, N. (2007). Analysis of a quantum memory for photons based on controlled reversible inhomogeneous broadening. *Physical Review A*, 75(3), 032327.
- [136] Rakonjac, J. V., Chen, Y. H., Horvath, S. P., & Longdell, J. J. (2018). Spin echoes in the ground and an optically excited state of $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ at near-zero magnetic fields using Raman heterodyne spectroscopy. *arXiv preprint arXiv:1802.03862*.
- [137] Kimble, H. J. (2008). The quantum internet. *Nature*, 453(7198), 1023-1030.
- [138] Northup, T. E., & Blatt, R. (2014). Quantum information transfer using photons. *Nature photonics*, 8(5), 356-363.
- [139] O'brien, J. L., Furusawa, A., & Vučković, J. (2009). Photonic quantum technologies. *Nature Photonics*, 3(12), 687-695.
- [140] Andrews, R. W., Peterson, R. W., Purdy, T. P., Cicak, K., Simmonds, R. W., Regal, C. A., & Lehnert, K. W. (2014). Bidirectional and efficient conversion between microwave and optical light. *Nature Physics*, 10(4), 321-326.
- [141] Equall, R. W., Sun, Y., Cone, R. L., & Macfarlane, R. M. (1994). Ultraslow optical dephasing in Eu $3+$: Y 2SiO_5 . *Physical review letters*, 72(14), 2179.
- [142] Rančić, M., Hedges, M. P., Ahlefeldt, R. L., & Sellars, M. J. (2018). Coherence time of over a second in a telecom-compatible quantum memory storage material. *Nature Physics*, 14(1), 50-54.
- [143] Gündoğan, M., Ledingham, P. M., Kutluer, K., Mazzer, M., & De Riedmatten, H. (2015). Solid state spin-wave quantum memory for time-bin qubits. *Physical review letters*, 114(23), 230501.

- [144] Laplane, C., Jobez, P., Etesse, J., Timoney, N., Gisin, N., & Afzelius, M. (2015). Multiplexed on-demand storage of polarization qubits in a crystal. *New Journal of Physics*, 18(1), 013006.
- [145] Lauritzen, B., Hastings-Simon, S. R., De Riedmatten, H., Afzelius, M., & Gisin, N. (2008). State preparation by optical pumping in erbium-doped solids using stimulated emission and spin mixing. *Physical Review A*, 78(4), 043402.
- [146] Baldit, E., Bencheikh, K., Monnier, P., Briaudeau, S., Levenson, J. A., Crozatier, V., ... & Goldner, P. (2010). Identification of Λ -like systems in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ and observation of electromagnetically induced transparency. *Physical Review B*, 81(14), 144303.
- [147] Welinski, S., Ferrier, A., Afzelius, M., & Goldner, P. (2016). High-resolution optical spectroscopy and magnetic properties of Yb^{3+} in Y_2SiO_5 . *Physical Review B*, 94(15), 155116.
- [148] Tiranov, A., Ortu, A., Welinski, S., Ferrier, A., Goldner, P., Gisin, N., & Afzelius, M. (2018). Spectroscopic study of hyperfine properties in $\text{Yb}^{3+}:\text{Y}_2\text{SiO}_5$. *Physical Review B*, 98(19), 195110.
- [149] Ortu, A., Tiranov, A., Welinski, S., Fröwis, F., Gisin, N., Ferrier, A., Goldner, P. & Afzelius, M., (2018). Simultaneous coherence enhancement of optical and microwave transitions in solid-state electronic spins. *Nature materials*, 17(8), pp.671-675.
- [150] De Riedmatten, H., Afzelius, M., Staudt, M. U., Simon, C., & Gisin, N. (2008). A solid-state light-matter interface at the single-photon level. *Nature*, 456(7223), 773-777.
- [151] Zhong, T., Rochman, J., Kindem, J. M., Miyazono, E., & Faraon, A. (2016). High quality factor nanophotonic resonators in bulk rare-earth doped crystals. *Optics express*, 24(1), 536-544.
- [152] Wyckoff, R. (1963). *Crystal Structures*, 2nd ed. John Wiley & Sons.
- [153] Abragam, A., & Bleaney, B. (2012). *Electron paramagnetic resonance of transition ions*. OUP Oxford.
- [154] Ranon, U. (1968). Paramagnetic resonance of Nd^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} in YVO_4 . *Physics Letters A*, 28(3), 228-229.
- [155] Cook, E. C., Martin, P. J., Brown-Heft, T. L., Garman, J. C., & Steck, D. A. (2012). High passive-stability diode-laser design for use in atomic-physics experiments. *Review of Scientific Instruments*, 83(4), 043101.
- [156] Wei, C., Holmstrom, S. A., Manson, N. B., Martin, J. P. D., He, X. F., Fisk, P. T. H., & Holliday, K. (1996). Raman heterodyne detected magnetic resonance: I. cw and coherent transient measurements. *Applied Magnetic Resonance*, 11(3-4), 521-538.

- [157] Blasberg, T., & Suter, D. (1994). Excitation of coherent Raman beats in rare earth solids with a bichromatic laser field. *Optics communications*, 109(1-2), 133-138.
- [158] Blasberg, T., & Suter, D. (1995). Determination of oscillator strengths in $\text{Pr}^{3+}:\text{YAlO}_3$ by Raman heterodyne and hole burning spectroscopy. *Journal of luminescence*, 65(4), 199-209.
- [159] Walther, A., Nilsson, A. N., Li, Q., Rippe, L., & Kröll, S. (2016). Fast all-optical nuclear spin echo technique based on EIT. *The European Physical Journal D*, 70(8), 1-9.
- [160] Serrano, D., Karlsson, J., Fossati, A., Ferrier, A., & Goldner, P. (2018). All-optical control of long-lived nuclear spins in rare-earth doped nanoparticles. *Nature communications*, 9(1), 1-7.
- [161] Koster, G. F., Dimmock, J. O., Wheeler, R. G., & Statz, H. (1963). *Properties of the thirty-two point groups* (Vol. 24). MIT press.
- [162] Di Bartolo, B. (2010). *Optical interactions in solids*. World Scientific Publishing Company.
- [163] Henderson, B., & Imbusch, G. F. (2006). *Optical spectroscopy of inorganic solids* (Vol. 44). Oxford University Press.
- [164] Shi, H. S., Zhang, G., & Shen, H. Y. (2001). Measurement of refractive indices and thermal refractive index coefficients of YVO_4 crystal. *J. Synth. Cryst.*, 30, 85-88.
- [165] Purcell, E. M., Torrey, H. C., & Pound, R. V. (1946). Resonance absorption by nuclear magnetic moments in a solid. *Physical review*, 69(1-2), 37.
- [166] Sumida, D. S., & Fan, T. Y. (1994). Effect of radiation trapping on fluorescence lifetime and emission cross section measurements in solid-state laser media. *Optics Letters*, 19(17), 1343-1345.
- [167] Kisel, V. E., Troshin, A. E., Tolstik, N. A., Shcherbitsky, V. G., Kuleshov, N. V., Matrosov, V. N., ... & Kupchenko, M. I. (2004). Spectroscopy and continuous-wave diode-pumped laser action of $\text{Yb}^{3+}:\text{YVO}_4$. *Optics letters*, 29(21), 2491-2493.
- [168] Ganem, J., Wang, Y. P., Boye, D., Meltzer, R. S., Yen, W. M., & Macfarlane, R. M. (1991). Nonexponential photon-echo decays of paramagnetic ions in the superhyperfine limit. *Physical review letters*, 66(6), 695.
- [169] Fisk, P. T. H., He, X. F., Holliday, K., & Manson, N. B. (1990). Anomalous lineshapes in Raman heterodyne detected EPR. *Journal of luminescence*, 45(1-6), 26-28.
- [170] Karlsson, J., Kunkel, N., Ikesue, A., Ferrier, A., & Goldner, P. (2017). Nuclear spin coherence properties of $^{151}\text{Eu}^{3+}$ and $^{153}\text{Eu}^{3+}$ in a Y_2O_3 transparent ceramic. *Journal of Physics: Condensed Matter*, 29(12), 125501.
- [171] Ahlefeldt, R. L., Hush, M. R., & Sellars, M. J. (2016). Ultranarrow optical inhomogeneous linewidth in a stoichiometric rare-earth crystal. *Physical review letters*, 117(25), 250504.

- [172] Bartholomew, J. G., Ahlefeldt, R. L., & Sellars, M. J. (2016). Engineering closed optical transitions in rare-earth ion crystals. *Physical Review B*, 93(1), 014401.
- [173] Elliott, R. J., & Stevens, K. W. H. (1953). The theory of magnetic resonance experiments on salts of the rare earths. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 218(1135), 553-566.
- [174] Abrahams, S. C., & Geller, S. (1958). Refinement of the structure of a grossularite garnet. *Acta Crystallographica*, 11(6), 437-441.
- [175] Reinemer, G. D. (2003). *Optical characterization of perturbed sites and C 3i sites in rare earth doped oxide crystals*. Montana State University.
- [176] Flinn, G. P., Jang, K. W., Ganem, J., Jones, M. L., Meltzer, R. S., & Macfarlane, R. M. (1994). Anomalous optical dephasing in crystalline Y₂O₃: Eu³⁺. *Journal of luminescence*, 58(1-6), 374-379.
- [177] Flinn, G. P., Jang, K. W., Ganem, J., Jones, M. L., Meltzer, R. S., & Macfarlane, R. M. (1994). Sample-dependent optical dephasing in bulk crystalline samples of Y₂O₃: Eu³⁺. *Physical Review B*, 49(9), 5821.
- [178] Ferrier, A., Tumino, B., & Goldner, P. (2016). Variations in the oscillator strength of the 7F₀→ 5D₀ transition in Eu³⁺: Y₂SiO₅ single crystals. *Journal of Luminescence*, 170, 406-410.
- [179] Wemple, S. H., & Tabor, W. J. (1973). Refractive index behavior of garnets. *Journal of Applied Physics*, 44(3), 1395-1396.
- [180] Ralph, J. E. (1969). Optical transitions in Tm³⁺ doped Y₃Ga₅O₁₂ near 2.0 μ. *Solid State Communications*, 7(15), 1065-1067.
- [181] De Riedmatten, H., & Afzelius, M. (2015). Quantum light storage in solid state atomic ensembles. In *Engineering the Atom-Photon Interaction* (pp. 241-273). Springer, Cham.
- [182] Ménager, L., Lorgeré, I., Le Gouët, J. L., Dolfi, D., & Huignard, J. P. (2001). Demonstration of a radio-frequency spectrum analyzer based on spectral hole burning. *Optics Letters*, 26(16), 1245-1247.
- [183] McAuslan, D. L., Longdell, J. J., & Sellars, M. J. (2009). Strong-coupling cavity QED using rare-earth-metal-ion dopants in monolithic resonators: What you can do with a weak oscillator. *Physical Review A*, 80(6), 062307.
- [184] Lauk, N., O'Brien, C., Fleischhauer, M., Blum, S., & Morigi, G. (2014). Interfacing superconducting qubits and optical photons via a rare-earth doped crystal. *Verhandlungen der Deutschen Physikalischen Gesellschaft*.

- [185] Walther, A., Rippe, L., Yan, Y., Karlsson, J., Serrano, D., Nilsson, A.N., Bengtsson, S. & Kröll, S., (2015). High-fidelity readout scheme for rare-earth solid-state quantum computing. *Physical Review A*, 92(2), p.022319.
- [186] Lutz, T., Veissier, L., Thiel, C. W., Cone, R. L., Barclay, P. E., & Tittel, W. (2016). Modification of phonon processes in nanostructured rare-earth-ion-doped crystals. *Physical Review A*, 94(1), 013801.
- [187] Hong, D. S., Meltzer, R. S., Bihari, B., Williams, D. K., & Tissue, B. M. (1998). Spectral hole burning in crystalline Eu_2O_3 and Y_2O_3 : Eu^{3+} nanoparticles. *Journal of luminescence*, 76, 234-237.
- [188] Malyukin, Y. V., Masalov, A. A., & Zhmurin, P. N. (2003). Single-ion fluorescence spectroscopy of a Y_2SiO_5 : Pr^{3+} nanocluster. *Physics Letters A*, 316(1-2), 147-152.
- [189] Macfarlane, R. M., & Dejneka, M. J. (2001). Spectral hole burning in thulium-doped glass ceramics. *Optics letters*, 26(7), 429-431.
- [190] Perrot, A., Goldner, P., Giaume, D., Lovrić, M., Andriamiadamanana, C., Gonçalves, R. R., & Ferrier, A. (2013). Narrow optical homogeneous linewidths in rare earth doped nanocrystals. *Physical review letters*, 111(20), 203601.
- [191] Heitjans, P., Masoud, M., Feldhoff, A., & Wilkening, M. (2007). NMR and impedance studies of nanocrystalline and amorphous ion conductors: lithium niobate as a model system. *Faraday discussions*, 134, 67-82.
- [191] Scholz, G., Stösser, R., Klein, J., Silly, G., Buzaré, J. Y., Laligant, Y., & Ziemer, B. (2002). Local structural orders in nanostructured Al_2O_3 prepared by high-energy ball milling. *Journal of Physics: Condensed Matter*, 14(8), 2101.
- [192] Bonarota, M., Ruggiero, J., Le Gouët, J. L., & Chanelière, T. (2010). Efficiency optimization for atomic frequency comb storage. *Physical Review A*, 81(3), 033803.
- [193] Kareiva, A. (2011). Aqueous sol-gel synthesis methods for the preparation of garnet crystal structure compounds. *Materials science*, 17(4), 428-436.
- [194] Anderson, P. W., Halperin, B. I., & Varma, C. M. (1972). Anomalous low-temperature thermal properties of glasses and spin glasses. *Philosophical Magazine*, 25(1), 1-9.
- [195] Phillips, W. A. (1972). Tunneling states in amorphous solids. *Journal of low temperature physics*, 7(3), 351-360.
- [196] Watson, S. K. (1995). Tunneling states in crystals with large random strains. *Physical review letters*, 75(10), 1965.

- [197] Macfarlane, R. M., Sun, Y., Cone, R. L., Thiel, C. W., & Equall, R. W. (2004). Optical dephasing by disorder modes in yttrium orthosilicate (Y_2SiO_5) doped with Eu^{3+} . *Journal of luminescence*, 107(1-4), 310-313.
- [198] Meltzer, R. S., Jang, K. W., Hong, K. S., Sun, Y., & Feofilov, S. P. (1997). Optical dephasing of rare earth ions in mixed crystalline and size-restricted systems. *Journal of Alloys and Compounds*, 250(1-2), 279-286.
- [199] Szeftel, J., & Alloul, H. (1978). Nuclear spin lattice relaxation in the amorphous state: Towards an understanding. *Journal of Non-Crystalline Solids*, 29(3), 253-281.
- [200] Askew, T. R., Stapleton, H. J., & Brower, K. L. (1986). Anomalous electron-spin relaxation in amorphous silicon. *Physical Review B*, 33(7), 4455.
- [201] Balzer-Jöllenbeck, G., Kanert, O., Steinert, J., & Jain, H. (1988). Low-temperature properties of nuclear spin relaxation in inorganic glasses. *Solid state communications*, 65(5), 303-309.
- [202] Aminov, L. K., Kurkin, I. N., & Lukoyanov, D. A. (1998). Some peculiarities of spin-lattice relaxation of impurity rare-earth ions in crystals caused by the structure defects. *Applied Magnetic Resonance*, 14(4), 447-456.
- [203] Georgescu, S., Constantinescu, S., Chinie, A. M., Stefan, A. S., Toma, O., & Bibicu, I. (2007, August). Optical and Mossbauer studies on YAG: Eu nanocrystals synthesized by a sol-gel method. In *ROMOPTO 2006: Eighth Conference on Optics* (Vol. 6785, p. 67850A). International Society for Optics and Photonics.
- [204] Li, X., Liu, H., Wang, J., Cui, H., Zhang, X., & Han, F. (2004). Preparation of YAG: Nd nano-sized powder by co-precipitation method. *Materials Science and Engineering: A*, 379(1-2), 347-350.
- [205] Pradhan, A. K., Zhang, K., & Loutts, G. B. (2004). Synthesis of neodymium-doped yttrium aluminum garnet (YAG) nanocrystalline powders leading to transparent ceramics. *Materials Research Bulletin*, 39(9), 1291-1298.
- [206] Xu, G., Zhang, X., He, W., Liu, H., Li, H., & Boughton, R. I. (2006). Preparation of highly dispersed YAG nano-sized powder by co-precipitation method. *Materials Letters*, 60(7), 962-965.
- [207] Lauritzen, B., Minář, J., De Riedmatten, H., Afzelius, M., & Gisin, N. (2011). Approaches for a quantum memory at telecommunication wavelengths. *Physical Review A*, 83(1), 012318.
- [208] Afzelius, M., Simon, C., De Riedmatten, H., & Gisin, N. (2009). Multimode quantum memory based on atomic frequency combs. *Physical Review A*, 79(5), 052329.
- [209] Amin, J., Dussardier, B., Schweizer, T., & Hempstead, M. (1996). Spectroscopic analysis of Er^{3+} transitions in lithium niobate. *Journal of luminescence*, 69(1), 17-26.

- [210] Saglamyurek, E., Sinclair, N., Jin, J., Slater, J.A., Oblak, D., Bussieres, F., George, M., Ricken, R., Sohler, W. & Tittel, W., (2011). Broadband waveguide quantum memory for entangled photons. *Nature*, 469(7331), pp.512-515.
- [211] Weis, R. S., & Gaylord, T. K. (1985). Lithium niobate: summary of physical properties and crystal structure. *Applied Physics A*, 37(4), 191-203.
- [212] Armenise, M. N. (1988). Fabrication techniques of lithium niobate waveguides. *IEE Proceedings J (Optoelectronics)*, 135(2), 85-91.
- [213] Sohler, W., & Suche, H. (1999). Integrated Optical Circuits and Components: Design and Application.
- [214] Hastings-Simon, S. R., Staudt, M. U., Afzelius, M., Baldi, P., Jaccard, D., Tittel, W., & Gisin, N. (2006). Controlled Stark shifts in Er³⁺-doped crystalline and amorphous waveguides for quantum state storage. *Optics communications*, 266(2), 716-719.
- [215] Thiel, C. W., Macfarlane, R. M., Böttger, T., Sun, Y., Cone, R. L., & Babbitt, W. R. (2010). Optical decoherence and persistent spectral hole burning in Er³⁺: LiNbO₃. *Journal of Luminescence*, 130(9), 1603-1609.
- [215] Thiel, C. W., Sun, Y., Macfarlane, R. M., Böttger, T., & Cone, R. L. (2012). Rare-earth-doped LiNbO₃ and KTiOPO₄ (KTP) for waveguide quantum memories. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 45(12), 124013.
- [216] Benchabane, S., Robert, L., Rauch, J. Y., Khelif, A., & Laude, V. (2009). Highly selective electroplated nickel mask for lithium niobate dry etching. *Journal of Applied Physics*, 105(9), 094109.
- [217] Courjal, N., Benchabane, S., Dahdah, J., Ulliac, G., Gruson, Y., & Laude, V. (2010). Acousto-optically tunable lithium niobate photonic crystal. *Applied Physics Letters*, 96(13), 131103.
- [218] Lacour, F., Courjal, N., Bernal, M. P., Sabac, A., Bainier, C., & Spajer, M. (2005). Nanostructuring lithium niobate substrates by focused ion beam milling. *Optical materials*, 27(8), 1421-1425.
- [219] Gheorma, I. L., Savi, P., & Osgood, R. M. (2000). Thin layer design of X-cut LiNbO₃ modulators. *IEEE Photonics Technology Letters*, 12(12), 1618-1620.
- [220] Ramadan, T. A., Levy, M., & Osgood Jr, R. M. (2000). Electro-optic modulation in crystal-ion-sliced z-cut LiNbO₃ thin films. *Applied Physics Letters*, 76(11), 1407-1409.
- [221] Robinson, H., Pitt, C. W., & Gibson, R. A. (1993). Silicon lithium niobate electro-optic waveguide modulator structures in the parallel-plate configuration. *Applied optics*, 32(21), 3981-3988.

- [222] Hu, H., Ricken, R., Sohler, W., & Wehrspohn, R. B. (2007). Lithium niobate ridge waveguides fabricated by wet etching. *IEEE Photonics Technology Letters*, 19(6), 417-419.
- [223] Knabe, B., Buse, K., Assenmacher, W., & Mader, W. (2012). Spontaneous polarization in ultrasmall lithium niobate nanocrystals revealed by second harmonic generation. *Physical Review B*, 86(19), 195428.
- [224] Grange, R., Choi, J.W., Hsieh, C.L., Pu, Y., Magrez, A., Smajda, R., Forró, L. & Psaltis, D., (2009). Lithium niobate nanowires synthesis, optical properties, and manipulation. *Applied Physics Letters*, 95(14), p.143105.
- [225] Morozovska, A. N., Eliseev, E. A., Svechnikov, G. S., & Kalinin, S. V. (2010). Pyroelectric response of ferroelectric nanowires: Size effect and electric energy harvesting. *Journal of Applied Physics*, 108(4), 042009.
- [226] Rüdiger, A., Schneller, T., Roelofs, A., Tiedke, S., Schmitz, T., & Waser, R. (2005). Nanosize ferroelectric oxides—tracking down the superparaelectric limit. *Applied Physics A*, 80(6), 1247-1255.
- [227] Kunkel, N., Bartholomew, J., Welinski, S., Ferrier, A., Ikesue, A., & Goldner, P. (2016). Dephasing mechanisms of optical transitions in rare-earth-doped transparent ceramics. *Physical Review B*, 94(18), 184301.
- [228] Bartholomew, J. G., de Oliveira Lima, K., Ferrier, A., & Goldner, P. (2017). Optical line width broadening mechanisms at the 10 kHz level in Eu³⁺: Y₂O₃ nanoparticles. *Nano letters*, 17(2), 778-787.
- [229] Feofilov, S. P. (2002). Spectroscopy of dielectric nanocrystals doped by rare-earth and transition-metal ions. *Physics of the Solid State*, 44(8), 1407-1414.
- [230] Zheng, H., Wang, X. J., Qu, S. X., Dejneka, M. J., & Meltzer, R. S. (2006). Dynamical processes of Ln³⁺ ions doped in LaF₃ nanocrystals embedded in transparent oxyfluoride glass. *Journal of luminescence*, 119, 153-160.
- [231] Meltzer, R. S., Zheng, H., & Dejneka, M. J. (2004). Photon echo studies of LaF₃: Pr³⁺ nanocrystals in glass. *Journal of luminescence*, 107(1-4), 166-175.
- [232] Beaudoux, F., Ferrier, A., Guillot-Noël, O., Chanelière, T., Le Gouët, J. L., & Goldner, P. (2011). Emission of photon echoes in a strongly scattering medium. *Optics express*, 19(16), 15236-15243.
- [233] Koch, C. C. (1993). The synthesis and structure of nanocrystalline materials produced by mechanical attrition: A review. *Nanostructured materials*, 2(2), 109-129.
- [234] Šepelák, V., Bégin-Colin, S., & Le Caer, G. (2012). Transformations in oxides induced by high-energy ball-milling. *Dalton Transactions*, 41(39), 11927-11948.

- [235] Michel, D., Mazerolles, L., Berthet, P., & Gaffet, E. (1995). Nanocrystalline and amorphous oxide powders prepared by high-energy ball milling. *European journal of solid state and inorganic chemistry*, 32, 673-673.
- [236] Bravina, S. L., Morozovska, A. N., Morozovsky, N. V., & Skryshevsky, Y. A. (2004). Low-temperature pyroelectric phenomena in lithium niobate single crystals. *Ferroelectrics*, 298(1), 31-42.
- [237] Bork, D., & Heitjans, P. (1998). NMR relaxation study of ion dynamics in nanocrystalline and polycrystalline LiNbO₃. *The Journal of Physical Chemistry B*, 102(38), 7303-7306.
- [238] Pooley, M. J., & Chadwick, A. V. (2003). The synthesis and characterisation of nanocrystalline lithium niobate. *Radiation effects and defects in solids*, 158(1-6), 197-201.
- [239] Heitjans, P., & Indris, S. (2004). Fast diffusion in nanocrystalline ceramics prepared by ball milling. *Journal of materials science*, 39(16), 5091-5096.
- [240] Chadwick, A. V., Pooley, M. J., & Savin, S. L. P. (2005). Lithium ion transport and microstructure in nanocrystalline lithium niobate. *Physica status solidi (c)*, 2(1), 302-305.
- [241] Kar, S., Logad, S., Choudhary, O. P., Debnath, C., Verma, S., & Bartwal, K. S. (2013). Preparation of lithium niobate nanoparticles by high energy ball milling and their characterization. *Univers. J. Mater. Sci*, 1(2), 18-24.
- [242] Wang, X., Ye, Z., Li, G., & Zhao, B. (2007). Influence of substrate temperature on the growth and optical waveguide properties of oriented LiNbO₃ thin films. *Journal of crystal growth*, 306(1), 62-67.
- [243] Budakoti, G. C., & Rawat, R. S. (2008). Enhancement in crystalline quality of LiNbO₃ films by slow annealing at low temperatures. *Journal of crystal growth*, 310(18), 4205-4208.
- [244] Jhans, H., Honig, J. M., & Rao, C. N. R. (1986). Optical properties of reduced LiNbO₃. *Journal of Physics C: Solid State Physics*, 19(19), 3649.
- [245] Dhar, A., & Mansingh, A. (1990). Optical properties of reduced lithium niobate single crystals. *Journal of applied physics*, 68(11), 5804-5809.
- [246] Simoes, A. Z., Zaghete, M. A., Stojanovic, B. D., Gonzalez, A. H., Riccardi, C. S., Cantoni, M., & Varela, J. A. (2004). Influence of oxygen atmosphere on crystallization and properties of LiNbO₃ thin films. *Journal of the European Ceramic Society*, 24(6), 1607-1613.
- [247] Jackel, J. L., Ramaswamy, V., & Lyman, S. P. (1981). Elimination of out-diffused surface guiding in titanium-diffused LiNbO₃. *Applied Physics Letters*, 38(7), 509-511.
- [248] Forouhar, S., Betts, G. E., & Chang, W. S. C. (1984). Effects of water vapor on modes in Ti-indiffused LiNbO₃ planar waveguides. *Applied physics letters*, 45(3), 207-209.

- [249] Schlarb, U., & Betzler, K. (1993). Refractive indices of lithium niobate as a function of temperature, wavelength, and composition: A generalized fit. *Physical Review B*, 48(21), 15613.
- [250] Zelmon, D. E., Small, D. L., & Jundt, D. (1997). Infrared corrected Sellmeier coefficients for congruently grown lithium niobate and 5 mol.% magnesium oxide-doped lithium niobate. *JOSA B*, 14(12), 3319-3322.
- [251] Veissier, L., Falamarzi, M., Lutz, T., Saglamyurek, E., Thiel, C. W., Cone, R. L., & Tittel, W. (2016). Optical decoherence and spectral diffusion in an erbium-doped silica glass fiber featuring long-lived spin sublevels. *Physical Review B*, 94(19), 195138.
- [252] Gog, T., Griebenow, M., & Materlik, G. (1993). X-ray standing wave determination of the lattice location of Er diffused into LiNbO₃. *Physics Letters A*, 181(5), 417-420.
- [253] Sole, J. G., Bausa, L. E., Jaque, D., Montoya, E., Murrieta, H., & Jaque, F. (1998). Rare earth and transition metal ion centers in LiNbO₃. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 54(11), 1571-1581.
- [254] Black, J. L., & Halperin, B. I. (1977). Spectral diffusion, phonon echoes, and saturation recovery in glasses at low temperatures. *Physical Review B*, 16(6), 2879.
- [255] Silbey, R. J., Koedijk, J. M. A., & Völker, S. (1996). Time and temperature dependence of optical linewidths in glasses at low temperature: Spectral diffusion. *The Journal of chemical physics*, 105(3), 901-909.
- [256] Heshami, K., England, D. G., Humphreys, P. C., Bustard, P. J., Acosta, V. M., Nunn, J., & Sussman, B. J. (2016). Quantum memories: emerging applications and recent advances. *Journal of modern optics*, 63(20), 2005-2028.
- [257] Sipahigil, A., Evans, R. E., Sukachev, D. D., Burek, M. J., Borregaard, J., Bhaskar, M. K., & Lukin, M. D. (2016). An integrated diamond nanophotonics platform for quantum-optical networks. *Science*, 354(6314), 847-850.
- [258] Hensen, B., Bernien, H., Dréau, A.E., Reiserer, A., Kalb, N., Blok, M.S., Ruitenbergh, J., Vermeulen, R.F., Schouten, R.N., Abellán, C. and Amaya, W., 2015. Loophole-free Bell inequality violation using electron spins separated by 1.3 kilometres. *Nature*, 526(7575), pp.682-686.
- [259] Maurer, P.C., Kucsko, G., Latta, C., Jiang, L., Yao, N.Y., Bennett, S.D., Pastawski, F., Hunger, D., Chisholm, N., Markham, M. and Twitchen, D.J., 2012. Room-temperature quantum bit memory exceeding one second. *Science*, 336(6086), pp.1283-1286.
- [260] Hong, S., Grinolds, M. S., Pham, L. M., Le Sage, D., Luan, L., Walsworth, R. L., & Yacoby, A. (2013). Nanoscale magnetometry with NV centers in diamond. *MRS bulletin*, 38(2), 155-161.

- [261] Powell, R. C. (1998). *Physics of solid-state laser materials* (Vol. 1). Springer Science & Business Media.
- [262] Kenyon, A. J. (2002). Recent developments in rare-earth doped materials for optoelectronics. *Progress in Quantum Electronics*, 26(4-5), 225-284.
- [263] Jüstel, T., Nikol, H., & Ronda, C. (1998). New developments in the field of luminescent materials for lighting and displays. *Angewandte Chemie International Edition*, 37(22), 3084-3103.
- [264] Wang, F., Han, Y., Lim, C.S., Lu, Y., Wang, J., Xu, J., Chen, H., Zhang, C., Hong, M. & Liu, X., (2010). Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. *Nature*, 463(7284), pp.1061-1065.
- [265] Downing, E., Hesselink, L., Ralston, J., & Macfarlane, R. (1996). A three-color, solid-state, three-dimensional display. *Science*, 273(5279), 1185-1189.
- [266] Ruan, X. L., & Kaviany, M. (2006). Enhanced laser cooling of rare-earth-ion-doped nanocrystalline powders. *Physical Review B*, 73(15), 155422.
- [267] Ferrier, A., Thiel, C.W., Tumino, B., Ramirez, M.O., Bausa, L.E., Cone, R.L., Ikesue, A. and Goldner, P., 2013. Narrow inhomogeneous and homogeneous optical linewidths in a rare earth doped transparent ceramic. *Physical Review B*, 87(4), p.041102.
- [268] Lutz, T., Veissier, L., Thiel, C. W., Cone, R. L., Barclay, P. E., & Tittel, W. (2016). Modification of phonon processes in nanostructured rare-earth-ion-doped crystals. *Physical Review A*, 94(1), 013801.
- [269] Yang, H. S., Feofilov, S. P., Williams, D. K., Milora, J. C., Tissue, B. M., Meltzer, R. S., & Dennis, W. M. (1999). One phonon relaxation processes in Y₂O₃: Eu³⁺ nanocrystals. *Physica B: Condensed Matter*, 263, 476-478.
- [270] Yang, H. S., Hong, K. S., Feofilov, S. P., Tissue, B. M., Meltzer, R. S., & Dennis, W. M. (1999). Electron-phonon interaction in rare earth doped nanocrystals. *Journal of luminescence*, 83, 139-145.
- [271] Liu, G. K., Zhuang, H. Z., & Chen, X. Y. (2002). Restricted phonon relaxation and anomalous thermalization of rare earth ions in nanocrystals. *Nano Letters*, 2(5), 535-539.
- [272] Mercier, B., Dujardin, C., Ledoux, G., Louis, C., Tillement, O., & Perriat, P. (2006). Confinement effects in sesquioxides. *Journal of luminescence*, 119, 224-227.
- [272] Förster, T. (2012). Energy migration and fluorescence. *Journal of biomedical optics*, 17(1), 011002. Translated from Förster, T.(1946) Energiewanderung und Fluoreszenz *Naturwissenschaften*, Vol. 33 (6), pp. 166–175.

- [273] Mezeix, L., & Green, D. J. (2006). Comparison of the mechanical properties of single crystal and polycrystalline yttrium aluminum garnet. *International journal of applied ceramic technology*, 3(2), 166-176.
- [274] Kaithwas, N., Dave, M., Kar, S., Verma, S., & Bartwal, K. S. (2010). Preparation of Nd: Y3Al5O12 nanocrystals by low temperature glycol route. *Crystal Research and Technology*, 45(11), 1179-1182.
- [275] Gong, H., Tang, D. Y., Huang, H., & Ma, J. (2009). Agglomeration control of Nd: YAG nanoparticles via freeze drying for transparent Nd: YAG ceramics. *Journal of the American ceramic society*, 92(4), 812-817.
- [276] Hänsch, T. W. (1972). Repetitively pulsed tunable dye laser for high resolution spectroscopy. *Applied Optics*, 11(4), 895-898.
- [277] Lamb, H. (1881). On the vibrations of an elastic sphere. *Proceedings of the London Mathematical Society*, 1(1), 189-212.
- [278] Strickler, S. J., & Berg, R. A. (1962). Relationship between absorption intensity and fluorescence lifetime of molecules. *The Journal of chemical physics*, 37(4), 814-822.
- [279] Schniepp, H., & Sandoghdar, V. (2002). Spontaneous emission of europium ions embedded in dielectric nanospheres. *Physical review letters*, 89(25), 257403.
- [280] Aubret, A., Pillonnet, A., Houel, J., Dujardin, C., & Kulzer, F. (2016). CdSe/ZnS quantum dots as sensors for the local refractive index. *Nanoscale*, 8(4), 2317-2325.
- [281] Scheel, S., Knöll, L., & Welsch, D. G. (1999). Spontaneous decay of an excited atom in an absorbing dielectric. *Physical Review A*, 60(5), 4094.
- [282] De Fornel, F. (2001). *Evanescent waves: from Newtonian optics to atomic optics* (Vol. 73). Springer Science & Business Media.
- [283] Garrett, K. W., & Rosenberg, H. M. (1974). The thermal conductivity of epoxy-resin/powder composite materials. *Journal of Physics D: Applied Physics*, 7(9), 1247.
- [284] Rettelbach, T., Säuberlich, J., Korder, S., & Fricke, J. (1995). Thermal conductivity of silica aerogel powders at temperatures from 10 to 275 K. *Journal of non-crystalline solids*, 186, 278-284.
- [285] Brodie, D. E., & Mate, C. F. (1965). Heat transfer in gas-filled powders at low temperatures. *Canadian Journal of Physics*, 43(12), 2344-2360.
- [286] Babbitt, W. R., Barber, Z. W., Bekker, S. H., Chase, M. D., Harrington, C., Merkel, K. D., Mohan, R.K., Sharpe, T., Stiffler, C.R., Traxinger, A.S., & Woidtke, A. J. (2014). From spectral holeburning memory to spatial-spectral microwave signal processing. *Laser Physics*, 24(9), 094002.

- [288] Fraval, E., Sellars, M. J., & Longdell, J. J. (2004). Method of Extending Hyperfine Coherence Times in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$. *Physical Review Letters*, 92(7), 077601.
- [289] Macfarlane, R. M., Yannoni, C. S., & Shelby, R. M. (1980). Optical line narrowing by nuclear spin decoupling in $\text{Pr}^{3+}:\text{LaF}_3$. *Optics Communications*, 32(1), 101-104.
- [290] Ohlsson, N., Nilsson, M., Kröll, S., & Mohan, R. K. (2003). Long-time-storage mechanism for $\text{Tm}:\text{YAG}$ in a magnetic field. *Optics Letters*, 28(6), 450-452.
- [291] Teplov, M. A. (1967). Magnetic resonance on pr^{141} nuclei in a $\text{pr}^{2+}(\text{sO}_4)_3 \cdot 8\text{H}_2\text{O}$ single crystal. *Zh. Eksp. Teor. Fiz*, 53, 1510-1515.
- [292] Abragam, A., & Bleaney, B. (1983). Enhanced nuclear magnetism: some novel features and prospective experiments. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 387(1793), 221-256.
- [293] Dillon Jr, J. F., & Walker, L. R. (1961). Ferrimagnetic resonance in rare-earth doped yttrium iron garnet. II. Terbium substitution. *Physical Review*, 124(5), 1401.
- [294] Menzer, G. (1929). XX. Die kristallstruktur der granate. *Zeitschrift für Kristallographie-Crystalline Materials*, 69(1-6), 300-396.
- [295] Lauro, R., Chanelière, T., & Gouët, J. L. L. (2009). Slow light using spectral hole burning in a $\text{Tm}^{3+}:\text{YAG}$ crystal. *arXiv preprint arXiv:0902.2657*.
- [296] Erickson, L. E. (1977). The nuclear quadrupole interaction in $\text{Pr}^{3+}:\text{LaF}_3$ —an optical-rf double resonance measurement of the ground electronic state. *Optics Communications*, 21(1), 147-149.
- [297] Silversmith, A. J., Radlinski, A. P., & Manson, N. B. (1985). Holeburning and ODNMR Study of a Eu^{3+} site in CaF_2 . *Le Journal de Physique Colloques*, 46(C7), C7-531.
- [298] Jones, E. D. (1968). Observation of the Tm^{169} nuclear magnetic resonance in thulium gallium garnet. *Journal of Physics and Chemistry of Solids*, 29(8), 1305-1308.
- [299] Schmidt, V. H., & Jones, E. D. (1970). Nuclear-Magnetic-Resonance Study of Thulium Aluminum Garnet. *Physical Review B*, 1(5), 1978.
- [300] McAuslan, D. L., Bartholomew, J. G., Sellars, M. J., & Longdell, J. J. (2012). Reducing decoherence in optical and spin transitions in rare-earth-metal-ion-doped materials. *Physical Review A*, 85(3), 032339.
- [301] Van Vleck, J. H. (1932). *The theory of electric and magnetic susceptibilities*. Clarendon Press.
- [302] Longdell, J. J., Alexander, A. L., & Sellars, M. J. (2006). Characterization of the hyperfine interaction in europium-doped yttrium orthosilicate and europium chloride hexahydrate. *Physical Review B*, 74(19), 195101.

- [303] Lovrić, M., Glasenapp, P., Suter, D., Tumino, B., Ferrier, A., Goldner, P., Sabooni, M., Rippe, L. & Kröll, S., (2011). Hyperfine characterization and spin coherence lifetime extension in Pr 3+: La 2 (WO 4) 3. *Physical Review B*, 84(10), p.104417.
- [304] Kielpinski, D., Meyer, V., Rowe, M. A., Sackett, C. A., Itano, W. M., Monroe, C., & Wineland, D. J. (2001). A decoherence-free quantum memory using trapped ions. *Science*, 291(5506), 1013-1015.
- [305] Tongning, R. C., Chanelière, T., Le Gouët, J. L., & Pascual-Winter, M. F. (2015, April). Optical clock transition in a rare-earth-ion-doped crystal: coherence lifetime extension for quantum storage applications. In *Journal of Physics: Conference Series* (Vol. 605, No. 1, p. 012037). IOP Publishing.
- [306] Pascual-Winter, M. F., Tongning, R. C., Chaneliere, T., & Le Gouët, J. L. (2012). Spin coherence lifetime extension in Tm 3+: YAG through dynamical decoupling. *Physical Review B*, 86(18), 184301.
- [307] Lauro, R., Ruggiero, J., Louchet, A., Alexander, A., Chanelière, T., Lorgeré, I., Bretenaker, F., Goldfarb, F. and Le Gouët, J.L., 2009. Thulium doped crystals for quantum information storage. *Journal of Luminescence*, 129(12), pp.1951-1954.
- [308] Li, Y., Hemmer, P., Kim, C., Zhang, H., & Wang, L. V. (2008). Detection of ultrasound-modulated diffuse photons using spectral-hole burning. *Optics express*, 16(19), 14862-14874.
- [309] Tay, J. W., Ledingham, P. M., & Longdell, J. J. (2010). Coherent optical ultrasound detection with rare-earth ion dopants. *Applied optics*, 49(23), 4331-4334.
- [310] Xu, X., Kothapalli, S. R., Liu, H., & Wang, L. V. (2010). Spectral hole burning for ultrasound-modulated optical tomography of thick tissue. *Journal of biomedical optics*, 15(6), 066018.
- [311] Louchet-Chauvet, A., Lauro, R., Goldner, P., Ramaz, F., Chanelière, T., & Le Gouët, J. L. (2011, February). High-resolution large dynamic range spectral filtering at 800 nm using Tm: YAG crystals. In *Advances in Photonics of Quantum Computing, Memory, and Communication IV* (Vol. 7948, p. 794805). International Society for Optics and Photonics.
- [312] Sellin, P. B., Strickland, N. M., Carlsten, J. L., & Cone, R. L. (1999). Programmable frequency reference for subkilohertz laser stabilization by use of persistent spectral hole burning. *Optics letters*, 24(15), 1038-1040.
- [313] Thorpe, M. J., Leibrandt, D. R., & Rosenband, T. (2013). Shifts of optical frequency references based on spectral-hole burning in Eu3+: Y2SiO5. *New Journal of Physics*, 15(3), 033006.

- [314] Cook, S., Rosenband, T., & Leibrandt, D. R. (2015). Laser-Frequency Stabilization Based on Steady-State Spectral-Hole Burning in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$. *Physical review letters*, 114(25), 253902.
- [315] Ball, M., Garton, G., Leask, M. J. M., Ryan, D., & Wolf, W. P. (1961). Low-temperature magnetic properties of some rare-earth garnet compounds. *Journal of Applied Physics*, 32(3), S267-S269.
- [316] Amittar, V., Taneja, S. P., & Puri, S. P. (1972). Crystal field investigations of $\text{Yb}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Er}^{3+}:\text{YA1G}$. *Journal of Physics and Chemistry of Solids*, 33(4), 813-818.
- [317] Bagdasarov, K. S., Zhekov, V. I., Lobachev, V. A., Murina, T. M., & Prokhorov, A. M. (1983). Steady-State Emission from a $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Er}^{3+}$ Laser ($\lambda = 2.94 \mu$, $T = 300 \text{ K}$). *Soviet Journal of Quantum Electronics*, 13(2), 262.
- [318] Payne, S. A., Chase, L. L., Smith, L. K., Kway, W. L., & Krupke, W. F. (1992). Infrared cross-section measurements for crystals doped with Er^{3+} , Tm^{3+} , and Ho^{3+} . *IEEE Journal of Quantum Electronics*, 28(11), 2619-2630.
- [319] Morrison, C. A., Wortman, D. E., & Karayianis, N. (1976). Crystal-field parameters for triply-ionized lanthanides in yttrium aluminium garnet. *Journal of Physics C: Solid State Physics*, 9(8), L191.
- [320] Gruber, J.B., Quagliano, J.R., Reid, M.F., Richardson, F.S., Hills, M.E., Seltzer, M.D., Stevens, S.B., Morrison, C.A. & Allik, T.H., (1993). Energy levels and correlation crystal-field effects in Er^{3+} -doped garnets. *Physical Review B*, 48(21), p.15561.
- [321] Koningstein, J. A., & Geusic, J. E. (1964). Energy levels and crystal-field calculations of Er^{3+} in yttrium aluminum garnet. *Physical Review*, 136(3A), A726.
- [322] Hellwege, K. H., Hüfner, S., Schinkmann, M., & Schmidt, H. (1966). Optical absorption spectrum and crystal field of erbium aluminum garnet (ErAlG). *Physik der kondensierten Materie*, 4(5), 397-403.
- [323] Zverev, G. M., Kolodnyi, G. Y., & Onishchenko, A. M. (1971). Nonradiative transitions between levels of trivalent rare-earth ions in yttrium-aluminum garnet crystals. *Sov. Phys. JETP*, 33, 497.
- [324] Devi, A. R., Jayasankar, C. K., & Reid, M. F. (1994). Comparative correlation crystal field analysis of $\text{Er}^{3+}(4f^{11})$ in garnet hosts. *Journal of alloys and compounds*, 207, 74-77.
- [325] Burdick, G. W., Gruber, J. B., Nash, K. L., Chandra, S., & Sardar, D. K. (2010). Analyses of $4f^{11}$ energy levels and transition intensities between stark levels of Er^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$. *Spectroscopy Letters*, 43(5), 406-422.

- [326] Ter-Gabrielyan, N., Fromzel, V., Merkle, L. D., & Dubinskii, M. (2011). Resonant in-band pumping of cryo-cooled Er $3+$: YAG laser at 1532, 1534 and 1546 nm: a comparative study. *Optical Materials Express*, 1(2), 223-233.
- [327] Zhou, D., Xu, X., Xia, C., Shen, D., Cheng, S., Li, D., ... & Xu, J. (2011). Spectroscopic analysis and lasing of Er: Lu 1.5 Y 1.5 Al 5 O 12 crystals. *JOSA B*, 28(10), 2543-2548.
- [328] Feofilov, S., Kulinkin, A., Ovanesyan, K., Petrosyan, A., & Dujardin, C. (2014). Anomalous discrete disorder response of high-symmetry impurity centers spectra in garnet solid solutions. *Physical Chemistry Chemical Physics*, 16(41), 22583-22587.
- [329] Feofilov, S. P., Kulinkin, A. B., Ovanesyan, K. L., & Petrosyan, A. G. (2016). Discrete zero-phonon Cr $3+$ lines in the spectra of Terbium–Yttrium–Lutetium Aluminum garnets solid solutions: Lattice compression and dilation. *Solid State Communications*, 226, 39-43.
- [330] Imbusch, G. F., Yen, W. M., Schawlow, A. L., McCumber, D. E., & Sturge, M. D. (1964). Temperature Dependence of the Width and Position of the E $2 \rightarrow A 2 4$ Fluorescence Lines of Cr $3+$ and V $2+$ in MgO. *Physical Review*, 133(4A), A1029.
- [331] Ashkin, A. (1970). Acceleration and trapping of particles by radiation pressure. *Physical review letters*, 24(4), 156.
- [332] Rahman, A. A., & Barker, P. F. (2017). Laser refrigeration, alignment and rotation of levitated Yb $3+$: YLF nanocrystals. *Nature Photonics*, 11(10), 634-638.
- [333] Ashkin, A., & Dziedzic, J. M. (1971). Optical levitation by radiation pressure. *Applied Physics Letters*, 19(8), 283-285.
- [334] Seletskiy, D. V., Epstein, R., & Sheik-Bahae, M. (2016). Laser cooling in solids: advances and prospects. *Reports on Progress in Physics*, 79(9), 096401.