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
Montana State University
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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

by

Richard Charles Martoglio

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of a thesis submitted by

Richard Charles Martoglio

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.

Dr. Lee Spangler  
(Signature)  
8/15/97  
Date

Approved for the Department of Chemistry

Dr. David Dooley  
(Signature)  
8/15/97  
Date

Approved for the College of Graduate Studies

Dr. Robert Brown  
(Signature)  
8/15/97  
Date
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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 (Tm$^{3+}$) 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.
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$_3$Al$_5$O$_{12}$ 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 matrix and dopant materials be free of outside impurities 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 $^3\text{H}_4$ manifold near 780 nm to the $^3\text{H}_6$ 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. Zverev, 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 $^3\text{F}_4 \rightarrow ^3\text{H}_6$ 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 ($^3\text{F}_4$).(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 $^3\text{H}_4$ 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 $^3\text{H}_4$ manifold to the $^3\text{H}_5$ manifold. At sufficiently large Tm$^{3+}$ concentrations, non-radiative energy decay to the $^3\text{F}_4$ manifold readily occurs(18). Non-radiative multiphonon emission dominates the energy decay from the $^3\text{H}_5$ to the $^3\text{F}_4$ manifold because of the small energy gap (2,000 cm$^{-1}$). This is followed by a long-lived radiatively dominated emission to the $^3\text{H}_6$ ground state (see Figure 2). These emission

![Diagram showing energy levels and transitions](image)

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 $^{3}F_4-^{3}H_4$ and $^{3}F_4-^{3}H_6$ manifolds. At large enough dopant-ion concentrations the emission from the $^{3}H_4$ to the $^{3}F_4$ 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 $^{3}F_4$ 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 $^{3}F_4$ manifold due to temperature increases within the sample can be avoided(9). The fundamental transition ($^{3}F_4-^{3}H_6$) 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 $^{3}F_4$ 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
as an energy transfer medium. Several studies have described the use of Tm$^{3+}$ in YAG with Ho$^{3+}$ and, or Cr$^{3+}$(20,22-29). One possible operating scheme is illustrated in Figure 3. When a Cr$^{3+}$, Tm$^{3+}$, Ho$^{3+}$ co-doping scheme is employed, the Cr$^{3+}$ ion is typically excited at an energy of approximately 16,000 cm$^{-1}$. This is followed by non-radiative decay to the Cr$^{3+}$ $^2$E manifold where there is sufficient overlap with the $^3$H$_4$ manifold of Tm$^{3+}$. Energy is transferred to the $^3$H$_4$ manifold predominantly non-

![Figure 3. IR lasing operation scheme for CTH:YAG.](image)
radiatively. Just as in Tm$^{3+}$:YAG energy decays to the $^{3}F_{4}$ manifold and the cross-relaxation process in Tm$^{3+}$ leads to the formation of two $^{3}F_{4}$ states. Energy is then transferred from the $^{3}F_{4}$ states to the $^{5}I_{7}$ Stark manifold of Ho$^{3+}$ followed by radiative emission to the $^{5}I_{8}$ ground state.

It has been suggested that due to the inability to pump Tm$^{3+}$ and Ho$^{3+}$ efficiently with a broad-band source, Cr$^{3+}$ must be utilized as the excitation medium to initiate the energy transfer process(23). Using a transition metal as a dopant ion is convenient because they typically exhibit broad absorption features and absorb a large fraction of excitation energy which is then available for transfer to a co-doped ion. A simple demonstration can show this process indirectly. When broad-band light is shown onto Cr$^{3+}$:YAG red light can be observed at the edges of the crystal exhibiting the radiative emission from the $^{4}T_{2}$ manifold to the $^{4}A_{2}$ ground state. However, when broad-band light is shown onto a crystal containing both Cr$^{3+}$ and Tm$^{3+}$, red emission is not observed at the edge of the crystal. This is due to the fact that energy is being readily transferred to the Tm$^{3+}$ via Cr$^{3+}$ because of sufficient overlap between the Cr$^{3+}$ emission and the corresponding absorption bands of Tm$^{3+}$(22).

Generally, when these types of crystals are grown they contain all three dopant materials. This allows the user greater flexibility when deciding which operating scheme to exploit. For example, Cr$^{3+}$, which has a broad visible absorption, may be more easily pumped by a visible source, as opposed to the Tm$^{3+}$ ion. Consequently, due to the different excitation methods, and, in turn, slightly different energy transfer processes, observed emission intensities and lifetimes may deviate significantly. This may be
desirable depending on how the laser will be used. The materials described above are of interest for use in solid-state systems because of their extremely long radiative lifetimes in the IR. These long lifetimes might permit the storage of a large amount of energy which is beneficial for use in pulsed laser systems(20).
CHAPTER 2

TIME-RESOLVED FOURIER TRANSFORM SPECTROSCOPY

Background

Standard Fourier transform infrared (FT-IR) and Fourier transform visible spectroscopy (FT-VIS) have been used in many analytical studies for the determination of specific absorption wavelengths characteristic for a particular material. FT spectroscopy (FTS) became a confidently used and accepted analytical technique in the late 1960's due to previous findings made by Fellgett and Jaquinot, as well as, the availability of computers (quick data reduction) and helium-neon lasers (moving mirror monitoring)(30). FT-IR absorption spectroscopy is a powerful tool in the study of organic compounds. Through detailed analysis of standard samples, functional groups such as ketones, ethers, and amines have been "fingerprinted", that is, their spectra reveal characteristic absorption bands at certain frequencies and, also, a unique band structure which aids in the structural elucidation of molecules.

FTS has many advantages over other spectroscopic techniques. Fellgett determined that all of the components that make up a spectrum may be evaluated simultaneously. Due to this fact, the derivation of spectra using an FT spectroscopic
device is approximately *1000 times faster* than using a traditional spectrometer (31) due to the multiplex advantage. A short time later Jaquinot stated that an interferometer is relatively unlimited in the amount of radiation that may enter the instrument, hence the Jaquinot or throughput advantage.

Perhaps the only substantial disadvantage to using an FT interferometer is the initial investment made. Modern FT instruments are priced from approximately $20,000 to $200,000, or more in some cases. While the investment is substantial, it is believed that the efficiency of analysis will more than offset the initial monetary sacrifices.

**Step-Scan FTS Technique**

Temporal analysis of radiative emission can be accomplished through the use of time-resolved spectroscopy (TRS) via step-scan FT (FT-TRS). The first step-scan interferometer was developed in 1966 (32). Widespread use of FT-TRS was not seen until very recently in the late 1980’s and has only recently been applied to the analysis of laser materials (4, 33). A recent study performed in 1996 concentrated on studies of transient chemical reactions using FT-TRS (34).

In order to perform step-scan measurements the instrument must function differently than in the normal rapid-scan mode. In the rapid-scan mode of analysis simultaneous collection of all the frequencies of light present at a given time takes place (spectral multiplexing). The moving mirror of the Michelson interferometer changes positions very rapidly at a velocity determined by the user, typically about 40kHz. This presents a problem for FT-TRS because there is no consideration of events occurring
over time at every scheduled mirror position. As long as there exists a continuous emission, rapid-scan mode would suffice for frequency determination. Even when employing a modulated source, if the lifetime of the emission is sufficiently long-lived (>1-2ms), rapid-scan mode can characterize the frequency, but step-scan via FT-TRS is always required to characterize temporal events.

Temporal analysis is achieved by holding the moving mirror stationary at every mirror increment during data collection. In this way the spectral multiplexing can be separated from the time-based events that occur after pulsed excitation(35). In normal, rapid-scan FTS it is important to keep the moving mirror velocity constant while data are obtained, whereas, in step-scan FTS it is important to keep the moving mirror position constant to ensure accurately obtained information for Fourier transformation(35).

These requirements are shown in Figure 4. For the step-scan mode the moving mirror position is on the y-axis and the length of time (arbitrary units) the mirror is held at each position is on the x-axis. The length of time at each scheduled mirror position is determined by the duration (temporal resolution) and number of time intervals. Each vertical column contains the information needed to construct the single frequency interferogram at the corresponding time interval. It can be seen that a number of interferograms that contain time and intensity information will be assembled whose amplitude is decreasing over time. The waveforms will then be Fourier transformed to yield a FT-TRS spectrum. Figure 5 again shows the formation of each interferogram at every mirror position and conversion to the time-resolved spectrum.
Formation of the Interferogram

"RAPID SCAN"

- the instrument collects frequency information at certain mirror positions as it moves back and forth
- this information is digitized to yield the actual points that make up the interferogram
- the Fourier transform is then performed to yield the observed spectrum

"STEP-SCAN"

- this model assumes one frequency only

Figure 4. Formation of the interferogram in rapid-scan mode vs. step-scan mode.
Figure 5. Derivation of the time-resolved spectrum.
Normalization of FT-TRS and Inherent Spectral Noise

Upon examination of the FT-TRS spectra (Figure 6) one notices baseline noise which decreases proportionally with decreasing signal. This noise is due directly to pulse to pulse fluctuations in the pump laser output which are manifested in the emission from the sample material.

Figure 6 exhibits this noise for an emission in Tm$^{3+}$:YAG. The upper spectrum is obtained by exciting the sample continuously by 780 nm diode laser output. A relatively noise-free FT-TRS spectrum is obtained when no fluctuations in the laser pump power occur. By manually changing the pump power as the data is collected, noise is artificially created as seen in the lower spectrum. The noise is random in the energy regime, but shows consistency in intensity.

If we assume that a single frequency is being emitted and reaching the detector we can more easily see how this noise is created in the interferogram. If the emission is consistent from pulse to pulse a smooth single frequency interferogram is constructed as in Figures 4 and 5. When intensity fluctuations occur, significant amplitude differences occur at the points where data is obtained by the instrument which leads to the construction of a completely different interferogram comprised of several different frequencies, but still contains the emission frequency of interest. The ratio of the noise to the signal is constant over time which is evident in all of the FT-TRS spectra. This effect can be represented for a multi-frequency emission by comparing interferograms at a given time in the clean and noisy spectra as shown in Figure 7. The lower traces exhibit the difference between the magnitudes of the 2 interferograms and resultant
Figure 6. Generation of systematic noise in FT-TRS spectra.
Figure 7. Interferograms and corresponding spectra.
noise upon Fourier transformation. The process of distributing the noise throughout the spectral region of study is perhaps a benefit, that is, the noise typically does not occur exclusively where emission signal is present. Consequently, for the more intense emission processes, useful information regarding emission lifetimes and frequencies may be obtained when there are significant pulse to pulse fluctuations. However, the ability to correct the interferogram at each time by considering a corresponding reference interferogram would allow for much clearer FT-TRS spectra and in turn more accurate integrations, emission trace extracts and lifetime determinations. IR normalization may require an additional detector for this region. Currently, this is a financial limitation which can be overcome in the near future.

FT-TRS Nomenclature

FT-TRS measurements performed in this study are described by specific nomenclature that corresponds to experimental parameters and spectral interpretation. The nomenclature is derived from the manufacturer software which controls the system. The following is a discussion of the terms used in FT-TRS. Figure 8 will be used as the reference step-scan spectrum for this discussion.

Each emission trace (spectrum) represents a "time slice" or more descriptively, the time interval between data sampling at each mirror position (temporal resolution). There is no theoretical limit on the number of time slices that may be taken for an experiment, however we are limited by computer datafile space. The spectrum in Figure 8 contains 200 time slices with 500 μsec temporal resolution. The magnitude of the
temporal resolution paired with the number of time slices determines the length of emission sampling (100,000 μsec). The signal to noise (S/N) ratio can be improved by a signal averaging technique known as co-adding. If 20 co-additions are selected the instrument will hold the moving mirror at a given position for 20 laser pulses before moving to the next mirror position. Consequently, 20 values that describe emission intensity and mirror position for each time slice will be obtained and averaged yielding a single point in each interferogram.

The IFS 66 has 2 different modes for acquiring time-resolved data. The internal ADC (IADC) mode is a 16-bit analog to digital converter that is used for studying emission events which occur in the μsec to msec regime. The maximum temporal resolution for IADC mode is 5 μsec. The electronics for IADC can process signals from
the detector with voltages that range from 0 to \( \pm 15 \) V. Typically, 10 to 12 V from the detector is rarely exceeded and no adjustments (aperaturing, for example) to the experimental design are necessary to ensure that the detector is not being saturated due to sample emission alone. The PAD82 mode uses a faster 8-bit analog to digital converter and has a maximum temporal resolution of 5 nsec and a minimum resolution of 8 \( \mu \)sec. However, the electronics that govern PAD82 require an input voltage from the detector of less than +1 V and more than 0 V. If the voltage does not fall within this specified range a usable, coherent spectrum cannot be obtained and, therefore, a more cautious approach to obtaining data is required.
CHAPTER 3

EXPERIMENTAL PROCEDURE

Aspects of experimental design, apparatuses, samples and procedures are outlined and presented in this chapter. Also, the stepwise method of laser material analysis is described, as well as modifications to the interferometer and the integration of light collecting optics to the experimental setup.

Sample Laser Materials

All crystalline laser materials used to acquire experimental results were obtained from Scientific Materials Corporation located in Bozeman, Montana. The materials used were of shown to be of sufficient purity through absorption measurements and in good physical condition.

The concentrations of the dopant ion in the respective samples are as follows: 5 Tm$^{3+}$ doped YAG crystals at 0.1, 0.25, 2.4, 4.0 and 5.2 atomic percent, 2 Tm$^{3+}$ doped YAlO$_3$ (YALO) crystals at 0.1 and 4 atomic percent, 2 Tm$^{3+}$ doped Y$_2$SiO$_5$ (YSO) crystals at 0.1 and 3 atomic percent, 2 Tm$^{3+}$ doped Y$_2$O$_3$ (YO) crystals at 0.1 and 3 atomic percent, and 1 Tm$^{3+}$ doped Lu$_3$Al$_5$O$_{12}$ (LAG) crystal at 2 atomic percent. In
each case, Tm$^{3+}$ substitutes for yttrium or lutetium.

The samples are generally rectangular or circular ranging in size from quarter to a sixteenth of an inch in thickness and an eighth of an inch to 1 inch in diameter or length. Most of the samples have polished edges. The Tm$^{3+}$:YO samples are a noted exception. Due to the complexity of the growing process, these samples are very small and lack uniformity. The samples are cleaned with high purity acetone prior to analysis to remove residues that may have accumulated on the surfaces.

**Experimental Apparatus**

The apparatus used for both absorption and emission experiments is shown in Figure 9. In all experiments a Bruker Instruments IFS 66 step-scan interferometer was used to obtain and analyze visible and infrared radiation (see Figure 10).

The IFS 66 consists of a Michelson interferometer using a HeNe laser for internal mirror positional referencing. The reference wavelength is 15,879.8 cm$^{-1}$ (632.99 nm). The maximum resolution for the IFS 66 is 0.1 cm$^{-1}$. The beamsplitters (BS, Figure 10) used for visible and infrared studies are respectively, quartz and calcium fluoride (CaF$_2$). Spectral ranges for these beamsplitter/detector combinations are shown in Figure 11. The device used for infrared measurements is a liquid nitrogen cooled Graseby-Specac indium antimonide (InSb) detector (D2, Figure 10) coupled with an external pre-amplifier that has a 120 nsec risetime and 60 nsec recovery time. The InSb/CaF$_2$ detector/beamsplitter combination is capable of detecting emitting wavelengths from nearly 16,000-2,000 cm$^{-1}$. The detector used for visible measurements is a silicon diode.
Figure 9. Apparatus for absorption and emission studies.
Figure 10. The Bruker IFS 66 step-scan interferometer.
Figure 11. Spectra for detector/beamsplitter combinations.
(D1, Figure 10) obtained from Bruker Instruments. This diode has a built-in preamplifier with a rise and recovery time of 15 and 25 nsec, respectively. Rise and recovery time measurements were performed by passing a scattered laser pulse of known wavelength through the interferometer and then measuring the temporal response of the detector in relation to the pulse. The Si/Quartz detector/beamsplitter combination can detect radiative emission from nearly 27,000-9,000 cm$^{-1}$.

All absorption measurements were made using a tungsten lamp (S1, Figure 10) as the source of visible and IR radiation.

The $^3H_4$ Stark manifold of Tm$^{3+}$ readily absorbs radiation supplied by an Opto Power Corporation CW diode laser operating near 12,800 cm$^{-1}$ (see Figure 2). Initial FT-TRS experiments were performed by modulating the diode output beam with a PTI mechanical chopper that, at 100 Hz, provided a pulse of 1 msec duration with relatively long rise and fall times. The beam diameter was 0.25 inches at the sample and was not focused.

A shorter pulse was necessary to more accurately model crystal behavior within an actual operating laser system. Currently, a Coherent Infinity 40-100 series Nd:YAG laser operating at the third harmonic (355 nm) is used to pump a Lambda-Physik OPO which, in turn can generate wavelengths of 400 nm to nearly 2.5 $\mu$m. The Infinity is capable of operating at 0.1 to 100 Hz repetition rate with a pulse duration of approximately 8nsec. The third harmonic's output intensity at 10 Hz repetition and 425 mJ fundamental (1064 nm) is approximately 2.0 W and at a higher repetition rate of 100 Hz and 375 mJ fundamental intensity the 355 nm output is approximately 16 W. The
linewidth of the 355 nm output is typically less than 0.008 cm\(^{-1}\). The 355 nm beam is
turned by two dichroic mirrors obtained from Newport Corporation into the Lambda-
Physik Scanmate OPO. Amplified tunable laser output is then achieved through the use
of the Scanmate. The "signal" (410-710 nm) and "idler" (710-2446 nm) beams allow for
excitation over a broad wavelength region. The signal beam for this system is typically
10 times more powerful than the idler, 20 to 30 mJ/pulse compared to 2.0 to 5.0
mJ/pulse. Filters supplied by Lambda-Physik allow the user to select the signal or idler
for sample excitation. An RG715 filter is nearly 0% transmissive to wavelengths shorter
than 714 nm (14,000 cm\(^{-1}\)) (see Figure 12) allowing for elimination of the signal output
from many dyes. An KG3 filter is nearly 0% transmissive to IR wavelengths below
12,000 cm\(^{-1}\) in energy, but passes visible radiation.

The output of the OPO is immediately turned by a fused silica prism obtained
from Virgo Optics and focused to a beam diameter of approximately 2 mm at the sample
by an f/12 lens. Samples are typically placed at the focal point incident to the beam at
an edge to allow for maximum absorption of pump light and to minimize the effects of
self-absorption or radiation trapping. Light emitting from the edge of the sample is then
collected. Radiation trapping within a material can change the bandshape of the observed
emission spectra and also lead to spurious long lifetimes(36). The pump beam must
also contact the volume of the material that is at the focal point, again to diminish the
self-absorption process.

Light emission is collected and focused into the interferometer by an off-axis
paraboloid mirror (f number=4.5) obtained from Bruker Instruments. Light enters the
Figure 12. Spectra for KG3 and RG715 optical filters.
instrument through the entrance at E1, is turned at the internal flipping mirror of the interferometer and proceeds through the instrument to the corresponding detector. For IR measurements performed in the 9,000-2,000 cm\(^{-1}\) range an Si filter is placed at E1. This filter eliminates nearly 100% of wavelengths less than 9,000 cm\(^{-1}\) and is approximately 50% transmissive to wavelengths greater than 9,000 cm\(^{-1}\). The RG715 filter is placed at I1 if the visible OPO beam is being used for excitation to eliminate visible wavelengths prior to reaching the InSb detector. Measurements performed from 14,000-2,000 cm\(^{-1}\) requires that only the RG715 filter be placed at E1.

Synchronization of the moving mirror to the excitation pulse is accomplished by triggering the IFS with TTL signals provided directly from the Infinity pump laser.

**The Material Characterization Process**

Upon receiving a sample laser material a series of steps are followed for complete characterization. Absorption spectra in both the visible and IR regions of the wavelength spectrum are obtained with sufficient resolution (<2.0 cm\(^{-1}\)) and signal averaging (>1000 scans). This allows the user to determine which Stark levels may be pumped to initiate energy transfer.

It is also beneficial to next obtain a continuous emission spectrum of sufficient resolution (typically, 8.0 cm\(^{-1}\)) if the sample possesses an absorption band that may be excited by an available continuous source. This allows identification of the strongest emission band(s). It may then be assumed that this emission has a relatively long lifetime (>5\(\mu\)sec). This determination is important because the instrument uses the two
aforementioned methods for acquiring FT-TRS data.

The last step of the characterization is finding the lifetimes of the radiative energy transfer processes. Generally, IADC is performed first and then temporal resolution is increased to "see" the faster processes that are occurring in the material and PAD82 becomes necessary for analysis.
CHAPTER 4

EXPERIMENTAL RESULTS

In this section data will be presented and briefly interpreted. Chapter 5 contains detailed discussion of the FT-TRS data, as well as the model generated to describe the kinetics of the materials studied and the theory upon which the model is based.

Absorption Spectra

Absorption spectra and energy levels for Tm$^{3+}$ doped into various materials at liquid helium or liquid nitrogen temperatures have been reported previously (37-41) and are of importance when making room temperature assignments. All absorption measurements in this study were performed at room temperature. Typically, absorption measurements made with the IFS 66 are resolved to $2.0 \text{ cm}^{-1}$. The number of scans performed (signal averaging) varies from 64 to 4096 depending on the desired S/N ratio. For Tm$^{3+}$:YAG materials, a sample of undoped YAG is employed for the background measurement with which the sample measurement is divided by to eliminate the spectral contributions caused by entities other than the Tm$^{3+}$ ion. A tungsten source was used for measurements for both the IR region (9,000 to 2,000 $\text{ cm}^{-1}$) and the visible region
The observation of phonon absorption due to the crystalline lattice was not possible as these absorptions most often occur below 2,000 cm\(^{-1}\)\(^{(37)}\). The decrease in detector/beam splitter response drastically diminishes the S/N ratio outside of the stated wavelength regions.

Absorption measurements were performed on all samples, but only the spectra for 4\% Tm\(^{3+}\):YAG, 4\% Tm\(^{3+}\):YALO, 3\% Tm\(^{3+}\):YSO and 3\% Tm\(^{3+}\):YO are shown because spectra for a given host crystal exhibit similar absorption features regardless of concentration. A correction was performed to eliminate baseline deviations across the spectrum so that the magnitudes of the absorptions could be compared between manifolds.

Absorption spectra are presented in Figures 13 through 17. The IR absorption spectrum for each sample is shown prior to the visible spectrum. The spectra exhibit the characteristic sharp line shapes of f electron transitions in rare-earth doped laser materials. Comparing the absorption spectra for Tm\(^{3+}\):YAG to data obtained by Gruber, et al.\(^{(37)}\) at 90 K reveals small shifts in maximum absorption energies. Gruber, et al.\(^{(37)}\) report the energies for absorption maxima of the \(^{1}G_{4}\), \(^{3}F_{3}\), \(^{3}H_{4}\), and \(^{3}F_{4}\) manifolds to be 21,757 cm\(^{-1}\), 14,679 cm\(^{-1}\), 12,720 cm\(^{-1}\) and 5,901 cm\(^{-1}\), respectively. These room temperature measurements show maxima occurring at 21,742 cm\(^{-1}\), 14,680 cm\(^{-1}\), 12,724 cm\(^{-1}\) and 6,146 cm\(^{-1}\) for the same manifolds. The room temperature spectra are considerably less resolved than the spectra obtained at low temperatures. Spectral broadening can be attributed to the upper levels of the ground state manifold being thermally populated leading to a larger number of absorption pathways from the
Figure 13. IR (top) and visible absorption spectra for Tm$^{3+}$:YAG.
Figure 14. IR (top) and visible absorption spectra for Tm$^{3+}$:LAG.
Figure 15. IR (top) and visible absorption spectra for Tm$^{3+}$:YALO.
Figure 16. IR (top) and visible absorption spectra for Tm$^{3+}$:YSO.
Figure 17. IR (top) and visible absorption spectra for $\text{Tm}^{3+}:\text{YO}$. 
ground state manifold to excited state manifolds. Also, inhomogeneous line broadening due to small spatial deviations of the Tm$^{3+}$ ion from site to site within the crystalline lattice may also contribute to spectral broadening (3,6). The absorption features near 22,000 cm$^{-1}$ of the 1G$_4$ manifold show diminished S/N compared to the remainder of the visible spectrum due to the aforementioned decrease of the instrument response. A larger number of scans may enhance the absorption features. Shifts in the maximum absorption values for each manifold vary approximately 100 to 400 cm$^{-1}$ as the host lattice is varied. The sharp peak centered at 15,798 cm$^{-1}$ in the visible spectra is the HeNe laser used for monitoring the moving mirror in the interferometer.

**Continuous Fluorescence Spectra**

Fluorescence spectra for various transitions at many temperatures for several Tm$^{3+}$ doped laser materials have been presented previously (1,37,39,40,42,43). The data obtained in this study are in agreement with the literature.

Tm$^{3+}$ is most often excited continuously by pumping the 1D$_2$ manifold (29,000 cm$^{-1}$), the 1G$_4$ manifold (21,700 cm$^{-1}$) or the 3H$_4$ manifold (12,800 cm$^{-1}$). A GaAlAs diode laser which operates continuously at approximately 12,820 cm$^{-1}$ (780 nm) and provides nearly 2W of continuous lasing power was used as the excitation source when observing IR emission. Off-resonance excitation of the 1G$_4$ Stark manifold was accomplished through the use of the 454 nm line of a continous Ar ion laser. Excitation at this wavelength allowed for the observation of visible fluorescence.

Continuous fluorescence spectra are typically resolved to 16 cm$^{-1}$ and 64 to 1024
scans are performed for signal averaging. Filters were rarely needed because the scattered laser light was not intense enough to saturate the detector. All emission experiments were performed at room temperature. The samples were excited by pumping at the edge of the face and the resulting emission was collected from the nearest side of the sample to minimize self-absorption processes.

Figures 18 through 22 (pgs. 42-46) show the fluorescence spectra which exhibit transitions from the $^1G_4$, $^3H_4$ and the $^3F_4$ manifolds to the $^3H_6$ ground state and other manifolds of higher energy. The emission frequency on the x-axis is in units of cm$^{-1}$ and the intensity units on the y-axis are arbitrary. The spectra have been corrected for variations in the instrument response over the entire spectrum. The tungsten filament used operates at a temperature of 3500 K. A blackbody calculation was performed and factored into the instrument response to eliminate the source's contribution to the response curve. The IR spectrum is presented prior to the visible spectrum for each sample. Again, only one set of spectra are shown for Tm$^{3+}$:YAG, YALO, YSO and YO.

Comparing the spectra, Tm$^{3+}$:YALO, Tm$^{3+}$:YSO and Tm$^{3+}$:YO exhibit relatively broad band-shapes and unresolved line-shapes, especially in the IR region. The spectra for Tm$^{3+}$:YAG and Tm$^{3+}$:LAG exhibit a much sharper line-shape in both the IR and visible spectral regions, however, all of the emission spectra are thermally broadened to a certain extent. The additional sharp line features in the visible spectra are caused by interference from the power supply of the Ar$^+$ source.
Figure 18. IR (top) and visible continuous emission spectra for Tm$^{3+}$:YAG.
Figure 19. IR (top) and visible continuous emission spectra for Tm$^{3+}$:LAG.
Figure 20. IR (top) and visible continuous emission spectra for Tm$^{3+}$:YALO.
Figure 21. IR (top) and visible continuous emission spectra for Tm\(^{3+}\):YSO.
Figure 22. IR (top) and visible continuous emission spectra for Tm$^{3+}$:YO.
The FT-TRS data is presented for each material or set of materials at every excitation wavelength used. In all plots, the x-axis is frequency in cm\(^{-1}\), emission intensity is on the vertical y-axis and time (increasing from front to rear, unless noted) is on the z-axis. A brief summary of the experimental parameters will be given for each material due to subtle differences in data acquisition. The spectra have not been corrected for differences in the response curves for the visible and infrared spectral regions. Experimentally determined lifetimes are presented in Tables I and II at the conclusion of this chapter.

**Excitation Via the \(^3\)H\(_4\) Manifold**

\textbf{Tm}^{3+}:YAG

Figure 23 shows the time-resolved fluorescence of the \(3F_4\rightarrow3H_6\) fundamental transition of 0.25 at.\% Tm\(^{3+}\):YAG. Each Tm\(^{3+}\) doped YAG sample was excited at 12,800 cm\(^{-1}\) (781.25 nm), using the idler OPO output, pumping the \(^3\)H\(_4\) manifold at either 10 or 15 Hz repetition rate. Idler output power for these experiments is on the order of 5 mJ/pulse. The interferometer was triggered on the positive edge of the TTL pulse from the Infinity system and no delays were used. Typically, for higher temporal resolution experiments (< 20 \(\mu\)sec) the IFS 66 is triggered prior to the laser pulse to view one or two traces before excitation, however this is impractical for the longer experiments. The RG715 filter was used inside the OPO cavity to eliminate the signal wavelength and an Si filter was placed inside the interferometer to cut wavelengths
greater than 9,000 cm$^{-1}$ in energy when desired. The slower 16 bit recorder was used for these experiments and the wavelength region from 9,000-2,000 cm$^{-1}$ was studied. Temporal resolution for these experiments was 500 µsec with 200 time slices (sampling) and 10 co-additions (signal averaging) performed. This yields a total sampling time of 100 msec. Generally, a sampling time that is at least 4 to 5 times longer than the lifetime of the transition of interest is used. The $^3F_4\rightarrow^3H_6$ transition is known to be approximately 10-12 msec in duration$^{(1,44,45)}$ and, therefore a laser repetiton rate of 20 Hz would be the maximum that would allow total relaxation to the ground state between pulses. The bandshape is relatively consistent between the 5 samples and

Figure 23. Time-resolved IR fluorescence spectrum for 0.25% Tm$^{3+}$:YAG. 400 µsec time resolution, 200 time slices, 10 co-adds.
exhibits the well-known 2μm transition, hence only one step-scan spectrum is shown for this process.

An integration of this transition over time yields a representative trace that appears to be purely exponential in behavior (see Figure 24). All trace plots are baseline corrected and normalized to a maximum intensity value of 1.0 for comparison between spectra.

The lifetime of the fundamental transition calculated from this data ranges from 11.21 to 11.79 msec with no observable dependence on the concentration of the dopant ion. Two additional bands centered at approximately 6,800 cm\(^{-1}\) and 4,300 cm\(^{-1}\) are readily observed and can be attributed to transitions originating from the \(^3\)H\(_4\) pump manifold. Increasing the time resolution was necessary to characterize the lifetimes of

![Figure 24. Decay of the \(^3\)F\(_4\)→\(^3\)H\(_6\) transition for the 0.25% Tm\(^3^+\):YAG sample.](image)
these faster emission processes. Inspecting Figure 25, one can see four emission bands centered at 12,700, 6,800, 5,500 (rising) and 4,300 cm\(^{-1}\). Experimental conditions were similar to the longer time-based experiment except that a Si filter was not used and a wavelength range of 15,750 - 2,000 cm\(^{-1}\) was studied. The 16 bit recorder was used for this experiment where the time resolution was 5 to 20 µsec with 200 time slices and 20 coadds (signal averaging) which yields 10 msec of total acquisition time. The faster 8 bit recorder was used for 5.25% Tm\(^{3+}\) where the temporal resolution was 1 µsec.

The emission band centered at about 6,800 cm\(^{-1}\) has been assigned to the \(^3\)H\(_4\)\(\rightarrow\)\(^3\)F\(_4\) transition. The weak band centered at about 4,300 cm\(^{-1}\) is the \(^3\)H\(_4\)\(\rightarrow\)\(^3\)H\(_5\) transition. An additional band centered at around 12,700 cm\(^{-1}\) is the \(^3\)H\(_4\)\(\rightarrow\)\(^3\)H\(_6\) transition. This band

---

**Figure 25.** Time-resolved IR fluorescence spectrum for 0.25% Tm\(^{3+}\):YAG. 20 µsec time resolution, 200 time slices and 20 co-adds.
appears to be relatively weak in comparison to the 6,800 cm\(^{-1}\) transition, however, the instrument response in this spectral region is quite small in comparison to the mid-IR region. The rising band centered at approximately 5,500 cm\(^{-1}\) shows the slow population of the upper-manifold of the fundamental \(3\text{F}_4 \rightarrow 3\text{H}_6\) transition. The decay process at 6,800 cm\(^{-1}\) is seen comparatively for 0.1\%, 0.25\%, 2.4\%, 4\% and 5.25\% Tm\(^{3+}\):YAG in Figure 26. Again, the emission bands appear similar in structure and location.

![Graph](image.png)

**Figure 26.** Decay of the \(3\text{H}_4 \rightarrow 3\text{F}_4\) transition at 6,800 cm\(^{-1}\) for the 5 Tm\(^{3+}\):YAG samples.

A noticeable difference is observed in the decay of the bands at 6,800 cm\(^{-1}\) and 4,300 cm\(^{-1}\). The decay is much faster for the 2.4\% sample and, in turn, even more rapid for the 5.25\% sample. The experimental lifetime for the 0.1\% and 0.25\% samples calculated from a single exponential fit are 500 \(\mu\)sec and 490 \(\mu\)sec, respectively. At 2.4\% Tm\(^{3+}\) the trace exhibits a fast non-exponential decay at early times becoming
exponential at longer times. It is believed that the decrease in the experimental emission lifetime from the $^3H_4$ manifold is due directly to concentration quenching. This effect has been previously observed by Becker, et al.(9) and Armagan, et al.(10) in Tm$^{3+}$:YAG. Approximate 1/e lifetimes of the $^3H_4$ decay for the 2.4%, 4% and 5.25% are 75 $\mu$s, 35 $\mu$s and 12 $\mu$s. The non-exponentiality of the decay curves for the higher concentrated samples can be shown by plotting the log of the intensity versus time shown in Figure 27. The rising population for the fundamental transition exhibits a

![Figure 27](image)

Figure 27. Log of intensity vs. time for the decay of the $^3H_4 \rightarrow ^3F_4$ transition at 6,800 cm$^{-1}$ for the 5 Tm$^{3+}$:YAG samples.

nearly identical trend as seen in Figure 28 where normalized intensity is plotted versus time.

It was believed that increasing the temporal resolution to 20 nsec would allow for the observance of the population for the transitions at 6,800 cm$^{-1}$ and 4,300 cm$^{-1}$ (see
Figure 28. Population of the $^{3}F_4 \rightarrow ^{3}H_6$ fundamental IR transition for the 5 Tm$^{3+}$:YAG samples.

Figure 25, page 53) for 0.25% Tm$^{3+}$:YAG. An Si filter was used to enhance the S/N ratio but all other experimental parameters were similar to the previous IR studies performed at less temporal resolution. The spectrum reveals that the risetime is in fact greater than the 180 nsec instrument response time and is shown comparatively for the 0.25% (open circles) and the 2.4% samples in Figure 29. The risetime of the other YAG samples could not be measured. Two possible explanations for this behavior are presented in Chapter 5.

**Tm$^{3+}$:YALO**

Experiments performed for Tm$^{3+}$:YAG were duplicated for the 0.1% and 4% Tm$^{3+}$:YALO samples. Exceptions in the experimental process include the pump wavelength and the repetition rate. A pump energy of 12,599 cm$^{-1}$ (793.7 nm) was used
Figure 29. Population of the $^3H_4 \rightarrow ^3F_4$ transition at 6,800 cm$^{-1}$ for 0.25% Tm$^{3+}$:YAG.

operating at 20 Hz. Figure 30 shows the $^3F_4 \rightarrow ^3H_6$ fundamental emission for 0.1% Tm$^{3+}$:YALO. The bandshape is consistent to that obtained via continuous excitation and the decay appears to be purely exponential in behavior (see Figure 31). The experimental lifetime obtained for the 0.1% sample was 5.18 msec and the lifetime for the 4% sample was 5.16 msec. Again two additional bands are observed at approximately 6,800 cm$^{-1}$ and 4,000 cm$^{-1}$. Upon removing the Si filter and examining a wavelength region of 15,750 - 2,000 cm$^{-1}$ four emission bands are readily observed as in YAG and are assigned to the same transitions as those for Tm$^{3+}$:YAG.

Integrating the $^3H_4 \rightarrow ^3F_4$ transition centered at 6,800 cm$^{-1}$ for the 0.1% and 4% samples yields the two distinctly different log curves shown in Figure 32. The experimental lifetime of this transition for the 0.1% sample is 630 $\mu$sec derived from
Figure 30. Time-resolved fluorescence spectrum for 0.1% Tm$^{3+}$:YALO. 250 μsec time resolution, 200 time slices, 10 co-adds.

Figure 31. Decay of the $^3F_4 \rightarrow ^3H_6$ transition for 0.1% Tm$^{3+}$:YALO.
fitting the decay to a single exponential function. A significant decrease in the experimental lifetime is observed and deviation from an purely exponential decay at 4% is also evident. The decrease in the lifetime is again believed to be due to the process of concentration quenching. The 1/e lifetime for the experimental decay from the $^3H_4$ manifold of the 4% sample is on the order of 12 µsec.

The rise of the fundamental transition exhibits behavior similar to that of the radiative decay from the $^3H_4$ manifold and is shown on the following page in Figure 33.

**Tm$^{3+}$: YSO**

Excitation wavelengths of 12,955 cm$^{-1}$ (771.90 nm) and 13,076 cm$^{-1}$ (764.75 cm$^{-1}$) were used to pump the Tm$^{3+}$: YSO samples. The experimental parameters used for the YAG and YALO samples describe the parameters employed here. Pump laser
repetition rates ranged from 20-25 Hz.

Integrated traces derived from the $^3F_4 \rightarrow ^3H_6$ fundamental transition are presented in Figure 34. The decay appears to be exponential in behavior and ranges in lifetime from 1.677 to 1.786 msec for 3% and 0.1% Tm$^{3+}$, respectively.

Increasing the temporal resolution allowed for observation of the faster radiative decay processes that occur after excitation. Integrated trace log curves for the $^3H_4 \rightarrow ^3F_4$ transition for the 2 samples are shown in Figure 35. The decay for the 3% sample could not be described by a single exponential function. 1/e lifetimes for the decay from the $^3H_4$ manifold in these 2 materials range from 10 to 140 µsec for 3% and 0.1% Tm$^{3+}$, respectively.
Figure 34. Decay of the $^3F_4 \rightarrow ^3H_6$ fundamental transition for Tm$^{3+}$:YSO.

Figure 35. Log of intensity versus time for the decay of the $^3H_4 \rightarrow ^3F_4$ transition at 6,800 cm$^{-1}$ for Tm$^{3+}$:YSO.
Tm$^{3+}$:YO

Tm$^{3+}$:YO was excited at 12,893 cm$^{-1}$ at 20 Hz or 25 Hz. The Tm$^{3+}$:YO samples exhibit exponential behavior for the $^3F_4 \rightarrow ^3H_6$ transition. The decay for this transition is shown in Figure 36. The 1/e lifetimes are 4.1 and 4.3 msec for the 0.1 and 3% samples, respectively. This difference in experimental lifetimes of this transition is believed to be due to a signal to noise error and not to the concentration differences of the 2 samples. Increasing the temporal resolution to 10 µsec allowed for the determination of the $^3H_4$ decay lifetime. The experimental lifetime decreases from 380 µsec to nearly 13 µsec from 0.1% to 3% Tm$^{3+}$ as shown in the log plot in Figure 37 on the next page.
Figure 37. Log of intensity versus time for the decay of the $^3H_4 \rightarrow ^3F_4$ transition at 6,500 cm$^{-1}$ for Tm$^{3+}$:YO.

**Tm$^{3+}$:LAG**

The 2% Tm$^{3+}$:LAG sample was excited at 12,800 cm$^{-1}$ at a pump laser repetition rate of 15 Hz. The lifetime of the fundamental transition was exponential in behavior with a lifetime of 11.230 msec. The decay from the $^3H_4$ manifold was again non-exponential with an $1/e$ lifetime of 115 $\mu$sec.

**Excitation Via the $^1G_4$ Manifold**

**Tm$^{3+}$:YAG**

All YAG samples were excited using 21,741 cm$^{-1}$ signal OPO output. Earlier experiments performed using the Coumarin 2 dye to generate this excitation energy required a pump laser repetition rate of 50 Hz to provide stable lasing output which in turn allowed for enhanced S/N. This repetition rate is most likely too fast to ensure
accurate lifetime determinations due to energy population residing in the upper manifolds when the sample is re-excited by the next pulse. Even so, it is still possible to observe trends in the experimental decay and locate new radiative processes occurring as the material is excited at increasing frequencies. Due to recent improvements in the pump laser output efficiency, studies have been performed at slower pump repetition rates (15 to 20 Hz) specifically for the 0.1%, 0.25% and 2.4% samples.

Two current limitations make visible studies a difficult task. The first is the inability to perform FT-TRS measurements on both "sides" of the HeNe reference frequency (15,798 cm\(^{-1}\)) simultaneously. Secondly, the Si diode detector employed is easily saturated by the excitation pulse and consequently a poor S/N ratio results. Due to these limitations a red pass filter or RG715 filter which eliminates energy of greater than 14,000 cm\(^{-1}\) before reaching the detector was employed. Also, the InSb detector was used in combination with either the CaF\(_2\) or quartz beamsplitter to study an energy region of 15,750 - 2,000 cm\(^{-1}\) or 14,000 - 2,000 cm\(^{-1}\) depending on which filter was used. The quartz beamsplitter allows for enhanced response in the red, but diminishes substantially in the IR spectral region.

Figure 38 (pg. 65) shows trace extracts 20 μsec after excitation at 12,800 cm\(^{-1}\) (upper spectrum) and 21,741 cm\(^{-1}\) for the 0.25% Tm\(^{3+}\):YAG sample. Several differences are immediately evident. There are overlapping radiative decay processes which occur at approximately 6,100 cm\(^{-1}\) and 12,500 cm\(^{-1}\). The 6,100 cm\(^{-1}\) decay process may be attributed to either the \(^1\)G\(_4\)→\(^3\)F\(_2\) transition or possibly the \(^3\)F\(_3\)→\(^3\)H\(_5\) transition. The latter of these is unlikely due to the proximity (1,800 cm\(^{-1}\)) of the \(^3\)H\(_4\)
Figure 38. Extracts at 20 μsec after red (upper) and blue excitation for 0.25% Tm$^{3+}$:YAG.
manifold to the $^3F_3$ manifold where the decay is predominantly phonon dominated. The overlap at 12,500 cm$^{-1}$ is most likely due to radiative emission from the $^1G_4$ manifold to the $^3H_5$ manifold. An additional emission band centered at 8,250 cm$^{-1}$ is assigned to the $^1G_4 \rightarrow ^3H_4$ transition. Upon closer examination of the lower spectrum a very weak band located at about 3,400 cm$^{-1}$ is seen. At this time it is unclear what causes this emission. Based on the absorption spectra, the energy of the assigned transitions are slightly less than the energy separation between the manifolds where the emissions occur. It is, therefore believed that these additional emission processes are made possible by phonon assisted transfer. The remaining emission bands are assigned to the same transitions as when excited by 12,800 cm$^{-1}$ energy.

The FT-TRS emission spectra for the YAG samples are similar in behavior from the standpoint of emission frequencies, but significant differences in the emission lifetimes are again evident. Only emission from the 0.1% and 0.25% sample could be described by a single exponential process.

**Tm$^{3+}$:YALO**

The 0.1 % and 4% Tm$^{3+}$:YALO were excited with 21,544 cm$^{-1}$ energy. All other experimental parameters described for the YAG samples were used when studying YALO. As in the YAG sample several additional emission bands are observed for the blue pumped spectrum. A very interesting feature of the emission centered at approximately 12,700 cm$^{-1}$ for the blue-pumped 0.1% sample is shown in Figure 39. Two integrated trace extracts are shown which represent emissions occurring at 12,700 cm$^{-1}$ (open circles) and 12,300 cm$^{-1}$ with time on the x-axis and normalized intensity on
the y-axis. The 12,700 cm\(^{-1}\) transition exhibits immediate decay after excitation, whereas the 12,300 cm\(^{-1}\) transition shows a slow rise followed by a significantly longer radiative decay. Figure 40 shows the time-resolved emission on a magnified scale for these two decays. The ability to identify these overlapping emission processes simultaneously is one of the biggest advantages of the FT-TRS method of analysis.

Like the YAG samples, as dopant ion concentration is increased to 4% a significant reduction in the experimental lifetime occurs for all transitions except the fundamental.

**Excitation Via the \( ^{1}D_{2} \) Manifold**

Based upon absorption data presented by Gruber, *et al.* (37) it was determined that the \( ^{1}D_{2} \) manifold of Tm\(^{3+}\) residing near 28,000 cm\(^{-1}\) could be excited off-resonance using the 354.7 nm tripled Nd:YAG output. UV excitation allows for the observation of
Figure 40. FT-TRS spectrum for 0.1% Tm$^{3+}$:YALO for the 13,000 cm$^{-1}$ region.

emission that may be occurring in either the visible or IR regions with reasonable S/N. A Schott UG33 filter was placed at a point outside the interferometer to eliminate unwanted UV radiation. The Si diode detector and the quartz beamsplitter were used for studying the entire visible spectral region. Only the 0.1%, 0.25% and 2.4% Tm$^{3+}$:YAG samples, as well as the 0.1% Tm$^{3+}$:YALO sample were studied in this region after UV excitation. This is due to a limitation that occurs when employing the Si diode detector for the PAD 82 studies required to characterize the more concentrated samples. A severe "echo" effect is observed which hinders the determination of accurate decay lifetimes. A solution to this problem is currently being investigated.
Tm$^{3+}$:YAG

Figure 41 exhibits the $^1G_4 \rightarrow ^3H_6$ blue emission of the 0.25% Tm$^{3+}$:YAG sample after 354.7 nm excitation. This decay process is quite rapid in comparison to the IR emission processes. The decay appears to be purely exponential and yields a lifetime of 40.2 µsec. A 1/e lifetime for the 2.4% sample is on the order of 25 µsec. Comparative log decay curves for the 3 concentrations studied are displayed in Figure 42.

It should be noted that upon UV excitation, green emission is visually observed emanating from the YAG samples. A very weak emission band located at approximately 19,000 cm$^{-1}$ is believed to be this emission, however, additional studies are needed to confirm this.
Examination of the 15,750 - 9,000 cm$^{-1}$ energy region reveals additional emission bands (see Figure 43). Two bands centered at nearly 15,000 cm$^{-1}$ and 13,200 cm$^{-1}$ are believed to be transitions from the $^1$D$_2$ manifold to the $^3$H$_4$ and $^3$F$_2$ manifolds, respectively. Lifetimes for these 2 transitions appear to be on the order of 40 $\mu$sec.

Inspection of the remainder of the spectrum into the IR region does not reveal additional radiative transitions.

**Tm$^{3+}$:YALO**

Identical experiments to those for Tm$^{3+}$:YAG were performed for the 0.1% Tm$^{3+}$:YALO sample. Emission bands at 22,000 cm$^{-1}$, 15,000 cm$^{-1}$, 13,000 cm$^{-1}$ and 12,700 cm$^{-1}$ are observed in the visible spectral region. Additional IR decay processes were not observed. The lifetimes for the exponentially decaying blue emission at 22,000 cm$^{-1}$...
Figure 43. Time-resolved visible (red) fluorescence spectrum for 0.25% Tm$^{3+}$:YAG.

cm$^{-1}$ and red emission at 13,000 cm$^{-1}$ are 16.94 $\mu$sec and 17.30 $\mu$sec, respectively. This reveals an interesting deviation from expected behavior. The IR radiative lifetimes of the 0.1% YALO sample are much longer than those for the 0.25% YAG, however the visible radiative lifetimes appear to be much shorter by comparison.
<table>
<thead>
<tr>
<th>Transition</th>
<th>Material</th>
<th>1/e Lifetime (μsec)</th>
</tr>
</thead>
<tbody>
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<td>$^3F_4 \rightarrow ^3H_6$</td>
<td>0.1% Tm$^{3+}$:YAG</td>
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<tr>
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<td>0.25% Tm$^{3+}$:YAG</td>
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<td>2.4% Tm$^{3+}$:YAG</td>
<td>11,350</td>
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<td>4.0% Tm$^{3+}$:YAG</td>
<td>11,170</td>
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<tr>
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<td>5.2% Tm$^{3+}$:YAG</td>
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<td>2% Tm$^{3+}$:LAG</td>
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<td>4% Tm$^{3+}$:YALO</td>
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<td>0.25% Tm$^{3+}$:YAG</td>
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<td>0.25% Tm$^{3+}$:YAG</td>
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</tr>
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<td></td>
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<tr>
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Table 1. continued

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<th>Transition</th>
<th>Material</th>
<th>1/e Lifetime (μsec)</th>
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<td>0.25% Tm$^{3+}$:YAG</td>
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Table 2. $^3F_4$ Manifold Population (Rise) Times For Tm$^{3+}$ Doped Materials.

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CHAPTER 5

DISCUSSION OF RESULTS

The following discussion examines the methods used to interpret the experimental data. An overview of the general experimental results is followed by a discussion concerning the generation of the decay curves and the methods used to fit the curves to yield approximate values for the experimental lifetimes. This is followed by the construction of a kinetic model which considers experimental parameters, as well as parameters generated through theoretical calculations.

General Experimental Results

Tm$^{3+}$:YAG

Experimental lifetimes obtained for the YAG samples appear to be consistent with results obtained in previous studies, however some variations do exist, especially in the lifetimes obtained for emission from the $^3H_4$ manifold. Values that have been reported for the fundamental lifetime ($^3F_4 \rightarrow ^3H_6$) at room temperature vary from approximately 10 msec to 12 msec (1,44-46) and do not show a concentration dependence.

The comparison of lifetimes from other manifolds has proven to be a complicated
task because of the large variance of dopant ion concentrations in the samples. Armagan, et al.(22) have reported room temperature lifetimes from the $^3\text{H}_4$ manifold to be approximately 400 $\mu$sec for 1% Tm$^{3+}$ and 450 $\mu$sec for 0.75% Tm$^{3+}$. Becker, et al.(9) report values of 535, 250 and 10 $\mu$sec for 0.07%, 0.7% and 4% Tm$^{3+}$, respectively. Closer inspection of the Becker data, however shows that erroneous 1/e lifetime values were reported. The actual values are approximately 20% longer in duration because the 1/e point chosen was not 36.7% of the initial intensity, but was nearly 74% which lead to the significantly shorter reported experimental lifetimes. Basiev, et al.(46) report a value of approximately 550 $\mu$sec for an undisclosed concentration of Tm$^{3+}$:YAG. We have found that the lifetime of the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition is on the order of 500 $\mu$sec for the 0.25% and 0.1% samples. The variance between our values and those obtained in other studies is due possibly to sample quality or variances in the magnitude of radiation trapping inherent in most experiments.

Power dependent studies were performed for the 0.25% and 2.4% samples Tm$^{3+}$:YAG. Pump power was varied from approximately 5 mJ/pulse to hundreds of $\mu$J/pulse with no change in the experimental lifetimes from the $^3\text{H}_4$ or $^3\text{F}_4$ manifolds. This is a limited consideration and a study of pump power needs to be performed for all of the materials.

Figure 28 (pg. 55) exhibits the rising population of the $^3\text{H}_4$ manifold after 12,800 cm$^{-1}$ excitation. This relatively long-lived rise may possibly be attributed to the process of radiation trapping. Another possible explanation for the rise is the process of inter-manifold energy transfer. Upon excitation, energy is transferred from higher energy...
Stark levels to lower energy Stark levels in the $^3H_4$ manifold via low energy phonons prior to radiative emission to the manifolds of lower energy. The latter explanation appears to be plausible because the sample is of low dopant ion concentration and thus should have a smaller probability of radiation trapping. Also, the risetime of the $^3H_4$ manifold significantly decreases as the dopant ion concentration is increased implying that either the inter-manifold energy transfer process becomes much less probable or the process of radiation trapping begins to diminish which seems unlikely due to the increasing proximity of dopant ions within the lattice.

**Tm$^{3+}$:YALO**

Hobrock and DeShazer (47) reported a lifetime of 630 $\mu$sec from the $^3H_4$ manifold in a Tm$^{3+}$:YALO sample of undisclosed dopant ion concentration. For the 0.1% sample we report an experimental lifetime of 630 $\mu$sec. The 1/e lifetime for the 4.0% sample is 10 $\mu$sec. Lifetimes for the emission from the first excited state are 5.12 msec and 5.14 msec for 0.1% and 4.0%, respectively which are very comparable to the value of 5.0 msec reported by Payne, *et al.* (48) for a 1% Tm$^{3+}$ sample.

An interesting trend was noticed when comparing the experimental lifetimes of the low concentration YAG and YALO samples. The lifetimes for the 0.1% YALO sample are longer than the 0.1% and 0.25% YAG sample in the IR region after 780 nm excitation, but are significantly shorter in the visible region after 355 nm excitation. This may be possibly attributed to a more efficient energy relaxation pathway in the YALO sample for these higher energy transitions. The trends in the experimental lifetimes obtained for the decay from the $^1G_4$ manifold for the two materials are
consistent with the radiative lifetimes obtained from the theoretical calculations derived by Morrison, et al. (49-51). The calculations consider crystal-field interactions and Judd-Ofelt parameters to generate theoretical radiative lifetimes, branching ratios and level-to-level line strengths. The trends in the lifetimes from the $^3\text{H}_4$ manifold do not agree with the calculations.

The decay from the $^1\text{G}_4$ manifold for the low concentration materials are exponential in behavior, therefore it is believed that no energy quenching processes are occurring.

**Generation and Fitting of Experimental Decay Curves**

**Generation of Decay Curves**

Experimental decay curves are generated through integration techniques supplied by the Bruker OPUS software. Several integration techniques were employed to determine which was the most reliable. Figure 44 shows an emission trace from a FT-TRS experiment. The integration method uses 2 portions of the spectrum (A-B & F-G) to correct for intensity contributions due to factors other than the emission itself (baseline correction). Two additional points are selected (C-E) to define the region where the most intense emission resides (D). The area under the single, most intense point is then integrated over time to yield a trace decay curve which represents the entire emission band as defined by the user. This technique yields better values at later times than other integration methods. The values obtained by this technique approach zero more reliably and a smaller baseline correction is then needed when the curve is mathematically fit.
Figure 44. Integration method employed to generate experimental trace decay curves. Regions A-B & F-G used to determine baseline. The highest point (D) is computer selected between the user defined C-E region.

Mathematical Fits of Experimental Decay Curves

Inokuti and Hirayama (12) (IH) in 1965, derived an expression that describes non-exponential decay processes in a physically meaningful manner. The IH theory is based upon a spherical volume of influence which contains an acceptor ion (A) that is surrounded by other acceptor ions and quenching ions (B) (the number of which depends on the concentration of dopant ion in the sample) by an average distance defined as $R_c(5,12,52)$. Upon excitation, the A ion that accepts the energy may transfer a significant portion of this energy to a B ion non-radiatively where it is then quenched. This non-radiative cross-relaxation process can then be described by a corresponding rate. As the dopant ion concentration is increased the probability of A→B interaction and energy transfer is also increased. Since it is believed that the observed non-exponential
behavior is due directly to an increase in dopant ion concentration (10), this model appears to be ideal in physically describing the non-exponential decay.

The expression shown below,

$$\phi = \phi_o \exp(-t/\tau_A - \Gamma(1-3/n) \frac{C}{C_0} (t/\tau_A)^{3/n})$$

considers the statistical average of interaction between A and B ions within the sphere of influence. In examining the above equation, two separate terms which describe the non-exponential decay are evident. $\tau_A$ is the experimentally determined lifetime for a sample that does not experience cross-relaxation. In this study the 0.1% results are used where $\tau_A$ is 510 $\mu$sec$^{-1}$.

The second term introduces non-exponential character into the decay. The value of the $\Gamma(1-3/n)$ term is derived from the $\Gamma$ mathematical tables. The value of $n$ is dependent on the type of multipole interaction that physically describes the A and B ion interaction. If a dipole-dipole interaction is considered, described by an $R^{-6}$ radius dependence (5,12), then $n=6$. Thus, for $\Gamma(0.5)$, a value of 1.77 is obtained from the gamma function tables. The $C/C_0$ term describes the ratio of B ions (C) to A ions where $C_0$ is defined as the critical concentration equivalent to $3/4\pi R^3(12)$. $R$ is the separation between A and B ions at $C_0$ where the cross-relaxation rate is equal to $1/\tau_A(12)$. $t/\tau_A$ in the second term is raised to the $1/2$ power due to the dipole-dipole A-B interaction dependence.

Using an equivalent form of the IH expression in the Kalidegraph mathematical software allowed for the iterative fitting of experimental data. The parameters that were
allowed to vary in the fit were $\phi_0$ and the $C/C_0$ concentration ratio. Figure 45 shows a representative log fit of the IH expression to actual data obtained for the 2.4\% Tm$^{3+}$:YAG sample. The IH equation yields similar fits at 4.0\% and 5.2\% Tm$^{3+}$:YAG, however deviations are slightly larger as concentration increases which can be seen in Figures 46 and 47 for 4.0\% and 5.2\%, respectively. Fits were improved for the 4.0\% and 5.2\% samples by varying the starting time of the experiment. There is a degree of uncertainty limited to the temporal resolution as to when the experiment starts after trigerring. The 5.2\% experiments, for example, used 1 $\mu$sec resolution, therefore the actual starting time of the experiment could vary from 0 to 1 $\mu$sec. The fit was enhanced by nearly 10\% by using a starting time of 0.9 $\mu$sec and the same was true for the 4.0\% fit.

![Figure 45. IH (solid line) fit to the $^3H_4\rightarrow^3F_4$ non-exponential decay for 2.4\% Tm$^{3+}$:YAG.](image-url)
Figure 46. IH (solid line) fit to the $^3H_4 \rightarrow ^3F_4$ non-exponential decay for 4.0% Tm$^{3+}$:YAG.

Figure 47. IH (solid line) fit to the $^3H_4 \rightarrow ^3F_4$ non-exponential decay for 5.2% Tm$^{3+}$:YAG.
The values obtained for \( C/C_0 \) increase with increasing concentration as expected. The increase in the values changes linearly with concentration from 0.25% to 4.0%, but the value obtained for the 5.2% sample deviates significantly from linearity. The reason for this is not clear at this time and additional studies at greater concentrations need to be performed to determine if additional A-B interactions are occurring.

It is possible that additional terms are necessary to describe the A-B electronic interaction as concentration is increased. Adding terms that account for dipole-quadrupole and quadrupole-quadrupole interactions did not improve the IH fit and actually made them worse for all of the more concentrated samples. The addition of a term which accounts for energy diffusion may improve the IH fit. Barnes, et al. (54) have stated that the self-quenching process can be significantly enhanced by the process of diffusion, especially as dopant ion concentration is increased.

Table III on the following page shows the values for relative ionic separation of \( \text{Tm}^{3+} \) ions within the crystalline lattice for the higher concentrated samples, as well as values for \( C/C_0 \) derived from the IH fit. The value for \( \text{Tm}^{3+}:\text{YAG} \) are plotted in Figure 48. The points are not linear and we predict that the \( C/C_0 \) ratio should be proportional to \( 1/R^3 \) based on the IH theory. This is not the case, however as the curve can be best fit with an \( 1/R^6 \) function. This implies that there may be an additional photophysical process besides the single cross-relaxation process that needs to be considered. Also, it may be possible that an enhanced placement of the ions occurs within the lattice as the dopant ion concentration is increased(52), meaning that ions substitute for \( \text{Y}^{3+} \) at sites nearer to each other than would be predicted. The cross-relaxation process would,
therefore, be of a larger magnitude than predicted based upon a normal placement of ions.

Table 3. Values for Relative Ionic Separation and $C/C_0$ Derived from the IH Fit.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ionic Separation(Å)</th>
<th>$C/C_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0% LAG</td>
<td>20.2</td>
<td>0.979</td>
</tr>
<tr>
<td>2.4% YAG</td>
<td>19.2</td>
<td>1.32</td>
</tr>
<tr>
<td>4.0% YAG</td>
<td>16.2</td>
<td>2.31</td>
</tr>
<tr>
<td>5.2% YAG</td>
<td>14.9</td>
<td>4.24</td>
</tr>
<tr>
<td>4.0% YALO</td>
<td>14.4</td>
<td>5.38</td>
</tr>
<tr>
<td>3.0% YO</td>
<td>14.3</td>
<td>6.60</td>
</tr>
</tbody>
</table>

Figure 48. Atomic concentration (%) versus $C/C_0$ derived from the IH fit for 2.4%, 4.0% and 5.2% $Tm^{3+}$:YAG.
Derivation of Rate Equations

The experimental results may be explained by deriving the kinetic rate equations for the populations of the $^3H_4$, $^3H_5$, $^3F_4$ and the $^3H_6$ manifolds of Tm$^{3+}$:YAG after 12,800 cm$^{-1}$ excitation. These equations are shown as follows:

Manifold 3 ($^3H_4$) $\frac{dN_3}{dt} = -(A_{30} + A_{31} + A_{32})N_3 - X_{CR}N_3N_0$

Manifold 2 ($^3H_5$) $\frac{dN_2}{dt} = +A_{32}N_3 - W_{21}N_2$

Manifold 1 ($^3F_4$) $\frac{dN_1}{dt} = +A_{31}N_3 + 2X_{CR}N_3N_0 + W_{21}N_2 - A_{10}N_1$

Manifold 0 ($^3H_6$) $\frac{dN_0}{dt} = +A_{30}N_3 + A_{10}N_1 - X_{CR}N_3N_0$

$N_i$ = population of level $i$
$A_{ij}$ = spontaneous radiative emission from manifold $i$ to manifold $j$
$W_{ij}$ = multiphonon emission from manifold $i$ to manifold $j$
$X_{CR}N_3N_0$ = non-radiative cross-relaxation term

The rate equations are written to include spontaneous emission, multiphonon emission and cross-relaxation processes. The derived equations exclude the excitation process to simplify the model, but no other assumptions are present. All time units are expressed in µsec. Figure 49 on the following page may be used as a reference for interpreting the assigned transitions.

The $A_{ij}$ terms are the calculated branching ratio obtained from calculations derived by Morrison, et al.(49,50) multiplied times the experimentally derived value of $k$ for the emission decay processes from manifolds 3 and 1. The calculated values obtained for the branching ratios of interest agree well with the experimental data for the 0.25%
sample. Comparisons were made by integrating the total volume under each decay process over the entire experimental sampling time after excitation and correcting for differences in the instrument response curve. Relative percentages of this area were then obtained and compared to the calculated branching ratio values. Variances on the order of 1-3% are evident.

Low Concentration Tm$^{3+}$:YAG

For the low concentration samples, 0.1% and 0.25%, the rate equations are identical to the above except the value for the cross-relaxation term is zero. Mathematica was used to determine numerical solutions to the set of simultaneous differential equations. The initial populations of manifolds 0, 1 and 2 were set to zero and the initial
population for manifold 3 was set to one. The $A_{ij}$ values were fixed at values determined from multiplying the calculated branching ratios and their respective experimental lifetime. These values are as follows: $A_{30} = 0.0019 \mu\text{sec}^{-1}$, $A_{31} = 0.00018 \mu\text{sec}^{-1}$, $A_{32} = 0.000017 \mu\text{sec}^{-1}$, $A_{10} = 0.000088 \mu\text{sec}^{-1}$.

It was found that the value for $W_{21}$ (multiphonon emission rate) is on the order of 0.1 to 0.01 $\mu\text{sec}^{-1}$, but variances by an additional order of magnitude could occur with minimal effects on the system. This insensitivity to the changes in $W_{21}$ can be attributed to the extremely small $A_{32}$ term which dictates that very little of the energy in manifold 3 ($^3H_4$) is actually transferred to manifold 2 ($^3H_5$). This is observed experimentally and since very little energy population proceeds to manifold 1 ($^3F_4$) via manifold 2, relatively large changes in the value for the $W_{21}$ non-radiative process will not affect the decay from manifold 3 or manifold 1. Lifetimes for the $W_{21}$ emission have been found to be on the order of 10 $\mu\text{sec}$ in other studies(55). We have measured the rise of the population in the $^3F_4$ manifold in the 2.4% sample after excitation into the $^3H_5$ manifold and do find this to be on the order of 10 $\mu\text{sec}$.

Decay curves for manifolds 3 ($^3H_4$) and 1 ($^3F_4$) generated by the model are shown compared to the experimental data in Figures 50 and 51. The modeled fits appear to be consistent with the experimental data. Examination of the rising population of the fundamental transition ($^3F_4 \rightarrow ^3H_6$) also agrees with experimental results.

**High-Concentration Tm$^{3+}$:YAG**

As the concentration of dopant-ion is increased the energy depopulation represented by the emission from manifold 3 to manifolds of lower energy deviates
Figure 50. Modeled decay (dashed) from manifold 3 ($^3\text{H}_4$) vs. 0.25% experimental decay.

Figure 51. Modeled decay (dashed) from manifold 1 ($^3\text{F}_4$) vs. 0.25% experimental decay.
significantly from exponential behavior. The population of manifold 1 mirrors this behavior.

The introduction of an appropriate cross-relaxation term into the kinetic equations produced decay curves that deviate from exponential behavior. The cross-relaxation involves non-radiative population of manifold 1 from manifolds 3 and 0 due to the resonance of these 2 transitions. It was decided that in order for this process to readily occur, significant population must reside in the manifold 0 ground state and this value should change linearly with changing concentration. The initial value for the population of manifold 3 remained 1. The $A_{ij}$ and $W_{ij}$ values remained the same as for the low concentration studies meaning that the branching ratios and the $k$ values were not changed. Reasonable fits of the radiative and non-radiative depopulation processes were then obtained for the 2.4%, 4.0% and 5.2% YAG samples by varying the magnitudes of the manifold 0 population and cross-relaxation terms. Table IV below provides a summary of the terms used to achieve fits to the experimental data.

Table 4. Summary of Terms Used for the Kinetic Model.

<table>
<thead>
<tr>
<th>Material</th>
<th>Level 0 Population</th>
<th>Cross-Relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4% YAG</td>
<td>0.735</td>
<td>0.02925</td>
</tr>
<tr>
<td>4.0% YAG</td>
<td>1.18</td>
<td>0.03656</td>
</tr>
<tr>
<td>5.2% YAG</td>
<td>1.34</td>
<td>0.08190</td>
</tr>
</tbody>
</table>
Figures 52, 53 and 54 show a comparison of the modeled non-exponential decay to the experimental decay for the 2.4%, 4.0% and 5.2% samples from level 3. The log of the intensity is on the y-axis and time in μsec is on the x-axis.

The terms derived from the model shown in Table IV seem to correlate with the changes in concentration and the trends in the parameters occur as expected. The cross-relaxation rate increases with increasing concentration as does $X_0$. The values do not change linearly with concentration as expected, however. This may be due to the possibility of an additional energy transfer process due to ionic interaction that is not being accounted for in the model. Analysis of samples of higher dopant ion concentrations would allow for the determination of a more accurate trend in these

![Log Intensity](image-url)

Figure 52. Modeled decay (dashed) from manifold 3 ($^3H_4$) vs. 2.4% experimental decay.
Figure 53. Modeled decay (dashed) from manifold 3 (\(^3\text{H}_4\)) vs. 4.0% experimental decay.

Figure 54. Modeled decay (dashed) from manifold 3 (\(^3\text{H}_4\)) vs. 5.2% experimental decay.
values. Comparison of the values for the cross-relaxation rate to studies performed by Armagan, et al. (10) at various temperatures show that the values obtained here are similar magnitudes at room temperature. The authors were able to describe the cross-relaxation process by the methods developed by Dexter, et al. (11). Differences in the rates of the cross-relaxation may therefore be due to the differences in the analysis procedures, however the value obtained by Armagan, et al. (10) for the 6% Tm\(^{3+}\):YAG sample also shows a large increase in the cross-relaxation rate and the rate does not change linearly with concentration from 0.75% to 6% Tm\(^{3+}\).

A recent study by Rustad, et al. (55) shows that additional cross-relaxation processes are possible. Two processes are described which involves the depopulation of manifold 1. The efficiency of these processes in this study are believed to be 0 (as Rustad, et al. found for a 6% sample) as there is none or very little non-exponential behavior in manifold 1. It is believed however that there is an additional cross-relaxation mechanism which is aiding in the depopulation of manifold 3 due to the behavior observed in the kinetic model. This may be occurring between levels 3 and 0, where the rates of the 3→0 and 0→3 pathways are different. Additional studies are necessary for a more complete understanding of this effect, however.
CHAPTER 6

CONCLUSIONS AND SUMMARY

Advantages and Limitations of FT-TRS

The FT-TRS method implemented to study these laser materials has exhibited many advantages, the most significant being the ability to observe several emission events simultaneously. This has enhanced our ability to understand the many photophysical processes that occur in these materials. For example, Figure 39 (pg. 67) shows overlapping decay processes in Tm$^{3+}$:YALO after blue excitation. The same type of overlap has been observed in Tm$^{3+}$:YAG in two different energy regions.

A recent area of interest has been the renewed study of CTH:YAG and TH:YAG(20,28,53,54,55,56). Cr$^{3+}$ has a broad absorption band in the visible that can be easily pumped at 590 nm and at high concentrations a large fraction of the pump energy can be absorbed and transferred to the Ho$^{3+}$, much more so than if the material were doped with Ho$^{3+}$ alone. In this way, a larger fraction of the pump energy may eventually be emitted at 2.1 $\mu$m enhancing laser performance.

Because these materials are very complex in the way that energy is transferred from ion to ion there are many parameters which are required to accurately model the
kinetics of the material. Of particular interest is the energy transfer time from Tm$^{3+}$ to Ho$^{3+}$ (see Figure 3). This process is reversible in nature and typically the transfer time is determined through modeling(55,56), but FT-TRS has enabled the direct determination of this time by measuring the difference in the population rates of the $^3F_4$ and $^5I_7$ manifolds. The difficulty in the measurement arises because the emission from these manifolds significantly overlap.

The population of these 2 manifolds is shown in Figure 55 and spectrally in Figure 56. This sample contains 6.5% Tm$^{3+}$ and 0.36% Ho$^{3+}$. We estimate the transfer time to be on the order of 80 to 100 $\mu$sec, however this time includes both the forward and reverse transfer processes occurring due to the overlap of the $^3F_4$ and $^5I_7$

![Figure 55. Population of the Tm$^{3+}$ $^3H_4$ (open circles) and Ho$^{3+}$ $^5I_7$ manifolds after 12,800 cm$^{-1}$ excitation.](image)
Figure 56. FT-TRS spectrum for the population of the $^3F_4$ and $^5I_7$ manifolds of Tm$^{3+}$ and Ho$^{3+}$, respectively in CTH:YAG.

Tm$^{3+}$ doped materials are much less complex as far as the number of actual emission events that are observed experimentally. A material such as Ho$^{3+}$:YAG or Er$^{3+}$:YAG consists of many more Stark manifolds than Tm$^{3+}$:YAG and consequently many more emission processes are evident. IR spectra obtained for Ho$^{3+}$:YAG show multiple emission processes simultaneously occurring on the nsec time scale. This ability to determine several kinetic parameters experimentally will aid in the study of these more complex materials.

While the advantages of FT-TRS are evident, currently we are experiencing many limitations which need to be overcome. The first of these is a limited experimental
spectral range. Acquiring additional beamsplitter/detector combinations will allow for broader spectral coverage and observation of additional energy transfer processes. Future plans include obtaining additional equipment to push detection capabilities to the far-IR and UV spectral regions. Spectral analysis in the far-IR region is most important because the ability to observe multiphonon emissions that occur from 1500 - 100 cm\(^{-1}\) would make energy transfer assignments and kinetic analysis much easier because lifetimes may be measured directly.

Secondly, we are experiencing spectral analysis complications due to detector saturation. The 8-bit PAD 82 experimentation requires cautious planning in order to obtain good spectra and the limited dynamic range is problematic for studying decays. Because of this, analysis of the same spectral region that is being excited is not currently possible due to detector saturation and possible damage to the electronics responsible for running PAD 82. This problem is currently being solved through the construction of a temporal filter that enables the elimination of the time space which contains response caused by the exciting laser pulse. The InSb detector response is relatively slow, on the order of 180 nsec, and a filter which allows for signal elimination on this time scale should be appropriate.

The addition of improved light collection optics may significantly enhance the S/N ratio for experiments that involve pump power dependences and for the study of low concentration samples. Most often a material that does not absorb a large fraction of the excitation energy does not efficiently emit light. Light collection schemes for enhancing S/N are being investigated at this time.
The effects of radiation trapping in spectroscopic measurements of laser materials are unavoidable for the most part. Proper sample placement and the use of samples that are of minimal thickness can significantly diminish this effect. A recent study by Hehlen(36) reveals the effects of radiation trapping that are inherent in most studies. By immersing the laser material of study into a refractive index-matched liquid Hehlen was able to obtain experimental lifetimes that were nearly 25% less than those analyzed in air because the critical angle at the air/crystal interface is diminished and total internal reflectance is minimized. Therefore, we estimate that the radiative lifetimes in our study may be as much as 25% too long in duration, however every effort was made to minimize the trapping effect.

Closing Remarks

The goal of this research was to implement and apply a method that would enable the rapid and accurate characterization of solid-state crystalline laser materials while exploring and exposing the advantages and limitations of the method. Methods that have been previously employed are quite satisfactory for the characterization process, but are generally more tedious and very time intensive. It was hoped that the ability to observe a broad spectral region would yield more information regarding energy transfer processes. The discovery of additional radiative transitions not observed previously may further the understanding of the complex energy transfer processes occurring in these materials.

At this time it is believed that the FT-TRS system has significantly enhanced the
ability to analyze crystalline laser materials. Reproducible results concerning experimental lifetimes, absorption band structure and material emission characteristics have been obtained and compare well with accepted results gathered through other studies. The limitations discussed previously can be overcome which will allow for even more rapid material characterization with equal or better accuracy and precision. Future applications for the FT-TRS method include cryogenic studies, 2 photon excitation and upconversion analysis. The instrumentation may also be used to study materials used in other applications, such as organic compounds and polymers.

The kinetic model developed to study these Tm$^{3+}$ doped laser materials has shown to describe the photophysical processes which occur after excitation. Additional studies are essential for enhancement of the model and developing a greater understanding of the nature of these materials. Studying materials over a larger concentration range and observing a greater region of the spectrum after excitation will lead to a more accurate representation of the kinetics, especially as the samples are excited at greater energies.
REFERENCES CITED
REFERENCES CITED


