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Optical properties of Tm^{3+} in the gehlenite matrix and sensitization of Ho^{3+} luminescence in potential Tm/Ho lasers

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Abstract

The Tm:Ho solid state lasers pumpable by laser diodes and emitting around 2.1 μm present interesting applications. In the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (CAS) gehlenite host, we have studied the Tm^{3+} emission, strongly dependent of the doping concentration, the Tm^{3+} - Tm^{3+} energy transfer leading to the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ broad emission [$\lambda_{\text{max}} = 1780 \text{ nm}$, using the [$^3\text{H}_4$, $^3\text{H}_6$] $\rightarrow$ [$^3\text{F}_4$, $^3\text{F}_4$] cross-relaxation scheme]. Furthermore, the Tm^{3+} - Ho^{3+} interactions have also been demonstrated in this study.

Introduction

In the recent years, considerable interest has been devoted to the 2 μm Tm, Ho solid state lasers pumpable by laser diodes which can be used in medicine and for LIDAR or military applications. In Tm/Ho doped crystals [1], Tm^{3+} acts as a sensitizer. When one Tm^{3+} ion is excited into the $^3\text{H}_4$ level, it gives rise through cross relaxation to two Tm^{3+} ions in the $^3\text{F}_4$ state which transfer their energy to the Ho^{3+} ions emitting around 2 μm . We are interested by the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (CAS) matrix with gehlenite structure which is a good host for lanthanides ions. Doped with Nd^{3+} ions, CAS has been demonstrated to lase [2] and to be suitable for diode pumping [3], since it presents broad absorption bands because of the existence of a structural disorder of this matrix. Significant amount of Tm^{3+} and Ho^{3+} can be substituted to Ca^{2+} in CAS while an equal number of Si^{4+} ions are replaced by Al^{3+} ions for charge compensation, leading to the formula $\text{Ca}_{2-x}\text{Ln}_x\text{Al}_{2+x}\text{Si}_{1-x}\text{O}_7$ with $\text{Ln}=\text{Tm}, \text{Ho}$. Rare-earth concentration of more than 10^{21} ions cm^{-3} ($x = 0.15$) can be obtained in Tm and Tm, Ho doped CAS crystals which have been grown by floating zone method in an arc-image furnace and by the Czochralski method.

$\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$ energy transfer

Absorption measurements under polarized light for Tm^{3+} in CAS, lead to the calculation of the Judd-Ofelt parameters ($\Omega_2 = 1.8 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.0 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.9 \times 10^{-20} \text{ cm}^2$) while the absorption at 4.2 K gives the energy levels diagram. From these values, the radiative lifetimes τ_{rad} and the branching ratio β_{IJ} are calculated. In

Table 1 are reported the variations of the experimental lifetimes of the fluorescent levels with the Tm^{3+} amount.

doping rate x	$\tau^1\text{D}_2$ (μs)	$\tau^1\text{G}_4$ (μs)	$\tau^3\text{H}_4$ (μs)
x = 0.001	21	255	264
x = 0.005	21	207	253
x = 0.02	19	145	189
x = 0.05	13	112	105
x = 0.10	7	45	34
x = 0.20	3	6	5
$\eta = (\tau_{\text{exp}}/\tau_{\text{rad}})$ for x = 0.001	33 %	35 %	21 %

Table 1 : Experimental lifetimes at different Tm^{3+} concentrations and radiative contribution η to the relaxation process.

For all the concentrations and the $^1\text{D}_2$, $^1\text{G}_4$ and $^3\text{H}_4$ emitting levels, strong lifetime variations occur with the concentration, revealing the cross-relaxation and energy migration effects. For instance, when Tm^{3+} is excited at 785 nm in the $^3\text{H}_4$ level which presents a broad absorption band (FWHM = 20 nm-see fig.1), the lifetimes decrease from 264 μs for the most diluted sample ($0.7 \cdot 10^{19} \text{ Tm}^{3+}$ ions cm^{-3}) to approximately 5 μs for $1.3 \cdot 10^{21} \text{ Tm}^{3+}$ ions cm^{-3} , showing cross-relaxation according to the scheme $[^3\text{H}_4, ^3\text{H}_6] \rightarrow [^3\text{F}_4, ^3\text{F}_4]$ and energy migration. From the lifetime measurements, one can estimate the cross-relaxation effect while $(1-(\tau_{\text{exp}}/\tau_{\text{rad}}))$ (table 1) gives the multiphonon non-radiative desexcitation probability for the diluted sample. In the Gehlenite host, strong non-radiative relaxations occur by the phonons [4]. The Tm^{3+} - Tm^{3+} cross-relaxation parameters are determined for the $^3\text{H}_4$ level. In this study, the R_0 parameter is found to be equal to 10.7 Å (leading to the formula $\text{Ca}_{1.947}\text{Tm}_{0.053}\text{Al}_{2.053}\text{Si}_{0.947}\text{O}_7$) and $C_{\text{DA}} = 0.69 \cdot 10^{-38} \text{ cm}^6 \text{ s}^{-1}$.

Fig 1: variation of the $^3\text{H}_4$ decay profiles with Tm^{3+} concentration ($\lambda_{\text{ext}}=785\text{nm}$, $\lambda_{\text{em}}=810\text{nm}$) and cross-relaxation scheme.

Fig 2: Emission spectra of Tm^{3+} :CAS in the visible range for x = 0.005 and x = 0.10 ($\lambda_{\text{ext}}=355 \text{ nm}$).

The cross-relaxation effect is also visible on the fluorescence spectra in the visible range (see fig.2). For the near infrared range, the intensity of the 3F_4 emission, measured on powdered samples, increases when cross-relaxation occurs and presents a maximum for a concentration of $3.3 \cdot 10^{20} \text{ Tm}^{3+} \text{ ions cm}^{-3}$ (see fig.3). The cross-relaxation which competes with the multiphonon relaxation in the lattice should decrease the heat released in the sample. For high Tm^{3+} content, reabsorption can occur and the excitation energy could migrate through the sample. Therefore, lifetimes of the 3F_4 level decrease from 2.2 ms to 0.3 ms (for $x = 0.02$ to $x = 0.2$ respectively). A decrease of the fluorescence intensity is also observed in the highly doped samples (see fig.3).

The emission band $^3F_4 \rightarrow ^3H_6$ is broad and is extended from 1.6 to 2 μm . It could be interesting for operating $\text{Tm}^{3+}:\text{CAS}$ as a quasi-four levels laser since the ground state splitting of Tm^{3+} in this host is around 808 cm^{-1} .

Fig.3 : fluorescence intensity of $\text{Tm}:\text{CAS}$ as a function of Tm^{3+} concentration ($\lambda_{\text{ext}}=785 \text{ nm}$, $P_{\text{ex}}=500 \text{ mW}$).

$\text{Tm}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer

The overlap between the Tm^{3+} emission spectrum ($^3F_4 \rightarrow ^3H_6$ transition) and the Ho^{3+} absorption spectrum ($^5I_8 \rightarrow ^5I_7$ transition) is significant and an efficient energy transfer between the two ions is observed (see figure 4). Under c.w. Ti : Sapphire laser excitation at 785 nm in the Tm^{3+} band, only the Ho^{3+} emission in the 1.8-2.1 μm range is observed fig.4-a (Tm^{3+} and Ho^{3+} concentrations of 6.6×10^{20} and $3.2 \times 10^{20} \text{ ions cm}^{-3}$ respectively). In that case the Tm^{3+} near infrared emission vanishes. When the Tm/Ho ratio increases up to a value of 10 (fig 4-b: $6.6 \times 10^{20} \text{ Tm}^{3+}$ and $0.7 \times 10^{20} \text{ Ho}^{3+} \text{ ions cm}^{-3}$) the Tm^{3+} emission is also present besides the Ho^{3+} one. $\text{Ho} \rightarrow \text{Tm}$ back transfer takes place and is temperature dependant as shown in fig 4-c.

Usually, one of the loss mechanisms in the $\text{Tm}-\text{Ho}$ system, which decreases the efficiency of the $\text{Tm} \rightarrow \text{Ho}$ energy transfer and increases the laser threshold is the

$[^3F_4, ^5I_7] \rightarrow [^3H_6, ^5I_5]$ up-conversion scheme [5,6]. This effect is not observed in the CAS laser material, mainly because of the short lifetime values of the 5I_6 and 5I_5 Ho^{3+} excited levels which are above the fluorescent 5I_7 one and because of the very weak absorption cross-section of these levels.

From the absolute fluorescence intensity of the $^5I_7 \rightarrow ^5I_8$ transition, it is possible to estimate the optimal doping concentrations of Tm^{3+} and Ho^{3+} in the CAS host. Laser oscillation from Ho^{3+} with a good tunability is expected to occur around $2.1\mu\text{m}$ in the $\text{Tm}:\text{Ho}:\text{CAS}$. In order to perform laser tests, single crystals of this material will be grown by the Czochralski method in our Laboratory.

Fig 4 : NIR emission in the $\text{Tm}:\text{Ho}:\text{CAS}$ under 785 nm excitation at 300 K [a) and b) : concentration effect (see text)] and [c) and d) : temperature effect].

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