SPECTROSCOPY OF Tm⁺³ : YLF AS A LASER MATERIAL
FOR DIODE LASER PUMPING

by

GIUSEPPE LA ROSA

Submitted to the Department of Materials Science and
Engineering in Partial Fulfillment of the Requirements of
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at the

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ABSTRACT

A detailed spectroscopic characterization of Tm:YLF was carried out to establish its potential as a solid state laser material under diode laser pumping. Fluorescence branching ratios and spectrally resolved stimulated emission cross sections have been obtained for transitions from the $^3H_4$ and $^3F_4$ metastable levels. Concentration dependent fluorescence lifetimes of both levels have been measured; establishing a strong concentration quenching of the $^3H_4$ level.

Thesis Supervisor: Hans P. Jenssen

Title: Principal Research Associate and Lecturer
Acknowledgements.

I would like to express my appreciation to my advisor Dr. Hans P. Jenssen to get me interested in the field of solid state lasers and help me a lot in understanding the spectroscopic issues in solid state laser materials. His outstanding experience in this field was essential in the shaping of this work.

Special thanks to Harry Chou and David Knowles, two fellow graduate students, for their numerous valuable suggestions and critical comments, which turned out to be one of the best ways of learning.

I would like also to thank all members of the Crystal Physics Laboratory for their technical assistance and fruitful discussions; in particular Mr. Peter Kloumann for helping me in solving many electronics problems I had to face in the course of this research and Mrs. E. Cook for assistance in administrative matters.
Dedication

To Marianna, whose love and encouragement has been essential to the making of this work
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1.1 Introduction

In recent years there has been a growing interest in the use of semiconductor diode lasers as optical pumping sources for solid state laser materials. The increase in system efficiency and component life time as well as a reduction of the thermal load of the laser medium have made these sources an attractive alternative to flashlamp pumping. Since less heat is absorbed in the gain medium during diode laser pumping thermo-optical effects are reduced and therefore a better quality beam and an increase in pulse repetition rate are possible. The degradation of the laser material resulting from high pump energy fluxes and a substantial content of UV radiation in the flashlamp spectrum is completely eliminated with diode pumping.

Soon after Ross (1) reported the first successful lasing of diode pumped Nd:YAG, this material has been widely investigated due to its combination of thermal, mechanical and spectroscopic properties that make it one of the most versatile laser materials.

On the other hand the properties of a good host, like YAG, become less important under diode laser pumping.

Trivalent rare earth ions with upper laser level lifetimes longer than the \( \text{F}_{3/2} \) lifetime in Nd:YAG (230 ns) can be used in energy storage applications, important in
pulsed laser operation.

Erbium, Holmium and Thulium have some long-living metastable states that make them particularly suitable for this kind of application. In addition, they exhibit broad absorption bands in the spectral region of the diode laser emission (750-860 nm).

The need of eye-safe laser wavelength for applications in atmospheric propagation has stimulated an investigation on the laser action of the $^3H_4 \rightarrow ^3H_5$ (λ = 2.3 um) and $^3F_4 \rightarrow ^3H_6$ (λ = 1.9 um) transitions in several Tm$^{3+}$ doped laser materials. The long $^3H_4$ fluorescence lifetime (larger than 1 ms in most host materials) and the practically unpopulated lower $^3H_5$ multiplet make the $^3H_4 \rightarrow ^3H_5$ an efficient four levels laser transition. Because of the weak absorption lines of Tm$^{3+}$, sensitation by Cr$^{3+}$ was required to achieve threshold at both 2.3 and 2.0 um using flashlamp pumping. The presence of Cr$^{3+}$, as a sensitizer, provides a broad band absorption in the visible and an efficient energy transfer to the $^3H_4$ multiplet (see figure (1.1)).

Laser action at 2.3 um was reported for the first time in the Tm:Cr:YAlO$_3$ crystal under flashlamp pumping at room temperature (2), but high threshold and low slope efficiencies were observed. The quasi three level character of the $^3F_4 \rightarrow ^3H_6$ transition makes difficult to achieve population inversion at room temperature. Laser oscillations were reported at 2.02 um in Tm:Cr:YAG by tungsten lamp pumping at 77 K (3).
Only recently (4) cw laser emission at 2.02 um has been reported at room temperature using a 12\% Tm$^{3+}$:YAG laser rod pumped by a laser diode. The low threshold for laser emission (17.2 mW) and the high slope efficiency (56\%) are due to a cross relaxation process, called concentration quenching, in which a Tm$^{3+}$ ion in the $^3H_s$ manifold transfers a fraction of its energy to another Tm$^{3+}$ ion in the ground state $^3H_s$, resulting in two Tm$^{3+}$ ions excited in the $^3F_s$ multiplet. Two 2.02 um photons are, therefore, emitted each time a pump photon is absorbed (see figure (1.2)).

A 3 at \% Tm$^{3+}$ doped LiYF$_4$, laser rod was used for the first time by M. D. Thomas et al. to achieve threshold between levels of the the $^3H_s$ and $^3H_s$ multiplets at room temperature pumped by a long pulsed alexandrite laser tuned at the Tm:YLF absorption line centered at 781 nm, simulating in this way GaAlAs laser pumping (5).

The $^3H_s$ $\rightarrow$ $^3H_s$ laser transition has also been observed by G. Kintz et al. (6) in a cascade laser operation together with the $^5I_s$ $\rightarrow$ $^5I_s$ (\( \lambda = 2.08 \text{ um} \)) transition of Ho from a laser diode pumped Tm:Ho:LiYF$_4$ crystal at room temperature. In this application the stimulated emission produced by the $^3H_s$ $\rightarrow$ $^3H_s$ transition populates very rapidly the $^3F_s$ multiplet through the $^3H_s$ $\rightarrow$ $^3F_s$ non radiative multiphonon process. The $^3F_s$ level transfers its energy to the Holmium $^5I_s$ level which is the upper level of the 2.08 um emission.

Cascade laser operation was also observed from Tm$^{3+}$ ions
in YAG crystals at 90 K (7) at 2.34 \( \text{um} \) (\( ^3\text{H}_4 \rightarrow ^3\text{H}_5 \)) and 1.93 \( \text{um} \) (\( ^3\text{F}_4 \rightarrow ^3\text{H}_4 \)) pumped by a Xenon discharge lamp (figure (1.3)). Laser operation of the \( ^3\text{F}_4 \rightarrow ^3\text{H}_6 \) transition in Tm:YLF by diode laser pumping the \( ^3\text{H}_6 \) multiplet is in principle possible either using a concentration quenching (at high Tm\(^{3+}\) concentration) or a cascade laser scheme (at low Tm\(^{3+}\) concentration) to achieve threshold.

The motivation of this study stems from the necessity to characterize spectroscopically Tm\(^{3+}\):YLF to evaluate its potential as a diode pumped laser material. An analysis of the fluorescence spectra of Tm\(^{3+}\) in LiYF\(_4\), produced by transitions from \( ^3\text{H}_4 \) to all lower multiplets (\( ^3\text{H}_5 \), \( ^3\text{F}_4 \), and \( ^3\text{H}_6 \)) (at 300 K) as well as from \( ^3\text{F}_4 \rightarrow ^3\text{H}_6 \) (at 300 and 77 K) has been carried out to determine both the \( \Pi \) (\( \vec{E} \parallel \vec{C} \), \( \vec{H} \perp \vec{C} \)) and \( \sigma \) (\( \vec{E} \perp \vec{C} \), \( \vec{H} \parallel \vec{C} \)) effective induced emission cross sections of these transitions and their corresponding branching ratios.

In addition the fluorescence lifetime of the \( ^3\text{H}_4 \) has been measured at 300 and 77 K as a function of Tm\(^{3+}\) concentration to obtain the radiative lifetime of this multiplet and study possible processes that can influence population inversion.

The rest of this chapter is devoted to describe the optical properties of Tm\(^{3+}\) as a free ion and in LiYF\(_4\). A short review of the most important spectroscopic parameters of laser materials is given with special reference to tetragonal
crystals. Chapter II describes the experimental set-up used to make the absorption, fluorescence and lifetime measurements. Chapter III ends this dissertation with an analysis of the data and a discussion of possible applications of Tm$^{3-}$:YLF under diode laser pumping.
Figure (1.1)  Fluorescence levels diagram of the 2.3 um Tm$^{3+}$:YAlO$_3$ laser sensitized with Cr$^{3+}$. 
Figure (1.3) Cascade laser operation of Tm$^{3+}$:YAG.

The $^3H_4 \rightarrow ^3H_5$ ( $\lambda = 2300$ nm) and $^3F_4 \rightarrow ^3H_6$ ($\lambda = 1800$ nm) transitions are simultaneously lasing.
Figure 1.2: Concentration quenching of the multiplet $^3F_4$ in Tm$^{3+}$.
1.2 Free Tm$^{3+}$ ion.

Thulium (Z=69) belongs to the lanthanides rare earth series which have a partially filled 4f$^n$ (1<n<14) electronic shell. It is found in a trivalent state (Tm$^{3+}$) in solids and its external electronic configuration being 4f$^{12}$5s$^2$5p$^6$.

The 4f$^{12}$ electrons are shielded by the outer 5s$^2$5p$^6$ electrons. Since all the electronic shells but the 4f$^{12}$ shell are spherically symmetric the hamiltonian describing the energy spectrum of the free ion is:

$$H = H_0 + H_e + H_{50}$$  \hspace{1cm} (1.1)

$H_0$ represents the central field contribution and it is given by:

$$H_0 = -\frac{k^2}{2m} \sum_i \Delta_i - \sum_i \frac{Z^*e^2}{r_i}$$  \hspace{1cm} (1.2)

The first term of $H_0$ is the kinetic energy of the 4f electrons while the second term represents their electrostatic interaction with the nucleus. Because these two terms of $H_0$ are spherically symmetric they do not remove any degeneracy of the 4f configuration. The next two terms in $H$ are the mutual Coulomb interaction of the 4f electrons:
\[ H_c = \sum_{i<j} \frac{\mathcal{L}_i^2}{r_{ij}} \]  

(1.3)

and the spin-orbit interaction:

\[ H_{so} = \sum_i \zeta_i(r_i) \vec{S}_i \cdot \vec{l}_i \]  

(1.4)

Both terms are responsible for the free ion energy level structure of the 4f electrons. A comparison between the experimentally observed energy levels and the theory confirms that both terms of the Hamiltonian \( H_c \) and \( H_{so} \) have the same magnitude in rare earth ions.

This approximation is called intermediate coupling to distinguish from the case in which \( H_c \gg H_{so} \) (Russel-Saunders coupling) and \( H_c \ll H_{so} \) (j-j coupling).

In the intermediate coupling approximation the energy levels of the \( 4f^{12} \) system are found diagonalizing the Hamiltonian \( H_c + H_{so} \) in the Russel-Saunders (RS) representation. The free ion energy spectrum has a multiplet structure, and each multiplet wavefunction is a linear superposition of the of the RS eigenstates \( |f^{12}, L, S, J, J_z \rangle \) with a fixed value of the total angular momentum \( J \) (since \((J, H_c + H_{so}) = 0\) \( J \) is still a good quantum number) and different values of the total spin \( S \) and orbital angular momentum \( L \). Normally a pure RS wavefunction (obtained assuming \( H_c \gg H_{so} \)) is considered to be the only component present. This is the case for the \( \text{Tm}^{3+} \) ground state, which
is mostly $^3H_6$ as obtained using Hund's rule.

But it is not so for some of the higher terms. For example the
second level of the Tm:YLF is a linear combination of $^3H_6$, $^3F_4$
and $^1G_4$ RS wavefunctions, even if $^3F_4$ is the main component.
Each multiplet has degeneracy $2J+1$ as given by the possible
values of $m_j$ ($m_j < |J|$) quantum number.

1.3 Lithium Yttrium Fluoride (YLF)

YLF is an optically transparent and insulating material
that crystallizes in the tetragonal scheelite structure
(CaWO$_4$). The space group given by the international tables of
x ray crystallography (19) is $C_{4v}^6$. The tetragonal unit cell
has four molecules ($Z=4$) with $a=5.2$ Å and $c=10.7$ Å. Table
(1.1) lists the Wyckoff (21) notation and the site symmetry of
each atom.

The refractive indices of YLF are $n_0=1.4485$ and $n_e=1.4708$
at $\lambda=1000$ nm (17). Kaminskii (20) reports 36 different laser
wavelengths for RE:YLF. The shortest and longest wavelength
available today are, actually, Ce$^{3+}$:YLF ($\lambda =0.3255$ um) and
Ho$^{3+}$:YLF ($\lambda =3.914$ um). Even if LiYF, is a relatively strong
material (see table (1.3)) its thermal properties are not as
good as YAG. It is clear from table (1.2) that heat
dissipation is a critical factor for YLF, if pumped by
flashlamps. The consequent thermal distortions impose an
upper bound on the average pump power and make necessary to
selectively pump this material to increase pumping efficiency.
<table>
<thead>
<tr>
<th>Ion</th>
<th>Pos.</th>
<th>Symm.</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>4(b)</td>
<td>$S_4$</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>Li</td>
<td>1(a)</td>
<td>$S_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>16(f)</td>
<td>$C_1$</td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
</tbody>
</table>

$x = 0.2820; \quad y = 0.1642; \quad z = 0.01815$

Table (1.1) Crystallographic data of LiYF$_4$.

<table>
<thead>
<tr>
<th></th>
<th>Nd:YLF</th>
<th>Nd:YAG</th>
<th>Nd:Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity at 300 K (W/m·K)</td>
<td>6.0</td>
<td>11</td>
<td>0.86</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient in 0 to 100 range</td>
<td>A axis $13\times10^{-6}$</td>
<td>$8\times10^{-6}$</td>
<td>$11\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>B axis $8\times10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Capacity at 300 K (J/C K)</td>
<td>0.79</td>
<td>0.5</td>
<td>0.88</td>
</tr>
<tr>
<td>Thermal lensing</td>
<td>$-60$ M</td>
<td>$+8$</td>
<td>$-        $</td>
</tr>
<tr>
<td></td>
<td>$=180$ M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (1.2) Comparison of thermal properties of YLF with YAG and Glass Nd doped crystals.
### Physical Properties of YLF

#### Mechanical

<table>
<thead>
<tr>
<th>Property</th>
<th>YLF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cm$^3$) undoped</td>
<td>3.99</td>
</tr>
<tr>
<td>Hardness (Moh)</td>
<td>5.07</td>
</tr>
<tr>
<td>Elastic Modulus (N/m$^2$)</td>
<td>$7.5\times10^{10}$</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.33</td>
</tr>
<tr>
<td>Strength (Kg/cm$^2$) (Modulus of rupture)</td>
<td>335</td>
</tr>
</tbody>
</table>

#### Thermal

<table>
<thead>
<tr>
<th>Property</th>
<th>YLF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity at 300 K (W/cm-K)</td>
<td>0.06</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient 0 - 100 K range</td>
<td></td>
</tr>
<tr>
<td>a axis</td>
<td>$13.8\times10^{-6}$</td>
</tr>
<tr>
<td>c axis</td>
<td>$9.0\times10^{-6}$</td>
</tr>
</tbody>
</table>

#### Crystalline Structure

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a axis (A)</td>
<td>5.167</td>
</tr>
<tr>
<td>c axis (A)</td>
<td>10.735</td>
</tr>
<tr>
<td>c/a ratio</td>
<td>2.078</td>
</tr>
</tbody>
</table>

Table(1.3) Physical properties of YLF.
1.4 Optical properties of Tm$^{3+}$:YLF

The particular optical properties of rare earth ions in crystals are determined by the presence of their partially filled 4f shell. The 4f electrons are localized near their own nucleus and they are shielded from the crystalline environment by the charge density of the outer closed 5s$^2$ and 5p$^6$ shells.

Therefore they interact very weakly with the charges of the surrounding ligands, conserving their free ion spectra in the host crystals. The effect of the crystal field is to partially remove the $2J+1$ degeneracy of the free ion multiplets according to the point symmetry of the site occupied by the rare earth ion in the crystal.

This is summarized for the trivalent rare earth ions in figure (1.4), which shows the indispensable energy level diagram prepared by Dieke and Crosswhite (1963). Although the details relate to RE$^{3+}$ in LaCl, the overall level structure is valid for other hosts, that is the energy centroids of the crystal field multiplets are "typical" of all host materials.

Tm$^{3+}$ goes substitutionally into Y$^{3+}$ sites in YLF. YLF has the scheelite structure (CaWO$_4$) and it belongs to the $C_{nv}$ space group with Y$^{3+}$ site having the point group symmetry $S_4$. Therefore each free Tm$^{3+}$ level, with a given $J$ and degeneracy $2J+1$, will split in LiYF$_4$ according to the irreducible representation $S$, group symmetry.
Having \( \text{Tm}^{3+} \) an even number of electrons its eigenstates will transform according to the irreducible representations \( \Gamma_1, \Gamma_2, \Gamma_3 \) and \( \Gamma_4 \) of the \( S_4 \) point group. \( \Gamma_3 \) and \( \Gamma_4 \) are both associated to double degenerate energy levels (Kramer's pair) and they are shortly called \( \Gamma_{3,4} \) in the literature.

H.P. Jenssen et al. (8) established the energy levels of the ground state \( 4f^{12} \) configuration of \( \text{Tm:YLF} \) from the analysis of the absorption and fluorescence spectra taken at 5 and 77 K. Their results are consistent with a \( \Gamma_2 \) ground state and each level being represented by the irreducible representation of the \( S_4 \) symmetry group.

Figure (1.5) shows a portion of the energy diagramm of \( \text{Tm}^{3+} \) in \( \text{LiYF}_4 \), as obtained by those authors.

The separation between initial and final Stark levels in a multiplet is of the order of 300 cm\(^{-1}\). Because of this small splitting an intramultiplet relaxation takes place so rapidly (\( \tau = 10^{-12} \) sec) that the multiplet population achieves thermalization before any decay process takes place.

Under these conditions the population density of the \( i^{th} \) component \( (n_i) \) of the I multiplet obeys the Boltzmann distribution law:

\[
n_i = f_i N_i
\]

(1.5)

where \( N_i \) is the total population density of the multiplet and \( f_i \)
is the fractional population at the temperature $T$.

Namely:

$$\rho_i = \frac{g_i \xi_i}{\sum_j g_j \xi_j} \frac{-\Delta E_i / kT}{\Delta E_j / kT} \quad (1.6)$$

being $g_i$ the degeneracy of the $j$ level and $\Delta E_j$ its energy respect to the lowest level in the multiplet.

The sum is carried out over all levels of the multiplet $I$.

Table (1.2) shows the fractional population of each level of the $^3H_s$, $^3H_s$, $^3F_s$, and $^3H_s$ multiplets at 300 and 77 K, its degeneracy and irreducible representations. The energy value of each level is also reported.

Electric and magnetic dipole transitions take place between levels of two different multiplets according to the selection rules predicted by group theory. The matrix element $\langle \psi_i, H_j, \psi_j \rangle$ of the operator $H_j$ between the $\psi_i$ and $\psi_j$ is different from zero if, calling $\Gamma_i$, $\Gamma_j$, and $\Gamma_i$ respectively the irreducible representation according to which $\psi_i$, $H_j$ and $\psi_j$ transform, the direct product $\Gamma_i \times \Gamma_j$ contains $\Gamma_j$ at least once (8), (9).

Now the matrix elements of the components of the electric dipole operator are proportional to those of the position operator, while the magnetic dipole operator transforms like the total orbital angular momentum $\mathbf{L}$. 

The selection rules for electric and magnetic dipole
transitions in the $S_4$ symmetry can be easily determined from the observation (8) that $z$ and $x,y$ transform respectively like $\Gamma_2$ and $\Gamma_{3,4}$ in $S_4$, while $L_z$ and $L_x, L_y$ transform like $\Gamma_3$ and $\Gamma_1$. The resulting electric and magnetic dipole selection rules are summarized in table (1.5).

The experimental data on RE$^{3-}$ doped crystals reveal that the radiation is mostly electric dipole in nature. Since the optical transitions are between levels of a particular $4f^{12}$ configuration the electric dipole radiation should be forbidden because the electric dipole operator is an odd operator (transforms like $x,y$ and $z$) and at the same time the transition matrix has even parity (Laporte selection rules).

If the crystal has not inversion symmetry Van Vleck (11) pointed out that electric dipole radiation can occur only because the $4f^n$ states have admixtures of $4f^{n-1}5d$ states.

Magnetic dipole transitions are allowed in the free ions if $\Delta J=0, \Delta L=0, \Delta S=0$.

Since, however, the RE$^{3-}$ free ion wavefunctions are not pure RS wavefunctions (intermediate coupling) $S$ and $L$ are not good quantum numbers any longer and in this case only the condition $\Delta J=0, \pm 1$ can be used to check if magnetic dipole transitions are allowed.
Figure (1.4) Energy level diagram of RE$^{3+}$ in LaCl$_3$ prepared by Dieke and Crosswhite.
Figure (1.5) Portion of energy level diagram of Tm$^{3+}$ in YLF as derived from (8).
<table>
<thead>
<tr>
<th>Multiplet</th>
<th>E (cm⁻¹)</th>
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<th>$\tilde{f}(77,K)$</th>
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Table (1.4) Portion of the energy levels of Tm$^{3+}$:YLF together with their Stark splittings, fractional population at 77 and 300 K and irriducible representation as obtained from (8).
Electric Dipole Selection Rules. (a)

<table>
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<th>$\Gamma_3$</th>
<th>$\Gamma_4$</th>
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<td>$\pi$</td>
<td>$\sigma$</td>
<td>$\sigma'$</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>$\pi$</td>
<td>$0$</td>
<td>$\sigma$</td>
<td>$\sigma'$</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>$\sigma$</td>
<td>$\sigma$</td>
<td>$\pi$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>$\sigma$</td>
<td>$\sigma$</td>
<td>$0$</td>
<td>$\pi$</td>
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</table>

Magnetic Dipole Selection Rules (b).

<table>
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<th>$\Gamma_3$</th>
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<td>$\pi$</td>
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<td>$\pi$</td>
<td>$0$</td>
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<td>$\Gamma_4$</td>
<td>$\pi$</td>
<td>$\pi$</td>
<td>$\sigma$</td>
<td>$0$</td>
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</table>

Table (1.5) Electric (a) and magnetic (b) dipole selection rules for allowed transitions in the $S_4$ symmetry. $\pi/\sigma$ mean allowed transitions for light polarized with $E$ parallel / perpendicular to the c axis. 0 means not allowed.
1.5 Spectroscopy of solid state laser materials.

The spectroscopic characterization of an impurity doped crystal is an essential step in evaluating its potential as solid state optically pumped laser material. Laser action is strongly dependent on an efficient excitation of the dopant ions, the ability of these ions to store this energy and the dominance of stimulated emission over a large variety of energy loss mechanisms.

In this paragraph we give a short overview of the most important spectroscopic parameters used to characterize a laser material.

Let us start by considering the atomic system whose energy diagram has the multiplet structure shown in figure (1.6). We assume that the arbitrary level \(i\) of the I multiplet has degeneracy \(g_i\) and energy \(E_i\) and that the population distribution within a multiplet obeys the Boltzmann Statistics (see (1.5) and (1.6)).

The fluorescence lifetime \(\tau_f\) of the multiplet I is the rate at which its population decays as result of the spontaneous emission for radiative transitions to lower energy multiplets and other decay processes such as multiphonon relaxation and energy transfer to other ions or impurities in the crystal.

In a multiphonon relaxation process a fraction of the
energy released by the ion is taken up by the lattice vibrations. The calculation of the multiphonon relaxation rate is very difficult since it requires a detailed knowledge of the electronic states and the phonon spectrum.

According to Riseberg and Moos (12) the multiphonon relaxation rate \( \omega_{ph} \) can be approximated by:

\[
\omega_{ph} = B \varepsilon^{\alpha \Delta E_g}
\]

(1.7)

where \( B \) and \( \alpha \) are characteristic of the host crystal, with negligible dependence on the dopant concentration.

In (1.7) \( \Delta E_g \) is the energy gap between the multiplet I and its next lower multiplet.

It is also possible for a dopant (called donor) to transfer part of its energy to a nearby ion (called acceptor) exciting it to an higher energy state.

When this energy transfer process is not radiative no photon is involved, but it is radiative if a photon is the carrier of the energy from the donor to the acceptor.

Dexter (13) considered the electric and magnetic multipolar interaction as well as the exchange interaction responsible for the non radiative energy transfer. Since these interactions become stronger as the donor acceptor distance decreases, the non radiative energy transfer increases with increasing concentration.

Sensitization is one of the most important applications of
energy transfer in optically pumped laser materials.
Light absorbed by the sensitizer ion is transferred to the
activators, with consequent more efficient absorption of the
pump radiation and therefore high pump efficiency.
An example of sensitization is the Cr sensitized Tm:YAG 2.3 um
laser discussed in the introduction (see figure (1.1)).

A further classical example of energy transfer process is
the so called "concentration quenching" in which a donor
transfers its energy to a similar ion (acceptor) in its
ground state by either a resonant or phonon assisted process.

A Tm³⁺ ion in YLF (at high Thulium concentration) when
excited at the ³H₂ multiplet undergoes the ³H₂ → ³F₁
transition exciting another Tm³⁺ ion from the ground state
multiplet ³H₅ to ³F₁ and one or more phonons are created to
conserve energy (see figure (1.2)).
An extensive review on energy transfer phenomena in rare earth
ions has been given by Watts (14).

The presence of defects and impurities is also of crucial
importance in modifying the fluorescence lifetime of a given
multiplet. One would expect that the crystal growth method
used to grow the material has a big influence especially at
high dopant concentration.

Following figure (1.6) we can write the fluorescence
lifetime \( \tau_\Phi \) as:

\[
\frac{1}{\tau_\Phi} = \frac{1}{\tau_R} + \sum K \omega_K
\]

(1.8)
where decay rate $w_k$ represents any other process but spontaneous emission. $\tau_R$ is the radiative lifetime from the multiplet I defined as follows. Calling $A_{ij}$ the probability per unit time that an ion at the level $i$ undergoes the $i \rightarrow j$ transition ($i>j$) releasing a photon by spontaneous emission (Einstein coefficient), its rate of radiative decay is defined by:

$$\frac{1}{\tau_{ij}} = A_{ij} \quad (1.11)$$

The radiative lifetime of the multiplet I is the statistical weighted average of all possible rates from the I multiplet. Therefore we have:

$$\frac{1}{\tau_R} = \sum_{ij} f_i A_{ij} \quad (1.12)$$

This quantity represents the storage ability of the system.

The fraction of ions decaying by spontaneous emission is given by:

$$\eta_R = \frac{\tau_f}{\tau_R} \quad (1.13)$$

and represents the radiative quantum efficiency of the system.
Suppose, now, that it is required to lase the $i \rightarrow j$ transition one wishes that a large portion of $1/\tau_R$ goes into $1/\tau_{i,j}$. This means that the branching ratio $\beta_{i,j}$, defined as the fraction of the total photon flux that are emitted through the $i \rightarrow j$ transition, should be as large as possible:

$$\beta_{i,j} = \frac{\tau_R}{\tau_{i,j}} \quad (1.14)$$

If in addition the laser cavity has length $L$ with end mirrors of reflectivity $R_1$ and $R_2$, the laser material achieves threshold (losses balance the gain) when the population inversion between the $i$ and $j$ levels ($i>j$):

$$\Delta n_{i,j} = n_i g_j - n_j g_i \quad (1.15)$$

is such that:

$$R_1 R_2 \exp \left[ 2L (g - \alpha) \right] = 1 \quad (1.16)$$

where $\alpha$ is the loss coefficient of the laser medium and $g$ is the gain due to stimulated emission at the laser wavelength:

$$g = \sigma_{i,j} \Delta n_{i,j} \quad (1.17)$$

where $\sigma_{i,j}$ is the induced emission cross section of the $i \rightarrow j$
transition. Therefore the stimulated emission cross section is the gain per unitary population inversion.

The inverse process to stimulated emission is absorption in which an ion at the level \( j \) \((j<i)\), excited by a photon of energy \( h \nu_{ij} \) equal to the energy difference between the \( j \) and \( i \) levels is raised to the level \( i \).

The intensity \( I_{ij}(x) \) of the monocromatic light of frequency at the distance \( x \) from the surface of incidence is:

\[
I_{ij}(x) = I_{ij}(0) \exp\left(-K_{ji} x\right)
\]  

(1.18)

where \( I_{ij}(0) \) is the intensity of the incident light.

\( K_{ji} \) is the absorption coefficient and it is defined as:

\[
K_{ji} = -\sigma_{ji} \Delta n_{ij}
\]  

(1.19)

where \( \sigma_{ji} \) \((j<i)\) is the absorption cross section and \( \Delta n_{ij} \) the population inversion.

Detailed balance considerations require that the following relation holds for the \( i \rightarrow j \) transition:

\[
\sigma_{ij} g_i = \sigma_{ji} g_j
\]  

(1.20)

This relation allows one to find the absorption cross section once the stimulated emission cross section is known. Defining the effective induced emission cross section as the
induced emission cross section per unit ion population ($f_i=1$) we have:

$$(\sigma_{ij})_{\text{eff}} = f_i \sigma_{ij}$$  \hspace{1cm} (1.21)

If absorption takes place from the ground state multiplet and we assume low pumping levels ($N_j=N_{\text{tot}}$) the absorption coefficient satisfies the property:

$$K_{ji} = \sigma_{ji} N_{\text{tot}} f_j$$  \hspace{1cm} (1.22)

where $f_j$ is the fractional population of the level $j$ in the ground multiplet and $N_{\text{tot}}$ is the total ion concentration in the crystal.

Combining (1.21) and (1.22) we can easily get:

$$K_{ji} = \frac{f_i}{f_i} \frac{g_i}{g_j} (\sigma_{ij})_{\text{eff}} N_{\text{tot}}$$  \hspace{1cm} (1.23)

The above relation can be used to calculate $K_{ji}$ once $(\sigma_{ij})_{\text{eff}}$ is known from the experiment. The important issue is to know how to calculate all these spectroscopic parameters from the analysis of measurements carried out on Tm:YLF crystals. This is the subject of next paragraph.
Figure (1.6) Typical energy level diagram of RE$^{3+}$ ions in crystals. An arbitrary level $i$ of the multiplet $I$ has degeneracy $g_i$, energy $E_i$, and fractional population $f_i$. A possible transition between the $i$ and $j$ levels is reported.
1.6 $\beta - \tau$ integral method applied to Tm:YLF

The calculation of the induced emission cross section, the branching ratios or other spectroscopic parameters discussed in paragraph (1.5) from the analysis of the fluorescence spectra is dependent on the particular structure of the crystal to be investigated.

For instance the tetragonal symmetry of YLF produces different polarized fluorescence and absorption spectra, depending if $\vec{E} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$ ( $\pi$ polarization ) or $\vec{E} \perp \vec{c}$ and $\vec{H} \parallel \vec{c}$, being $\vec{c}$ the direction of the optical axis of the crystal. Obviously this is not expected in crystals having cubic symmetry, since in this case both $\pi$ and $\sigma$ spectra should be coincident.

The method used in this study to calculate the effective induced emission cross section for a given transition in Tm:YLF is a generalization to a tetragonal crystal of the method discussed in (15) for Nd:YAG.

We start considering the case of steady state pumping of the $I$ multiplet with spontaneous emission occuring to a set of lower multiplets $J$ ( $J < I$ ) (see figure (1.6)). Following Mc-Cumber (16) we define a spontaneous emission $A_{ij}^{(w)}(\vec{K},\nu)$ function such that $A_{ij}^{(w)}(\vec{K},\nu)d\Omega d\nu$ is the probability per unit time that a photon, associated to the $i \rightarrow j$ transition is emitted in the direction of the unit vector $\vec{K}$ into the solid angle $d\Omega_\vec{K}$, within the frequency interval $d\nu$ around $\nu$ and
with one of the two possible independent polarizations $(d=x, y)$.

According to its definition (1.12) the radiative lifetime of the multiplet $I$ satisfies the condition:

$$\frac{1}{\tau_R} = \sum_{\kappa} \left( \sum_{i,j} A_{ij}^{(d)}(x, \nu) d\Omega_{k,d} d\nu \right)$$

where the sum $\sum_{\kappa}$ is carried out over both states of polarization and $\sum_{i,j}$ over all possible $i \rightarrow j$ transitions between levels of the multiplet $I$ and its lower multiplets $J$ ($J < I$). The observed spectral fluorescence intensity of the $i \rightarrow j$ transition is given by:

$$I_{ij}^{(d)}(x, \nu) d\Omega_{k,d} d\nu = G n_i A_{ij}^{(d)}(x, \nu) h \nu d\Omega_{k,d} d\nu$$

(1.25)

being $n_i$ the population density of the upper level $i$ and $G$ a calibration factor representing the fraction of fluorescence collected by the detection system.

Dividing both sides of (1.25) by $h \nu$, carrying out the integration in $d\Omega_{k,d}$ and $d\nu$ and finally summing over all possible $i \rightarrow j$ transitions and the two states of polarization (1.25) becomes:

$$\frac{G N_k}{\tau_R} = \sum_{\kappa} \left( \sum_{i,j} I_{ij}^{(d)}(x, \nu) d\Omega_{k,d} \frac{d\nu}{hn} \right)$$

(1.26)

where $I_{ij}^{(d)}(x, \nu)$ represents the fluorescence signal.

So that replacing (1.26) into (1.25) we finally get:
\[ A_{ij}^{(\omega)}(k', \nu) = \frac{I_{ij}^{(\omega)}(k', \nu)}{\iota k h \nu \tau_R \left[ \sum_i \left( \sum_j I_{ij}^{(\omega)}(k', \nu) d\Omega_R \frac{d\nu}{h \nu} \right) \right]} \] (1.27)

The reader is referred to Appendix A for the evaluation of the integral \( I = \sum_i \left( \sum_j I_{ij}^{(\omega)}(k', \nu) d\Omega_R \frac{d\nu}{h \nu} \right) \) in the case of a tetragonal crystal.

Assuming that only electric dipole transitions are allowed in the observed fluorescence spectra it is shown there that:

\[ I = \frac{8 \pi}{3} \left( [I^{(\pi)}(\nu) + 2 I^{(\sigma)}(\nu)] \frac{d\nu}{h \nu} \right) \] (1.28)

where \( I^{(\pi)}(\nu) \) and \( I^{(\sigma)}(\nu) \) are the total fluorescence signals respectively for purely \( \pi \) and \( \sigma \) polarized radiation and the integral is carried out over the entire fluorescence spectrum. Under these conditions (1.27) can be rewritten:

\[ A_{ij}^{(\omega)}(k', \nu) = \frac{I_{ij}^{(\omega)}(k', \nu)}{\iota k h \nu \tau_R \frac{8 \pi}{3} \left( [I^{(\pi)}(\nu) + 2 I^{(\sigma)}(\nu)] \frac{d\nu}{h \nu} \right)} \] (1.29)

The stimulated emission cross section \( \sigma_{ij}^{(\omega)}(k', \nu) \) is related to the spontaneous emission function \( A_{ij}^{(\omega)}(k', \nu) \) by:

\[ \sigma_{ij}^{(\omega)}(k', \nu) = \frac{c^2}{n^2 \nu^2} A_{ij}^{(\omega)}(k', \nu) \] (1.30)

Using (1.28) and converting to wavelength units relation (1.30) becomes:

\[ \sigma_{ij}^{(\omega)} = \frac{5}{6 \pi n^2 \tau_R \iota k} \int \frac{I_{ij}^{(\omega)}(\lambda)}{[I^{(\pi)}(\lambda) + 2 I^{(\sigma)}(\lambda)] \lambda} d\lambda \] (1.31)
The effective induced emission cross section \( \sigma_{ij}^{\text{eff}} \) is obtained from (1.31) assuming that \( f_i \) is equal to 1. This quantity is going to be calculated from the analysis of the polarized fluorescence spectra.

The fraction of the total photon flux from the multiplet \( I \) which goes into the multiplet \( J \) for a given polarization \( \alpha \) defines the branching ratio \( \beta_{I \rightarrow J}^{(\alpha)} \) (see (1.14)).

Experimentally this quantity is determined by the integration over the relative fluorescence spectra:

\[
\beta_{I \rightarrow J}^{(\alpha)} = \frac{C^{(\alpha)} \int_{I \rightarrow J} I^{(\alpha)}(\lambda) \lambda \, d\lambda}{\int \left[ I_{\pi}(\lambda) + 2 I^{(\sigma)}(\lambda) \right] \lambda \, d\lambda} \tag{1.32}
\]

The integration at the numerator is carried out numerically over the entire fluorescence spectrum produced by the \( I \rightarrow J \) transition, while \( C^{(\pi)} = 1 \) and \( C^{(\sigma)} = 2 \).

Note that these derivations have been carried out assuming that all possible transitions are electric dipole in nature. As already shown this may not be the case if, for instance, the transition between multiplets is such that \( \Delta J = \pm 1 \).

In this case magnetic dipole transitions are allowed.

Since the magnetic dipole moment is orthogonal to the direction of the electric field of the emitted radiation, while the electric dipole moment is parallel to it we can obtain the stimulated emission cross section and the branching ratio for a given transition directly from (1.31) and (1.32) simply switching \( I^{(\pi)} \) with \( I^{(\sigma)} \) in the integral at the
denominators and the corresponding values of $C_{(d)}^{(d)}$.

It is therefore important to distinguish experimentally between electric and magnetic dipole transitions. This is accomplished by comparing the $\pi$ and $\sigma$ spectra with those ones obtained when the crystal is rotated such that the direction of propagation of the light $\vec{K}$ coincides with the $\vec{c}$ axis of the crystal ($\delta$ spectra). If the transition is electric dipole in nature the $\sigma$ polarized lines will show up in the $\delta$ spectrum and the latter one will be just a replica of the $\sigma$ spectrum. On the other hand if the transition is magnetic dipole only $\pi$ lines will appear in the $\delta$ spectrum.

Therefore it is possible to check the nature of a given transition from the analysis of the absorption or fluorescence spectra by comparing the $\pi$ and $\sigma$ lines with the $\delta$ lines.

If it has been established experimentally that electric and magnetic dipole transitions at the same time produce the observed spectra (1.31) and (1.32) can still be used once the integral at the denominator is replaced with:

$$I = \frac{3\pi}{\hbar} \left[ \int_{\text{dir. dip.}} \left( I_{\pi}^{(d)} + 2 I_{\sigma}^{(d)} \right) d\lambda + \int_{\text{magn. dip.}} \left( I_{\pi}^{(d)} + 2 I_{\sigma}^{(d)} \right) d\lambda \right] \tag{1.33}$$

In our analysis it has been shown that only electric dipole transitions are allowed therefore (1.31) and (1.32) are used to calculate $(\phi_{e_i}^{(d)})$ and $\beta_{I \to J}^{(d)}$. 
2.1 Crystal Growth of Tm$^{3+}$:YLF crystals.

The Tm$^{3+}$ crystals used in this study were grown from the melt in a purified argon atmosphere using a computer controlled modified Czochralski/ top seeded method by the MIT Center for Materials Science and Engineering Crystal Growth Facility (18),(22).

The concentration of the dopant ion in a crystal is given by:

$$C_s = Kc_0 (1-g)^{-1} \quad (2.1)$$

where $c_0$ is the initial concentration of the dopant in the melt, $g$ the fraction of the melt which has been solified. $K$ is the segregation coefficient defined as the ratio of the dopant concentration in solid to the concentration in the melt, that is:

$$K = C_{solid}/C_{melt} \quad (2.2)$$

Since $K$ results close to one for Tm$^{3+}$ in YLF the dopant concentration in the crystal was assumed to be the same as in the melt.

Tm$^{3+}$ goes substitutionally into the Y$^{3+}$ sites in YLF.

Tm$^{3+}$:YLF crystals of 0.5, 1 and 10 at % Tm$^{3+}$ concentration
were grown along the a axis direction. All crystals were cut with two faces perpendicular to the c axis and were optically polished. All crystals were of high optical quality.
2.2 Fluorescence measurements.

Figure (2.1) shows the experimental set up used for the fluorescence spectroscopy. Fluorescence measurements were taken by exciting the sample with the 796 nm line of a GaAlAs Cw gain guided laser diode, which directly pumps the $^3H_4$ multiplet from $^3H_6$.

Figure (2.2) displays the observed light-current response. The diode laser was always operated at 600 mA and its output power was around 250 mW.

The fluorescence from the sample was focused on the entrance slit of a Mc-Pherson 0.3 meter spectrometer with interchangeable gratings.

The light entering the entrance slit was mechanically chopped by a HMS chopper operating at 200 Hz and polarized in the desired direction by a calcite polarizer.

The spectrometer transmits only a particular wavelength component of the beam to the exit slit, by using a diffraction grating as dispersive element. The grating was rotated by a stepping motor to scan a desired wavelength range. To prevent detection of the overlapping fluorescence from scattered light or high order grating responses convenient corning glass filters were used.

At the same time the use of different gratings was required depending on the wavelength region of interest.

In the region between 700 - 2000 nm a 600 grooves/mm grating
was used. This grating is blazed at 1600 nm and its linear dispersion is 53.1 Å/mm. The region between 2000 and 2600 nm was investigated using a 300 grooves/mm grating, whose blaze wavelength is 3000 nm and linear dispersion 106.1 Å/mm. The region of interest was split in three parts, where a convenient filter and grating were used as shown in table (2.1). For detection a dry - ice cooled RCA 7012 photomultiplier ( S - 1 type ) was used in the 700 - 1000 nm region and a liquid - nitrogen cooled In - As diode detector was employed in the 1000-2600 nm region.

The signal from the photodetector was sent to PAR-5301 lock-in amplifier. A reference signal at the chopper frequency ( 200 Hz ) was simultaneously supplied by the chopper controller. The lock-in amplifies the detector signal and mixes it with the reference signal. The use of low pass filters reduces noise ( the time constant used was 0.3 sec ) from the spectrum and allows collection of only those data arriving at the reference frequency.

Since the observed fluorescence was very weak (specially for the ^3H_s --> ^3H_u transition ) a slit width of 0.5 mm was chosen to increase the signal to the noise ratio. The resolution achieved was, therefore, 2.5 nm in the 700 - 2000 nm and 5.3 nm in the 2000-2600 nm region. A Data General Nova computer was used for data storage and further analysis of the fluorescence spectra.

When low temperature measurements ( 77 K ) were required
a variable temperature Janis optical dewar was used. A temperature controller allowed control of the temperature to better than 1 K, as long as the liquid nitrogen flow was kept constant.

The crystal used for the fluorescence measurements had 1 at % Tm³⁺ concentration.

All fluorescence spectra were corrected for the relative spectral response of the detecting system used. This was achieved by using an EPI - 1363 tungsten lamp placed at 50 cm from the entrance slit of the spectrometer and operated at 8.3 amps. The light of this lamp was apertured and reflected into the entrance slit by a MgSO₄ diffusive reflector.

Special attention was paid to the dependence of the grating spectral responsivity on the state of polarization of the incident light. In order to use just one spectral responsivity for both Π and Φ spectra the sample was mounted with the c axis oriented at 45 degrees with respect to the direction of the grating grooves, while the polarizer direction was oriented either along the c axis ( Π spectrum ) or perpendicular to it ( Φ spectrum ).

Under these conditions the direction of the polarizer was symmetric with respect to the direction of the grooves (45 degrees) and only one system response spectrum was required to analyze the data. All spectral response data were run with the polarizer oriented 45 degrees with respect to the direction of the grooves and in exactly the same conditions already described for each run.
Figure (2.3) shows the spectral responsivity curves so obtained. Note the presence of water absorption lines in the regions around 1400, 1900 and 2200 nm. These lines were determined to be of no importance in our analysis since the observed peaks do not lie in these regions.

The fluorescence spectra corrected for the spectral responsivity (see appendix B) were obtained by dividing the observed fluorescence spectra by the spectral responsivity spectra for each state of polarization.
Figure (2.1) Experimental Set-up used to obtain the fluorescence spectra.
Figure (2.2) Observed light-power response of the GaAlAs diode laser used in fluorescence measurements.
<table>
<thead>
<tr>
<th>Wavelength region</th>
<th>Filter</th>
<th>Grating</th>
<th>Reciprocal dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 - 1300</td>
<td>RG645</td>
<td>600 gr/mm</td>
<td>53.1 A/mm</td>
</tr>
<tr>
<td>1200 - 2100</td>
<td>RG1000</td>
<td>600 gr/mm</td>
<td>53.1 A/mm</td>
</tr>
<tr>
<td>2000 - 2600</td>
<td>Germanium</td>
<td>300 gr/mm</td>
<td>106.1 A/mm</td>
</tr>
</tbody>
</table>

Table (2.1) Filters and gratings used in the 700 - 2600 nm wavelength region for the fluorescence measurements. The linear dispersion of each grating is also reported.
Figure (2.3) Spectral responsivity spectrum of the detecting system used in the fluorescence measurements.
2.3 Lifetime measurements

The experimental setup used to make lifetime measurements is shown in figure (2.4). The fluorescence lifetime was measured by using a Molelectron DL-II tunable dye pulsed laser, pumped by a Nitrogen laser. Its pulse duration was around 10 - 20 nanoseconds and the pumping was selected by choosing a convenient dye ( RB + NBAP ), whose power energy spectrum matches an absorption line of the multiplet to be pumped.

The Tm⁺⁺ ions were excited from the ground state multiplet to the ³F₃ (λ = 690 nm).

The ³F₃ multiplet decays very rapidly (τ << 10 us) by multiphonon relaxation to the ³H₄ multiplet providing this way an efficient feeding of this multiplet.

The lifetime of the ³H₄ multiplet was measured by observing the fluorescence decay of the ³H₄ → ³H₆ transition by using an 800 nm interference filter in combination with a dry ice cooled RCA 7102 photomultiplier (S-1 type). A long pass filter RG1000 together with a liquid nitrogen cooled In-As detector were used to measure the lifetime of the ³F₃ level by observing the fluorescence decay of the ³F₃ → ³H₆ transition. This measurement was also made by pumping the ³F₃ multiplet.

A PAR 113 wideband (dc-300 kHz) low noise preamplifier was
used to amplify the signal, while the averaging and processing were carried out by a data 6000 waveform analyzer.

The samples used had different concentration (0.5, 1 and 10 at % Tm concentration) to study the dependence of the fluorescence lifetime on concentration.
Figure (2.4)  Experimental set up used for lifetime measurements.
2.4 Absorption Measurements.

The absorption measurements were all performed using a Perkin - Elmer Lambda 9 UV/VIS/NIR Spectrophotometer (23). This instrument features a double beam, double monochromator optical system.

The beam, produced by a halogen lamp in the VIS/NIR region, is dispersed by two holographic gratings (1440 lines/mm in VIS and 360 lines/mm in the NIR region) and conveniently filtered so that a near monochromatic beam is produced. A chopper splits this beam in a reference beam and a sample beam.

The radiation passing through the sample and the reference beam are detected by a photomultiplier in the visible, while a PbS detector is used in the near infrared region.

Prior to the absorption measurements a background correction was run in the same conditions the absorption spectra were taken to set the zero baseline.

If \( I_0 \) is the intensity of the reference beam and \( I \) that one of the transmitted beam the absorption coefficient is obtained as function of the wavelength from the ratio:

\[
K = \frac{\log_{10}(I_0/I)}{(\log_{10} e) d}
\]
where \( d \) is the sample thickness.

The absorption spectra in the region of the \( ^3H_4 \) multiplet were made in both states of polarization \( \Pi \) and \( \sigma \) using a 1\% at Tm\(^{3+}\):YLF crystal at room temperature.

The slit width was fixed to 1 nm resolution and scanning speed of 30 nm/min was chosen together with a response time of 1 sec. In addition the \( \delta \) spectra were run to check the nature of the transitions.

The \( \Pi \), \( \sigma \) and \( \delta \) absorption spectra in the region of the \( ^3F_4 \) multiplet (1500 - 2100 nm) were run in the same conditions. Only the slit width was adjusted as function of the wavelength to keep the PbS detector sensitivity fixed to a value of 2.
Chapter III

Analysis of the results

3.1 Analysis of the lifetime measurements.

Table (3.1) shows the measured fluorescence lifetime of the $^3\text{H}_4$ multiplet of Tm$^{3+}$ in YLF observed for different Tm$^{3+}$ concentrations (0.5, 1 and 10 at%) at 300 and 77 K. The room temperature dependence of the $^3\text{H}_4$ fluorescence lifetime on Tm concentration is shown in figure (3.1).

The decrease of the fluorescence lifetime of this multiplet at increasing concentration is due to a non radiative de-excitation which proceeds by the cross relaxation process (called concentration quenching) ($^3\text{H}_4$, $^3\text{H}_4$) $\rightarrow$ ($^3\text{F}_4$, $^3\text{F}_4$) (see figure (1.2)), producing two Tm ions excited into $^3\text{F}_4$ from a ($^3\text{H}_4$, $^3\text{H}_4$) pair.

Because concentration quenching is a non radiative process the fluorescence signal becomes very weak at high Tm$^{3+}$ concentrations making the detection very difficult. The fluorescence lifetime at low concentration has mainly a radiative component ($\tau_R$ is assumed to be 2.05 ms at room temperature). In addition $\tau_f$ ($^3\text{H}_4$) is not strongly dependent on temperature between 77 and 300 K.

The observed fluorescence decay of the $^3\text{F}_4$ multiplet is
strictly speaking exponential indicating that no energy
transfer process takes place in this case, as expected.
The radiative lifetime is, therefore, considered to be equal
to the observed fluorescence lifetime of the 1 at % Tm sample,
that is $\tau_R = 13.5$ ms at 300 K and $\tau_R = 16.5$ ms at 77 K.

The $^3H_5$ multiplet decays directly to $^3F_4$ by multiphonon
relaxation. No direct measurement of its fluorescence
lifetime has been made, but relation (1.7) was used to
estimate its value. As already discussed in paragraph (1.5)
the multiphonon relaxation rate of a level depends
exponentially on the energy gap between this level and the
next lower one and it is an intrinsic property of the host
material.

Figure (3.2) shows the observed energy gap dependence of
the multiphonon relaxation rates in YLF. From this figure it
is easy to calculate the following values of the constants
and B appearing in (1.7): $\alpha = 3.4 \times 10^{-3}$ (cm) and
$B = 3.8 \times 10^7$ (sec$^{-1}$).

Considering, now, that the energy gap between the $^3H_5$ and the
$^3H_4$ multiplets amounts to be 2309 cm$^{-1}$ the fluorescence
lifetime of the $^3H_4$ multiplet is 67 ms. This very short
lifetime is typical of levels decaying by multiphonon
relaxation.
fluorescence lifetime vs. at % Tm

for Tm:YLF at 300 K.

Figure (3.1)

Room temperature fluorescence lifetime of the $H_4^-$ multiplet as function of Tm concentration observed in Tm:YLF.

- Experimental data
- Other sources: M.D. Thomas, Sanders Associates, Inc.
Figure (3.2) Energy gap dependence of the Multiphonon Relaxation Rates in YLF.
<table>
<thead>
<tr>
<th>x at %</th>
<th>T(300 K)</th>
<th>T(77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.10 ms</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.05 ms</td>
<td>2.40 ms</td>
</tr>
<tr>
<td>1.0</td>
<td>1.34 ms</td>
<td>1.20 ms</td>
</tr>
<tr>
<td>5.0</td>
<td>66.0 us</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>25.0 us</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>8.5 us</td>
<td>6.1 us</td>
</tr>
</tbody>
</table>

Table (3.1)

Fluorescence lifetime of the $^3$H$_4$ multiplet observed at 300 and 77 K for different Tm concentrations.

- □ experimental data
- □ other sources (M.D. Thomas, Sanders Associates Inc.)
3.2 Analysis of the absorption spectra.

The room temperature absorption spectra in the wavelength region of the \( ^3\text{H}_4 \) multiplet are shown in figure (3.3) for both the \( \Pi \) and \( \sigma \) polarization.

The similarity between the \( \sigma \) and \( \delta \) spectra (see figure (3.4)) confirms that all the transitions are electric dipole type.

A comparison between the wavelengths of the observed absorption peaks with the wavelengths of the transitions allowed by the electric dipole selection rules helped us to single out those transitions responsible for producing the observed \( \Pi \) and \( \sigma \) lines.

The electric dipole selection rules applied to the \( S_2 \) symmetry allow three \( \Pi \) transitions from the \( ^1\text{I}_2 \) ground state to the three levels in \( ^3\text{H}_4 \), having energy 12825, 12741 and 12621 cm\(^{-1}\). Only two of these transitions are observed in the spectrum at 300 K and they have wavelengths respectively \( \lambda = 792 \) nm (0 \( \rightarrow \) 12621 cm\(^{-1}\)) and \( \lambda = 780 \) nm (0 \( \rightarrow \) 12825 cm\(^{-1}\)).

The strongest absorption line is centered at \( \lambda = 780 \) nm and the observed value of K is 1.06 cm\(^{-1}\). Considering that the Tm:YLF crystal used in these measurements had 1 % at Tm\(^{3+}\) concentration (\( N_{\text{cm}} = 1.38 \times 10^{20} \) cm\(^{-3}\)) the effective absorption cross section at 780 nm is \( 7.68 \times 10^{-21} \) cm\(^2\). This absorption
is particularly attractive for diode laser pumping because its linewidth of 8 nm full width half maximum is large compared to 1 nm for the strongest absorption line in Nd:YAG.

No \( \pi \) transitions to \(^3\!H_6\) from higher levels of \(^3\!H_4\) show up in the room temperature absorption spectrum. The \( \delta \) spectrum of the \(^3\!H_6\) multiplet has not well resolved lines to be discussed here. Figure (3.5) shows the two observed absorption transitions from \(^3\!H_6\) in Tm:YLF.

The absorption spectra of the \(^3\!F_4\) multiplet (1500 - 2100 nm) are shown in figure (3.6) and (3.7) at room temperature and figure (3.9) and (3.10) at 77 K respectively for both \( \pi \) and \( \delta \) polarization.

A room temperature \( \delta \) spectrum figure (3.8) once more confirms that all transitions are electric dipole in nature. In this case three \( \pi \) transitions are expected from the ground state to the \(^3\!F_4\) multiplet and they correspond to 5605, 5757 and 5967 cm\(^{-1}\) (\( \Gamma_2 \rightarrow \Gamma_1 \) transition).

In addition two \( \pi \) transitions should be observable from the second level of \(^3\!H_4\) (31 cm\(^{-1}\)) to the \(^3\!F_4\) manifold and their final levels have energy 5760 and 5977 cm\(^{-1}\).

All these lines appear in the \( \pi \) spectrum and the strongest observed line is produced by the 31 \( \rightarrow \) 5977 cm\(^{-1}\) transition (\( \lambda = 1682 \) nm) and its effective absorption cross section is \( 1.34 \times 10^{-20} \) cm\(^2\).

The absorption spectrum at 77 K shows better resolved lines with respect to the ones observed at room temperature.
Four lines are observed and the strongest one is centered at

\[ \lambda = 1682 \text{ nm} \] and its effective absorption cross section is

\[ \sigma_{\text{abs}} = 3.11 \times 10^{-20} \text{ cm}^2. \]

Since the multiplet \(^3 F_4\) contains only two levels \( \Pi_{3,4} \) (5760 and 5977 cm\(^{-1}\)) only 2 \( \sigma \) lines are possible from the ground level of \(^3 H_6\).

At the same time 5 \( \sigma \) lines are generated by electric dipole transitions from the first excited level (31 cm\(^{-1}\)) in \(^3 H_6\). Therefore 7 \( \sigma \) lines are possible from the first two levels of \(^3 H_6\). All of them are observed at 77.

The strongest line is centered at 1737 nm and it is produced from the 0 --> 5760 cm\(^{-1}\) transition. Its effective absorption cross section is \[ \sigma_{\text{abs}} = 1.19 \times 10^{-20} \text{ cm}^2 \] and it is not shifted as function of temperature. Figure (3.11) shows all transitions observed at 77 K.
Figure 3.3: Room temperature absorption spectra in the wavelength region of the $3_{H_4}$ multiplet observed in Tm:YLF. 

---

ABS. COEFF. (1/cm)
ABS.COEFF. TM(1%) YLF 300 K

Figure (3.4). Room temperature absorption spectrum in the wavelength region of the $^3H_4$ multiplet observed in Tm:YLF.
Figure (3.5) \( \Pi \) transitions observed at room temperature in the wavelength region of the \( ^3H_4 \) multiplet. The strongest line is observed at \( \lambda = 780 \) nm (marked arrow) and \( \sigma_{ab} = 7.6 \times 10^{-21} \text{ cm}^2 \).
Figure (3.6) Room temperature Ti absorption spectrum observed in the wavelength region of the $^{3}P_{4}$ multiplet in Tm:YLF.
Figure (3.7) Room temperature absorption spectrum observed in the wavelength region of the $^3H_4$ multiplet in Tm:YLF.
Figure (3.8) Room temperature absorption spectrum observed in the wavelength region of the $^{3}F_4$ multiplet in Tm:YLF.
ABS. COEFF. TM(1%):YLF 77 K

Figure (3.9) 6 absorption spectrum observed at 77 K in the wavelength region of the $^3P_4$ multiplet in Tm:YLF.
Figure (3.10) \( \Pi \) absorption spectrum observed at 77 K in the wavelength region of the \( ^3P_4 \) multiplet in Tm:YLF.
Figure (3.11)  $\sigma$ (a) and $\pi$ (b) electric dipole transitions producing the absorption lines observed in the wavelength region of the multiplet $^3P_4$ at 77 K. The strongest line is observed in the $\pi$ spectrum at $\lambda=1682$ nm (marked arrow) and its absorption cross section is $3.07 \times 10^{-20} \text{ cm}^2$. 
3.3 Evaluation of the effective induced emission cross section and branching ratios from the analysis of the fluorescence spectra.

The effective induced emission cross section of Tm:YLF in both states of polarization was obtained from the $\Pi$ and $\sigma$ fluorescence spectra, corrected for the spectral responsitivity of the detecting system used, by adopting the $\beta-\tau$ integral method applied to a tetragonal crystal described in paragraph (1.6). Relation (1.31) shows the result of that analysis.

The main difficulty of this method is the determination of the radiative lifetime of the upper multiplet. Since the fluorescence lifetime is directly measurable from the experiment a knowledge of the quantum efficiency $\eta_R$ (see formula (1.13)) is required. Direct measurements of $\eta_R$ are often difficult and subject to error.

In our case, because of concentration quenching, the radiative lifetime of the $^3H_4$ multiplet was assumed to be coincident with the fluorescence lifetime observed for the the Tm:YLF crystal with 0.5% at Tm$^3$ concentration, that is $\tau_R = 2.05$ ms at 300 K (see Table (3.1)).

Since Tm$^{3+}$ ions excited at $^3F_4$ are expected to relax only by radiative decay to $^3H_4$, the radiative
lifetime of the $^3F_4$ multiplet was assumed to be coincident to the observed fluorescence lifetime, that is $\tau_K = 13.5$ ms at 300 K and 16.5 ms at 77 K.

The refractive index of Tm$^{3+}$:YLF was assumed to have the value 1.44. A numerical integration of each $\Pi$ and $\sigma$ fluorescence spectra in the entire wavelength region of interest (700 - 2600 nm) was also carried out to evaluate the integral (1.27) in the assumption that all transitions are electric dipole in nature.

The correct estimation of this quantity is of critical importance in evaluating $\sigma_{\text{eff}}$ from the fluorescence spectra. A wrong zero baseline or a non adequate truncation of the numerical integration can change its value significantly. Figures (3.12) to (3.14) display the polarized room temperature effective induced emission cross section spectra examined in the three regions from 700 to 900 nm, from 1200 to 1700 nm and from 2100 to 2600 nm. These regions correspond respectively to transitions from the $^3H_4$ multiplet to the $^3H_{5/2}$, $^3F_4$, and the $^3H_{5/2}$ ground manifold.

The $\sigma$ spectra were found to be identical to the $\sigma$ spectra showing once more that all transitions are electric dipole. The line having the highest value of $\sigma_{\text{eff}}$ at 300 K was observed in $\Pi$ spectrum of the $^3H_4 \rightarrow ^3H_{5/2}$ transition and it is centered at $\lambda = 2303$ nm ($\sigma_{\text{eff}} = 2.4 \times 10^{-20}$ cm$^2$) being the 12621 and 8285 cm$^{-1}$ the initial and final levels, respectively. The observed large linewidth (10 nm) of this
transition should be instrumental.

The $^3H_4 \rightarrow ^3H_5$ spectra were the most difficult to measure since the fluorescence signal was very weak. In order to increase the signal to the noise ratio a lower spectral resolution (5 nm) was used. An incorrect baseline of these spectra introduces an error of almost 7.5% in evaluating the integral (1.27). Taking all sources of error into account the relative error made in estimating $\sigma_{\text{eff}}$ in all the transitions from $^3H_4$ amounts to less than 13%.

The line having the second highest value of $\sigma_{\text{eff}}$ is produced by the $12644 \rightarrow 5760$ cm$^{-1}$ ($\gamma_{3/4} \rightarrow \gamma_{5/4}$) transition and it is peaked at $\lambda = 1452$ nm. The calculated value of $\sigma_{\text{eff}}$ is $0.8 \times 10^{-20}$ cm$^2$.

The total splitting of the $^3H_4$ multiplet is only 311 cm$^{-1}$ and all levels are significantly populated at room temperature. All the strongest lines in the polarized spectra originate from the two lower levels of the $^3h_4$ multiplet however.

One more wavelength region (1600 - 2000 nm) was investigated corresponding to transitions from $^3F_4$ to the ground state multiplet $^3H_4$. The $\sigma_{\text{eff}}$ spectra at 77 K and 300 K are shown in figure (3.15) to (3.18) for both $\pi$ and $\sigma$ polarizations.

Since at 77 K the first level of the $^3F_4$ multiplet has 84% of its total population, we expect that the strongest
fluorescence lines obtained in both $\Pi$ and $\sigma$ spectra are produced by transitions from this level (5605 cm$^{-1}$) to levels of the $^3H_6$ multiplet. Its irreducible representation is $\Gamma_1$ and only three $\Pi$ lines are allowed by the electric dipole selection rules ($\Gamma_1 \rightarrow \Gamma_2$).

Two of these lines were observed in the $\Pi$ spectrum at 77 K and they are centered at $\lambda = 1873$ and 1888 nm. The final states of the corresponding transitions are respectively the fourth (282 cm$^{-1}$) and the fifth (310 cm$^{-1}$) ones in $^3H_6$. The two $\sigma$ lines observed at $\lambda = 1794$ and 1912 nm correspond to transitions between the 5605 cm$^{-1}$ to 31 cm$^{-1}$ and 375 cm$^{-1}$ energy levels respectively.

All $\Pi$ and $\sigma$ lines observed in 1600 - 2000 nm region at 77 K are shown in figure (3.19).

The line having the highest value of $\sigma_{\text{eff}}$ at room temperature is the one peaked at $\lambda = 1912$ nm. Its value is $3.5 \times 10^{-21}$ cm$^2$. The linewidth is 20 nm at 300 K and it does not change at 77 K. The 77 K cross section has the higher value of $1.3 \times 10^{-20}$ cm$^2$ as expected by the increase of the 5605 cm$^{-1}$ level population. No shift of the 1912 nm line is observed between 300 and 77 K.

Broad lines due to vibronics appear in the spectra. These structures are due to the coupling of the 4f electrons with the lattice vibrations (9), which makes transitions in the joint electron - phonon system possible.

The $\Pi$ and $\sigma$ lines that are observed to be common
to the absorption and the fluorescence spectra can be used to check the experimental accuracy. The measured absorption coefficient ($K_{s, p}$) can be compared to the one calculated from relation (1.22) (which we call $K_{s, 10}$).

Table (3.2) lists the $\pi$ and $\delta$ lines common to both the absorption and fluorescence spectra, as well as the corresponding transitions, the calculated $\alpha_{\pi}$ and the temperature. Table (3.3) shows the obtained values of $K_{s, 10}$ and $K_{s, p}$ for each observed common transition. The absorption coefficient obtained by these two methods are in agreement within 10 %.

The branching ratios of each of the $\pi$ and $\delta$ transitions from the $^3H_4$ and $^3F_4$ levels obtained at 300 and 77 K are shown in table (3.4). Almost 75 % of the ions decaying radiatively from $^3H_4$ go to the $^3H_4$ multiplet, while the total feeding of the $^3F_4$ multiplet from $^3H_4$ is only 24 % at low Tm concentration ($x<1\%$) and room temperature.
Figure (3.12) Room temperature effective induced emission cross section spectra observed in the 700 - 900 nm wavelength region \((3\text{H}_4 \rightarrow 3\text{H}_5)\). Continuous curve is spectrum. Dashed curve is spectrum.
Figure (3.13) Room temperature effective induced emission cross section spectra observed in the 1200-1700 nm wavelength region ($^3P_4 \rightarrow ^3F_4$). Contious curve $\pi$ spectrum. Dashed curve $\sigma$ spectrum.
Figure (3.14) Room temperature effective induced emission cross section spectra observed in the 2100 - 2600 nm wavelength region ($^{3}H_{4} \rightarrow ^{3}H_{5}$).
Continuous curve "A" spectrum.
Dashed curve "6" spectrum.
Figure (3.15) Room temperature induced emission cross section measured in 1600-2000 nm region ($^{1}D_4 \rightarrow ^{3}H_6$).

\( \Pi \) spectrum.
Figure 3.17 Induced emission cross section measured in the 1600-2000 nm region at 77 K ($^3F_4 \rightarrow ^3H_6$). π spectrum.
Figure (3.18) Induced emission cross section measured in the 1600-2000 nm region ($^3F_4 \rightarrow ^3H_6$) at 77 K. 6 spectrum.
Figure (3.19) $^3\text{P}_4 \rightarrow ^3\text{H}_6$ electric dipole transitions observed in the $\Sigma$ (a) and $\Pi$ (b) fluorescence spectra at 77 K.
<table>
<thead>
<tr>
<th>T(K)</th>
<th>Transition</th>
<th>$\lambda$ (nm)</th>
<th>$\sigma_{\text{eff}}$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>5605 -- 31</td>
<td>1794</td>
<td>2.2 $10^{-20}$</td>
</tr>
<tr>
<td>77</td>
<td>5757 -- 0</td>
<td>1737</td>
<td>0.64 $10^{-21}$</td>
</tr>
<tr>
<td>77</td>
<td>5760 -- 31</td>
<td>1746</td>
<td>1.85 $10^{-21}$</td>
</tr>
<tr>
<td>300</td>
<td>5605 -- 31</td>
<td>1794</td>
<td>3.10 $10^{-21}$</td>
</tr>
<tr>
<td>300</td>
<td>12619 -- 0</td>
<td>792</td>
<td>4.3 $10^{-21}$</td>
</tr>
</tbody>
</table>

Table (3.2)  $\sigma$ and $\Pi$ lines observed in common in the fluorescence and absorption spectra. The corresponding transitions and are reported.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\lambda$ (nm)</th>
<th>$K_{\text{exp}}$(cm$^{-1}$)</th>
<th>$K_{\text{calc}}$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>1794</td>
<td>0.66</td>
<td>0.78</td>
</tr>
<tr>
<td>300</td>
<td>1794</td>
<td>0.23</td>
<td>0.25</td>
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<tr>
<td>77</td>
<td>1737</td>
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</tr>
<tr>
<td>300</td>
<td>1746</td>
<td>0.42</td>
<td>0.31</td>
</tr>
<tr>
<td>300</td>
<td>792</td>
<td>0.90</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table (3.3) Values of $K_{\text{exp}}$ (observed from the absorption spectra) and $K_{\text{calc}}$ (calculated from (1.22)).
<table>
<thead>
<tr>
<th>Transition</th>
<th>$\pi$</th>
<th>$\sigma$</th>
<th>$T(\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{H}_6$</td>
<td>0.33</td>
<td>0.42</td>
<td>300</td>
</tr>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{F}_4$</td>
<td>0.03</td>
<td>0.04</td>
<td>300</td>
</tr>
<tr>
<td>$^3\text{H}_4 \rightarrow ^3\text{H}_5$</td>
<td>0.08</td>
<td>0.09</td>
<td>300</td>
</tr>
<tr>
<td>$^3\text{F}_4 \rightarrow ^3\text{H}_6$</td>
<td>0.26</td>
<td>0.74</td>
<td>300</td>
</tr>
<tr>
<td>$^3\text{F}_4 \rightarrow ^3\text{H}_6$</td>
<td>0.25</td>
<td>0.75</td>
<td>77</td>
</tr>
</tbody>
</table>

**Table (3.4)** Calculated branching ratios as obtained from the numerical integration of both $\pi$ and $\sigma$ spectra using relation (1.32).
3.4 Conclusions.

The spectroscopic analysis carried out in this study indicates that Tm:YLF is suitable as a laser material for laser diode pumping.

The room temperature absorption spectra in the region of the $^3H_4$ multiplet exhibit two absorption lines at $\lambda = 780$ and 792 nm that can be directly diode pumped.
The fluorescence lifetime measurements helped us to determine how the $^3H_4$ multiplet relaxes as function of concentration.
The polarized fluorescence spectra allowed the calculation of the effective induced emission cross section of the transitions from the $^3H_4$ and $^3F_4$ multiplets and their branching ratios, while the electric dipole selection rules were used to find the levels involved in each observed line.
All this information is useful in establishing possible laser schemes initiating from levels in the $^3H_4$ and $^3F_4$ multiplets, having $^3H_4$ as a pump band.
Table (3.5) summarizes the spectroscopic properties of those transitions believed to have the highest potential in the 700 -2600 nm wavelength region, while figure (3.20) shows their initial and final levels.

Three transitions originate from the $^3H_4$ manifold.
The $^3H_4 \rightarrow ^3H_4$ transition peaked at $\lambda = 2303$ nm satisfies all requirements for cw room temperature operation at low Tm concentration. At less than 1 at % Tm, the radiative
lifetime of the \(^3\)H\(_6\) multiplet is essentially equal to its fluorescence lifetime (\(T_R = 2.05\) ms) and the radiative quantum efficiency is therefore practically 100%.

The \(^3\)H\(_6\) level decays rapidly by multiphonon relaxation so that its population is negligible. The relative large value of the effective induced emission cross section (\(\sigma_{\text{eff}} = 2.4 \times 10^{-20}\)) should also make threshold reasonably low at room temperature.

The slow decay of the \(^3\)F\(_5\) multiplet appears to be the main obstacle to obtain stimulated emission of the \(^3\)H\(_6\) \(\rightarrow\) \(^3\)F\(_5\) transition at 1452 nm. If the host was doped with Tb or Eu the \(^3\)F\(_5\) level would probably relax more rapidly, increasing the chances of cw operation. Since these ions have no multiplets in the energy region between the \(^3\)H\(_6\) and \(^3\)F\(_5\) manifolds the lifetime of the \(^3\)H\(_6\) multiplet should not be modified by introducing them in the host. However it must be determined first that these impurity ions do not have absorption lines around 2.303 nm for this scheme to work.

The last transition \(^3\)H\(_6\) \(\rightarrow\) \(^3\)H\(_6\) is centered at 792 nm. Since the terminal level is the lowest one in \(^3\)H\(_6\) a three level laser scheme is applicable in this case and is therefore not practical.

The \(^3\)F\(_5\) \(\rightarrow\) \(^3\)H\(_6\) transition exhibits a possible laser line at 1912 nm. Its lower level has the energy 357 cm\(^{-1}\) and a quasi three level laser scheme describes its laser operation. The low feeding efficiency of the \(^3\)F\(_5\) multiplet from \(^3\)H\(_6\) at
low Tm concentration (\( \eta = 0.24 \)) combined with the small value of the effective induced emission cross section (\( \sigma_{\text{eff}} = 3.5 \times 10^{-21} \text{cm}^2 \)) makes cw laser action difficult to achieve at room temperature.

The cascade laser scheme \(^3H_4 \rightarrow ^3H_6 (\lambda_1) \rightarrow ^3F_4 \rightarrow ^3H_6 (\lambda_2)\) at \( \lambda_1 = 2303 \) and \( \lambda_2 = 1912 \text{ nm} \) can be used to improve this feeding. Stimulated emission from the 2303 nm transition will increase the rate of radiative decay from \(^3H_4\) to \(^3H_6\) making the feeding efficiency of the \(^3F_4\) multiplet almost equal to 1. Concentration quenching of the \(^3H_4\) multiplet fluorescence lifetime at sufficiently high Tm concentration (\( x > 1 \% \)) should increase further this value to 2.

With the measured concentration dependence of this quenching it should be possible to predict the optimum concentration of Tm in YLF for this transition.

The long fluorescence lifetime of the \(^3F_4\) multiplet (13.5 ms at room temperature) suggest laser action of the 1912 nm transition under \( Q \) switching operation. In this application the optical \( Q \) of the cavity defined as the ratio between the stored energy and the round trip loss in the cavity is temporarily decreased so that threshold is prevented from occurring. During this period the population inversion of the laser material builds up to levels higher than its normal values allowing higher energy storage in the medium. This energy is proportional to the fluorescence lifetime of the upper laser level. When the \( Q \) factor is
turned up to its normal cavity values an higher power pulse is released. The 1912 nm line should be suitable for this kind of application particularly at low temperature.

Diode laser pumping is certainly a new way to expand the range of applications of solid state laser materials. A number of interesting topics concerning the possibility of broader wavelength selection, increased efficiency over flashlamps and improved frequency and power stability obtainable from these pumping sources still remain to be explored. Their solution as well as an expected decrease in diode laser costs may lead to a new era in solid state laser technology.
Figure (3.20)
Portion of the energy levels diagram of Tm:YLF. The transitions corresponding to \( \lambda \approx 792, 1452, 1912 \) and 2303 nm are shown.
<table>
<thead>
<tr>
<th>Transition</th>
<th>$\lambda$ (nm)</th>
<th>$\sigma_{em}$ $(10^{-20}\text{cm}^2)$</th>
<th>Upper level lifetime (ms)</th>
<th>Lower level lifetime (ms)</th>
<th>Total branching ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3H_4 \rightarrow ^3H_5$</td>
<td>2303</td>
<td>2.4</td>
<td>2</td>
<td>0.067</td>
<td>0.17</td>
</tr>
<tr>
<td>$^3H_4 \rightarrow ^3F_4$</td>
<td>1452</td>
<td>0.8</td>
<td>2</td>
<td>13.5</td>
<td>0.07</td>
</tr>
<tr>
<td>$^3H_4 \rightarrow ^3H_6$</td>
<td>792</td>
<td>0.41</td>
<td>2</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>$^3F_4 \rightarrow ^3H_6$</td>
<td>1912</td>
<td>0.35</td>
<td>13.5</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Table (3.5)

Spectroscopic properties of possible laser transitions from the $^3H_4$ and $^3F_4$ multiplets of Tm:YLF at room temperature and 1 at 8 Tm concentration.
Appendix A

Evaluation of the fluorescence integral for Tm:YLF.

To find out the directional and polarized dependence of the spontaneous fluorescence intensity for an uniaxial crystal like Tm:YLF let us define a spherical coordinate system for the direction of emission made up of the angle $\Theta$ between the unit vector $\vec{K}$ and the c axis, the angle $\Phi$ between the projection of $\vec{K}$ on a plane perpendicular to the c axis and some arbitrary direction on this plane (x axis). The orientation of polarization (transverse to $\vec{K}$) is given by the angle $\Psi$. This angle is defined in such a way that $\Psi = 0$ gives the $\sigma$ polarization, perpendicular to the c axis.

Figure (A.1) describe this coordinate system.

After some geometrical calculations one finds that the angular dependence of the fluorescence intensity given by electric dipole $i \rightarrow j$ transition ($\vec{E} \parallel \vec{p}, \vec{H} \perp \vec{p}$) is:

$$I_{ij}(\nu, \Theta, \Phi, \Psi) = I_{ij}^{(\sigma)} \left[ \cos^2 \Psi + \sin^2 \Psi \cos^2 \Theta \right] + I_{ij}^{(\pi)} \sin^2 \Psi \sin^2 \Theta \quad (A.1)$$

where $I_{ij}^{(\pi)}$ and $I_{ij}^{(\sigma)}$ are the spontaneous emission intensities respectively for pure $\pi$ and $\sigma$ polarized radiation. Notice that $I_{ij}$ does not depend on the angle $\Phi$ as it should be expected from symmetry considerations.
Relation (A.1) tells us that the angular dependence of
for \( \psi = 0 \) (\( \sigma \) polarization) is:

\[
I_{ij} (\psi, \Theta, \phi, 0) = I_{ij}^{(\sigma)} \quad (A.2)
\]

while that one for \( \psi = \frac{\pi}{2} \) (\( \pi \) polarization) is:

\[
I_{ij} (\psi, \Theta, \phi, \frac{\pi}{2}) = I_{ij}^{(\sigma)} \cos^2 \Theta + I_{ij}^{(\pi)} \sin^2 \Theta \quad (A.3)
\]

Since for a given \( i \rightarrow j \) transition we want to evaluate the
sum \( \sum_{\psi} I_{ij}^{(\psi)} (\psi, \Theta, \phi, \psi) d\Omega, \frac{d\psi}{h\psi} \) (\( \psi = 0 \Rightarrow \alpha = \sigma \)),
considering (A.2) and (A.3) this sum becomes:

\[
\int_0^{\infty} \frac{d\psi}{h\psi} \int_0^{2\pi} d\phi \int_0^{\pi} \left[ I_{ij}^{(\sigma)} (\psi) (1 + \cos^2 \Theta) + I_{ij}^{(\pi)} (\psi) \sin^2 \Theta \right] \sin^2 \Theta d\Theta \quad (A.4)
\]

After carrying out the integration we get:

\[
\frac{6\pi}{3} \int_0^{\infty} \frac{d\psi}{h\psi} \left[ I_{ij}^{(\pi)} (\psi) + 2 I_{ij}^{(\sigma)} (\psi) \right] \quad (A.5)
\]

If the \( i \rightarrow j \) transition is magnetic dipole in nature (\( \vec{E} \perp \vec{m} \)
and \( \vec{H} \parallel \vec{m} \)) the fluorescence intensity angular dependence is:

\[
I_{ij} (\psi, \Theta, \phi, \psi) = I_{ij}^{(\pi)} \left[ \cos^2 \psi + \sin^2 \psi \cos^2 \Theta \right] + I_{ij}^{(\sigma)} \sin^2 \psi \sin \Theta \quad (A.6)
\]

Carrying out the same sum and integration as before we get:

\[
\frac{6\pi}{3} \int_0^{\infty} \frac{d\psi}{h\psi} \left[ I_{ij}^{(\sigma)} + 2 I^{(\pi)} \right] \quad (A.7)
\]
Figure (A.1) Spherical coordinate system introduced to describe the fluorescence intensity of an uniaxial crystal. The direction of the c axis coincides with the z direction. The direction of the polarization $\mathbf{P}$ ($\mathbf{K} \perp \mathbf{P}$) makes an angle $\psi$ with the x axis, such that $\psi = 0$ gives the $\sigma$ polarization.

$\Theta$ is the angle between the z and $\mathbf{K}$ ($\mathbf{K}$ determines the direction of propagation of the emitted light), while $\phi$ is that one between the projection of $\mathbf{K}$ on the xy plane and the x axis.
Appendix B

Calibration of the fluorescence spectra.

The evaluation of the induced emission cross section of a given transition requires the knowledge of the fluorescence spectra corrected for the spectral responsivity of the set-up used to carry out these measurements. Paragraph (2.2) describes the experimental set up to evaluate the spectral responsivity. In this appendix we give the basic theory underlying this calibration.

Calling $T(\lambda)$ the spectral irradiance of the Tungsten lamp, $K$ the fraction of $T(\lambda)$ entering the entrance slit, $S(\lambda)$ the responsivity of the grating, $F(\lambda)$ the filter transmission and finally $D(\lambda)$ the detectivity of the detector used, the observed intensity is:

$$T_{\text{exp}}(\lambda) = K \ D(\lambda) \ S(\lambda) \ F(\lambda) \ T(\lambda) \quad (B.1)$$

(we assume that the polarizer has a flat response).

Defining the spectral responsivity:

$$\alpha(\lambda) = D(\lambda) \ S(\lambda) \ F(\lambda) \quad (B.2)$$

it follows:
\[ \alpha(\lambda) = \frac{T_{\text{exp}}(\lambda)}{K \cdot T(\lambda)} \quad (B.3) \]

Running a fluorescence spectrum we actually measure:

\[ I_{\text{exp}}(\lambda) = G \cdot \alpha(\lambda) \cdot I_{\text{true}}(\lambda) \quad (B.4) \]

where \( I_{\text{true}}(\lambda) \) is the observed intensity (Volts/nm), \( I_{\text{true}}(\lambda) \) is the true intensity and \( G \) the fraction fluorescence entering the slit. So that:

\[ I_{\text{true}}(\lambda) = \frac{I_{\text{exp}}(\lambda)}{G \cdot \alpha(\lambda)} \quad (B.5) \]

From (B.5) it follows that it is necessary to know \( \alpha(\lambda) \) in order to find the true spectral fluorescence intensity.

Obviously these spectra are not absolute since we don't know the geometrical factors \( G \) and \( K \). On the other hand we are interested in our analysis to relative quantities of the form:

\[ \frac{I_{\text{true}}(\lambda)}{\int I_{\text{true}}(\lambda) \cdot \lambda \, d\lambda} \quad (B.6) \]

therefore the knowledge of these parameters is not important at all.
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