Spectroscopic evaluation of several thulium doped laser materials via Fourier transform time-resolved spectroscopy
by Richard Charles Martoglio

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry (MONTANA STATE UNIVERSITY Bozeman, Montana August 1997
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Abstract:
A new technique for. the analysis of solid-state laser materials named Fourier Transform Time-Resolved Spectroscopy (FT-TRS) has been developed and implemented. FT-TRS has advantages over previous analysis techniques, primarily the time in which complete material characterization can be accomplished. The technique uses interferometric methods to collect sample emission after excitation over a broad spectral range while simultaneously characterizing the emission lifetime. In this way, analysis time is shortened considerably while providing information regarding absorption frequencies, emission frequencies and emission lifetimes which are essential for understanding the kinetics of the many photophysical processes which occur in these materials.

The interferometer used for our FT-TRS experiments can resolve spectral features to 0.25 cm-1 over a range of nearly 23,000 cm"1 (25,000-2,000 cm-1). Temporal resolution to 20 nsec has been achieved. The implementation of an optically parametric oscillating laser enables material excitation from 23,000-5,500 cm-1.

FT-TRS has been used for the analysis of several different thulium (Tm3+) doped laser materials. The technique has proven to yield results consistent with earlier studies performed using different instrumentation. Emission rise and decay lifetimes for several electronic transitions have been determined. Mathematical fitting methods developed by Inokuti and Hirayama have proven to fit non-exponential emission decay that occurs in these materials. Subsequently, the kinetics which describe the many energy transfer events occurring after excitation have been investigated which has yielded the magnitudes of these radiative and non-radiative energy transfer processes.

SPECTROSCOPIC EVALUATION OF SEVERAL THULIUM DOPED LASER MATERIALS VIA FOURIER TRANSFORM TIME-RESOLVED SPECTROSCOPY

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

A new technique for the analysis of solid-state laser materials named Fourier Transform Time-Resolved Spectroscopy (FT-TRS) has been developed and implemented. FT-TRS has advantages over previous analysis techniques, primarily the time in which complete material characterization can be accomplished. The technique uses interferometric methods to collect sample emission after excitation over a broad spectral range while simultaneously characterizing the emission lifetime. In this way, analysis time is shortened considerably while providing information regarding absorption frequencies, emission frequencies and emission lifetimes which are essential for understanding the kinetics of the many photophysical processes which occur in these materials.

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CHAPTER 1

INTRODUCTION

General

Laser based analysis systems have been implemented in many areas of scientific research, as well as in monitoring applications and medicine. Examples include the study and identification of environmental pollutants through remote sensing (LIDAR), the determination of molecular orientation at a surface (SERS), the process of soft-ionization in laser desorption mass spectrometry (MALDI) and the development of surgical lasers. The creation of new laser technology and the improvement of laser designs currently in use is of paramount significance when considering the increasing complexity and importance of their roles in real world applications. As more demands are being made upon the scientific community to improve laser performance advances are also required in the analysis of the materials that serve as the lasing media.

Solid-state lasers are proving to be a practical source of light emission in the aforementioned areas of research. These lasers are very durable, are usually compact in size, quite powerful and generally can be operated at a variety of repetition rates. Coherent photon output in solid-state systems is dependent on the crystalline lasing

medium implemented. Laser performance is directly dependent on the optical properties of the lasing medium, such as emission. Spectroscopic analysis methods allow for a better understanding of the physical processes which occur in these crystalline materials. Based on the studies of these processes, materials may be evaluated and possibly improved.

Statement of the Problem

Currently, there are several hundred crystalline materials that have the potential for use in solid-state lasers. New materials may be developed at rapid rates, with crystal growth times generally on the order of a few days up to two weeks. Additionally, many growers have the capability of creating a variety of finished products in a single growing period. For example, Scientific Materials Corporation of Bozeman, MT created nearly fifty different materials in a two month span. Due to this ability to quickly manufacture materials and the limitations of current material analysis techniques it is the goal of this research to develop and apply a spectroscopic method that allows for rapid and accurate material characterization. Upon characterization, information may then be fed back to the grower to aid in their engineering processes or determine if the material is suitable for use in an operating laser system.

The method employed will allow for developing a better understanding of energy transfer processes which occur (radiative and nonradiative) after excitation. Spectroscopic results obtained via the new method will be compared to known and accepted data for validation of the method. In addition, a working kinetic model based

upon experimental results will be generated. During the initial studies of this project we hope to exploit the advantages of the technique while uncovering problems and limitations.

Spectroscopy of Rare-Earth Crystalline Laser Materials

The spectroscopic parameters of laser materials have been studied for over 30 years. Johnson, *et al.* in 1965 and 1966 studied emission from several different rare-earth ions doped into yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG)(1).

Solid-state laser materials tend to have many absorption bands which are made up of relatively narrow line features. The materials absorb light over a broad wavelength region, but do so selectively due to the narrow line widths. In order to fully characterize a material it is beneficial to selectively excite the sample at many different energies and often at different sites within a particular absorption manifold. Upon excitation the material may then emit light. The emission is typically narrow band, but can occur over a broad wavelength region. Most spectroscopic emission data has been obtained by using either a laser or conventional source such as a tungsten or mercury lamp to excite the material. Emitting wavelengths from the material are typically dispersed using a monochromator and impinged on a photo-sensitive detector responsive to the wavelength(s) of interest. Emission lifetimes may be measured after pulsed excitation with the addition of an oscilloscope or a boxcar with sufficient temporal resolution capabilities. The determination of the emission lifetimes with a high degree of accuracy and precision is necessary to determine energy transfer rates. This method of analysis

is a very reliable and proven one, but is quite tedious and time-consuming.

The above characteristics of these materials shed light upon the requirements needed to effectively perform spectroscopic analyses. It is imperative that a narrow band source be employed that is tunable over a large frequency range (ultra-violet to near-infrared) to fully exploit the absorption features of the material. Recent laser developments (Optical Parametric Oscillation, OPO) have made this possible. Also, because many emissions occur within a nanosecond time frame, short output pulses are required. Since emission lifetimes can vary significantly for different processes (from milliseconds for emission from the first excited state to nanoseconds for inter-manifold transitions), variation of the laser output repetition rate is essential to allow for complete relaxation between pulses.

The device employed to detect and analyze emitting radiation must operate over a wide spectral range with sufficient resolution capabilities. In order to analyze data rapidly the system must simultaneously pass, detect and resolve as many emitting wavelengths as possible and the system must resolve the emission in 3 dimensions: intensity, wavelength and time. This is the major time limiting factor of previous analysis designs. We have found that the solution to the above requirements is the technique of step-scan interferometry and is outlined in Chapter 2.

The Chemistry and Physics of Laser Materials

The materials used in this study were grown by the Czochralski technique. The materials are conceived by starting with the compounds that will form the crystalline

lattice. It is imperative that these compounds be free of dopant or impurity ions, such as Nd^{3+} and OH^-, respectively. Typically, an iridium crucible is used to contain the "melt" which consists of the lattice precursors. The growing process is carried out at temperatures above 2200 degrees celcius. The dopant ion is introduced into the melt when it reaches the correct temperature for material formation. The crystal is then pulled slowly from the melt, for example, 0.6 mm/hr during Nd:YAG crystal formation(2). The temperature of the melt must be rigorously controlled by the grower to ensure that the dopant ion is distributed properly throughout the crystal as it is pulled. The dopant ion replaces a matrix ion (yttrium) at certain sites in YAG (see Figure 1), for example, which leads to a material that is capable of producing radiative emission that

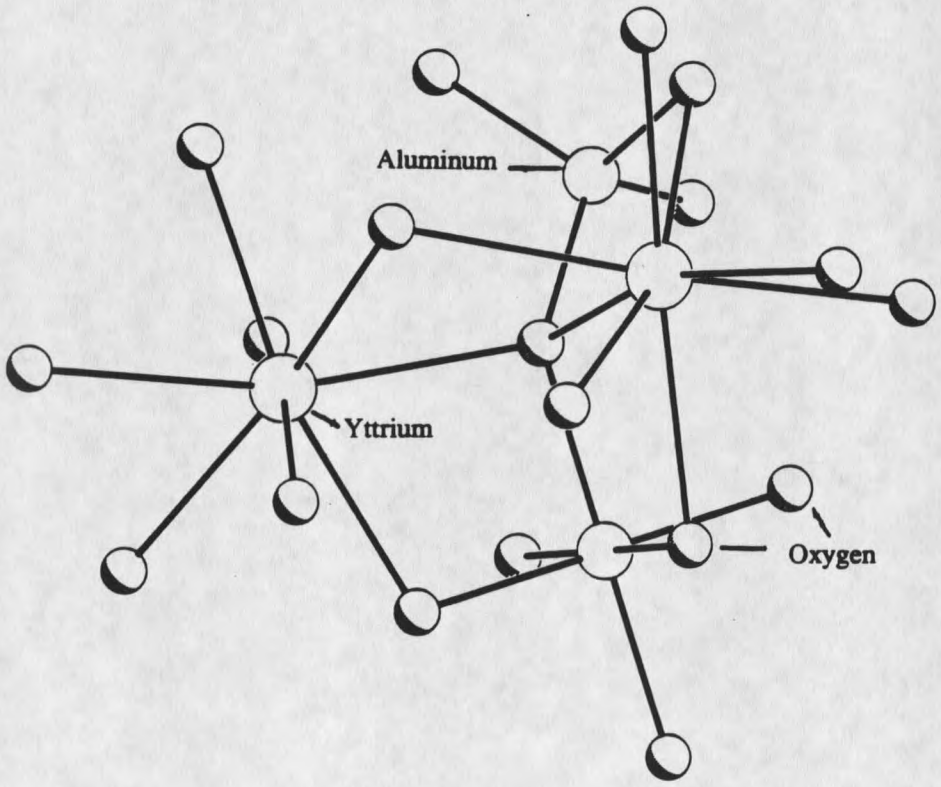

Figure 1. The YAG crystal lattice.

may be used for lasing under proper conditions(3). Again, it is important that the matrixand dopant materials be free of outside imputrities such as the hydroxide ion. Hydroxide ion impurities with magnitudes of 1 to 4% in Nd^{3+}:YAG have shown to cause a decrease of approximately 50% in lasing output power(4). This decrease is believed to be due to direct interaction of the Nd^{3+} ion with the OH^- impurity that resides in the dodecahedral site of the YAG lattice.

Stark Level Employment In Operating Schemes

It has been stated that the initial action to be taken when performing spectroscopic analyses of solid-state laser media is the identification and location of the characteristic absorption bands (Stark manifolds) and their corresponding features (Stark levels)(3). This process is most easily accomplished by light absorption methods. This determination allows for selective excitation, experimental emission energy transfer assignments and determination of other energy transfer processes such as upconversion and cross-relaxation, for example. While pre-existing calculated and experimental absorption data is a valuable resource, it is important to perform absorption measurements when samples are obtained for study, due to the possibility of changes in the optical properties caused by impurities.

Stark manifold location and level structure is governed by the electrostatic interaction of the 4f electrons with one another, the spin-orbit coupling of the electrons and the influence of the lattice crystal field.(5) The Coulombic interaction generates the ^{2s+1}L terms which are generally separated by thousands of cm^{-1}. The spin-orbit coupling splits the total angular momentum J states. The influence of the crystal field

then splits the Stark manifolds into their fine structure (Stark levels) with a degeneracy equal to 2J+1(5). The strength of the crystal field interaction with the dopant ion determines the energy spacing of the Stark levels within a given manifold. Most often, materials grown using rare-earth metals with a +3 charge experience a weak interaction with the crystal field due to the inner 4f electrons being shielded from the surrounding environment (host lattice) by the outer 5s and 5p electrons.(3,5,6) Consequently, the energy spacing between Stark levels is small, typically on the order of 10-100 cm^{-1}. Often, many different lattice materials are grown with the same dopant ion. This is done so that small energy shifts of the Stark levels may be accomplished leading to a laser material that may be employed in a desired application.

The crystal field is also responsible for inducing oscillator strength into specific transitions. The magnitude of the oscillator strength reveals the probability of radiative energy transfer between given Stark levels.

Dopant Ion Concentrations

Spectroscopic analysis of emission from the material as dopant concentration is varied over a large gradient is required in order to investigate ion-ion interactions(3). An experiment performed by Zhekov, *et al.*(7), described the effects of varying the concentration of Er^{3+} ions doped into YAG. The authors found that the optimum amount of doped Er^{3+} was 15% when observing the IR fluorescence decay at approximately 6,000 cm^{-1} . At very low (0.5%) and very high (100%) amounts of Er^{3+} the experimental lifetime decreased dramatically from a maximum lifetime of 9 msec obtained at 6% Er^{3+} to 6.5 msec and 0.25 msec, respectively. These results were

confirmed by Shi, *et al.*(8) in a similar study. Similarly, Becker, *et al.*(9), as well as Armagan, *et al.*(10) showed that as the Tm^{3+} concentration in YAG was increased the lifetime of the experimental emission from the $^3H_4$ manifold near 780 nm to the $^3H_6$ ground state became significantly shorter.

When high dopant ion concentrations are used self-quenching becomes an issue of concern. Self-quenching, often called concentration quenching or cross-relaxation, is a non-radiative, resonant energy transfer that can depopulate the upper laser level and have a detrimental effect on the lasing process as in the case of Er^{3+}:YAG.(7,8) Self-quenching is due solely to dopant ion-dopant ion interactions. As the concentration of the dopant ion increases the ions become closer to each other spatially. It has been determined by Dexter, *et al.*(11), as well as, Inotaki and Hirayama(12), that this cross-relaxing quenching process is generally dominated by electric dipole-dipole interactions described by an R^{-6} distance dependence. The process may also be dependent on the energy of the exciting photons(8), as well as the temperature of the crystal.

Temperature Effects

Radiative and non-radiative emission lifetimes in Tm^{3+} doped laser materials are substantially affected by changes in temperature. Zvervev, *et al.*(13), observed that for Tm^{3+}:YAG as temperature was increased from 77 to 900 degrees K the experimental emission lifetime of the $^3F_4 \rightarrow {}^3H_6$ transition decreased from 8.5ms to 2.5ms. This effect was described as temperature quenching. The decrease in lifetime is due to an increase in the probability of stimulated nonradiative (vibronic) transitions that depopulate the upper-laser manifold of the material ($^3F_4$)(14). In effect, as temperature increases, the

non-radiative processes (phonons, eg.) that occur within a sample begin to dominate the radiative processes. It is known that non-radiative decay events, as well as their reliance on variance in temperature are determined by the size of the dopant ion and its symmetry within a lattice(15). Therefore, for Tm^{3+} doped into different lattices, lifetimes may decrease over a temperature gradient with varying degrees of magnitude. It should be noted that a decrease in fundamental lifetime did not occur until the temperature reached approximately 475 K. A similar trend has been observed for lasing output power in three Tm^{3+} doped materials. As the crystal temperature was raised from 258 to 303 K the output power in Tm:YAG, Tm:YLAG and Tm:LAG decreased 8%, 7% and 11%, respectively(16).

Based on theoretical calculations, Riseberg and Weber(5) have shown that as temperature is increased from 0 to 400 degrees K, the rate of non-radiative multiphonon emission increases substantially and varies depending on the number of phonons involved in the emission. This supports the theory that as temperature is increased non-radiative decay becomes very significant and can have a detrimental effect on radiative energy transfer.

Thulium

Tm^{3+} has been used as an activator ion in laser materials for approximately 30 years(1,2) and is the main ion of focus in our studies. Tm^{3+} follows a quasi-four-level laser operating scheme with one metastable state when introduced as the dopant ion in YAG, where one Y^{3+} ion is replaced by one Tm^{3+} ion(3,17).

Most often, the $^3H_4$ Stark manifold near 12,800 cm^{-1} is pumped to initiate the energy transfer process where simultaneous radiative and non-radiative emissions occur from the $^3H_4$ manifold to the $^3H_5$ manifold. At sufficiently large Tm^{3+} concentrations, non-radiative energy decay to the $^3F_4$ manifold readily occurs(18). Non-radiative multiphonon emission dominates the energy decay from the $^3H_5$ to the $^3F_4$ manifold because of the small energy gap (2,000 cm^{-1}). This is followed by a long-lived radiatively dominated emission to the $^3H_6$ ground state (see Figure 2). These emission

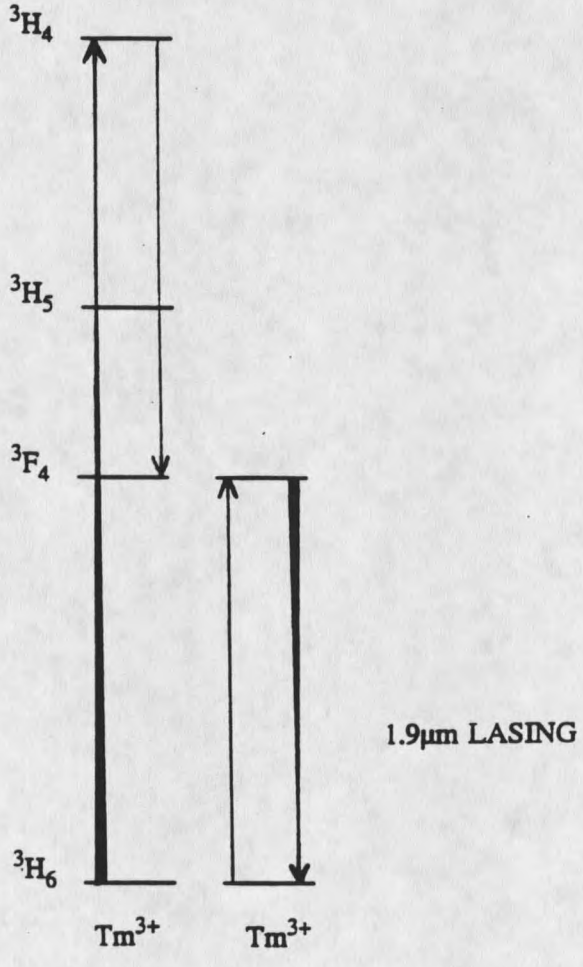

Figure 2. 2μm lasing operation scheme for Tm^{3+}:YAG.

processes have been studied previously(1,9,18,20,21).

An additional and very important photophysical process that occurs in Tm^{3+}:YAG is also shown in Figure 2. This is the cross-relaxation process which occurs due to the resonance caused by the energy gap between the $^3F_4$-$^3H_4$ and $^3F_4$-$^3H_6$ manifolds. At large enough dopant-ion concentrations the emission from the $^3H_4$ to the $^3F_4$ manifold of one Tm^{3+} is quenched by a neighboring Tm^{3+} within the lattice due to their proximity to one another(19). The cross-relaxation is not detrimental to the fundamental lasing transition because it aids in the population of the $^3F_4$ upper-laser manifold. This process is responsible for nearly doubling the pump quantum efficiency(20) and is important because losses in radiative emission from the $^3F_4$ manifold due to temperature increases within the sample can be avoided(9). The fundamental transition ($^3F_4 \rightarrow {}^3H_6$) in Tm^{3+} is of particular importance because water has absorption bands at this wavelength. A laser operating at this wavelength may be applied in studies of the environment, body tissues and remote sensing (LIDAR)(21).

Co-Doped Materials

Tm^{3+} may be introduced into various lattices with co-dopant ions such as Cr^{3+},Ho^{3+} and Er^{3+} with varying concentrations. Early studies by Johnson, *et al.*(1) have shown how co-dopant strategies can enhance laser performance. The IR emission from the $^3F_4$ manifold to the ground state near 5,200 cm^{-1} in 1 atomic % Tm^{3+}:YAG was enhanced by a factor of 40 by replacing 50% of the yttrium ions in the YAG matrix with erbium ions.

Most often, when Tm^{3+} is used in a co-doped laser material, its role is to serve