

Spectral-luminescent properties of Tm:YLF crystal

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Abstract

Luminescence of Tm³⁺-doped YLF single crystals is analyzed with respect to intensity, Stark structure, transition probabilities and lifetime of separate levels in samples with different Tm concentration. The probabilities of the self-quenching process in this crystal are estimated both experimentally and theoretically. The possibility of diode-pumped IR lasing is considered.

Keywords: Luminescence; Self-quenching; lifetime

1. Introduction

Success in the development of high-power laser diodes attracts specific interest to RE-doped fluorides, since their narrow absorption bands perfectly match the radiation bands of laser diodes, making them promising both for laser-diode pumping and sensitization in infrared IR lasers.

When considering laser schemes in activated crystals, all the energy transfer processes involved in these schemes should be examined. To increase the populating efficiency for the working levels of laser transitions, non-radiative energy-transfer processes both between the co-doping and lasing ions and also between the activator ions themselves are extensively used nowadays. These processes are of most importance in crystals with high concentration of doping ions, because they induce not only quenching of one level and excitation of other levels, but also the processes from the excited states, in particular, up-conversion from the hidden levels of lasing ions. That is why, in this study, we estimate the probabilities of energy-transfer processes in the YLF crystals studied; namely, migration, self-quenching and up-conversion at non-linear coupling of the excited states of dopant ions.

2. Results and discussion

2.1. Studied object

Studies were performed on Tm:YLF crystals, which have recently attracted great attention as laser medium

in biological and medical research. These ions are highly suitable for 780-nm diode pumping and so can be used both as lasing ion and also as co-dopant for, for example, 2 μ m Ho:Tm:YLF lasers. The host crystal can be pumped directly by laser-diode radiation because the holmium ion does not have absorption bands matching laser-diode radiation.

The Tm ions in YLF crystals isooptically substitute yttrium ions up to 100% without worsening the crystal quality. YLF crystals are uniaxial, positive, with scheelite structure, space symmetry group is C_{6h} , point symmetry group at the Y³⁺ site is S_6 . Rare-earth ions have predominantly one structure type of impurity centers. The lines in the optical spectra are polarized, narrow, and inhomogeneously broadened.

The Tm Stark structure and crystal-field parameters, and the intensities of radiative transitions for Tm:YLF were reported in Refs. [1,2].

2.2. Experimental and calculation methods

In order to estimate the energy-transfer rates, we employed the method of second quantum-mechanical calculation whose possibilities were demonstrated in Refs. [3-7]. To use this method, information about the Stark structure of the levels, phonon spectrum, and inter-multiplet transition line strengths is required. Since the necessary parameters for the Tm:YLF crystals were described in the literature in insufficient detail, we have studied the absorption and IR emission spectra of Tm ions in YLF. Determining the oscillator strengths of the absorption transitions, we obtained the line strengths; the intensity parameters for the radiative

transitions between the excited 3F_4 states were calculated by the Judd–Ofelt method [8,9].

2.3. Absorption and luminescence spectra

Absorption spectra of annealed crystals were recorded in the 3800–38 300 cm^{-1} range, including also the superexcited transition in the 3P_2 state. Of great interest were transitions to the lower excited states 3H_4 , 3H_5 and 3F_4 , involved in the Tm IR laser schemes, and also in the laser-diode pumping of 2- μm Ho laser in co-doped $\text{Tm}_2\text{Ho}_2\text{YLF}$, since the Tm absorption band in the range 750–800 nm (3H_4 – 3H_5) perfectly matches the emission spectrum of the GaAlAs laser diode. The highest absorption cross-section which we obtained in Tm_2YLF ($\sigma = 0.64 \times 10^{-20} \text{ cm}^2$) belongs to the p-polarized 781-nm line (3H_4 – 3H_5) (see Fig. 1).

From the absorption spectra recorded, we determined the oscillators and line strengths for the transitions from the ground states. Using the calculated transition probabilities for the transitions between the excited states, we obtained the intensity parameters Q and then calculated the line strengths S for these transitions using the theoretical values of transition probabilities. Results obtained are shown in Table 1, in comparison with the results of Ref. [2].

These data were used for calculating the spectroscopic parameters of the energy-transfer process. Since the only

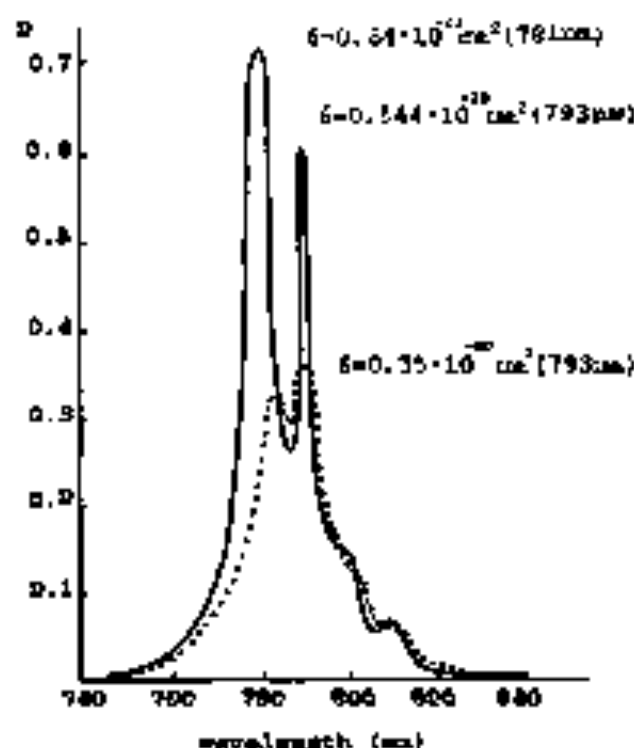


Fig. 1. Polarized absorption spectra of the 3H_4 – 3H_5 transition in $\text{Tm}_2(\text{Yb})\text{YLF}$ crystals: solid line, p-polarized, annealed line, s-polarized, quenched.

Table 1
Empirical parameters for Tm_2YLF crystals calculated from the absorption spectra Q , (10^{20} cm^2)

Q_1	Q_2	Q_3	Ref.
2.43	1.08	0.60	[2]
2.43	1.28	0.60	This work

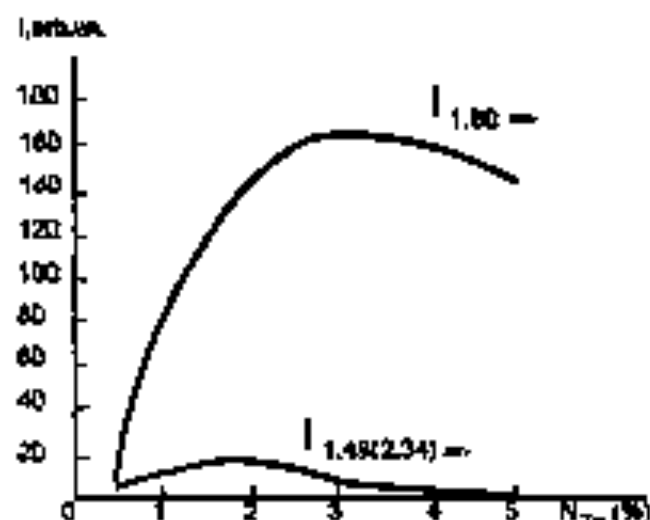


Fig. 2. Concentration dependence of the 1.88- μm (3F_4 – 3H_4) and 1.48- μm (3H_4 – 3F_4) luminescence intensity in Tm_2YLF crystal, T=300 K.

excited 3H_4 state is excited by 781-nm laser-diode radiation, we consider in detail the energy-transfer process involving this level.

We examined concentration dependences of Tm luminescence intensity for the transitions from the 3H_4 , 3F_4 and 3H_5 levels. In our experiments, crystals with 1, 2, 3 and 5 at.% of Tm with the dimensions $5 \times 5 \times 3 \text{ mm}^3$ were studied. Fig. 2 shows the experimental concentration dependences of the 1.88- μm (3F_4 – 3H_4) and 1.48- μm (3H_4 – 3F_4) luminescence transitions. The former corresponds to the transition from the 3H_4 state, interesting because the achievement of 2.34- μm Tm laser attracted great attention as a tool in medical and biological treatments. As is seen, the 1.88- μm and 1.48- μm transitions show maxima at different Tm concentrations. It is probably caused by redistribution of populations in 3H_4 and 3F_4 levels with Tm concentration and quenching of the 3H_5 level.

2.4. Luminescence kinetics, experimental self-quenching rates

Concentration dependence of the decay time of the 3H_4 level was measured for the same concentration series from the decay curves of luminescence at the exponential stages using the formula $I(t) = I_0 \exp(-t/\tau)$, where $\tau^{-1} = \tau_0^{-1} + B^{3H_4}$, the $\tau_0 = 1.5 \mu\text{s}$ value is the 3H_4 level lifetime measured at

0.5 at.% of Tm ($N = 7 \times 10^{18} \text{ cm}^{-3}$) and N^{3H_2} is the self-quenching rate. Experimental values of N^{3H_2} are listed in Table 2. As is seen (Fig. 3), the measured lifetimes fit the quadratic concentration dependence.

2.5. Calculations of the Tm:YLF energy-transfer microparameters and macrorate

As was noted, only the 3H_4 level is excited with 3H_1 -nan laser-diode pumping, from which the excitation decays via either non-radiative $^3H_4 \rightarrow ^3H_2$ or radiative $^3H_4 \rightarrow ^3H_2$, $^3H_4 \rightarrow F_4$ and $^3H_4 \rightarrow H_4$ transitions. An increase in the thulium concentration induces the probability of migration and self-quenching of the 3H_4 term due to the interionic coupling according to the following schemes:

- (i) $(^3H_4 \rightarrow ^3H_4) + (^3H_4 \rightarrow ^3H_4)$ — migration,
- (ii) $(^3H_4 \rightarrow F_4) + (^3H_4 \rightarrow F_4) + 2h\nu$ — self-quenching
- (iii) $(^3H_4 \rightarrow F_4) + (^3H_4 \rightarrow H_4) - h\nu$ — self-quenching

To estimate the energy-transfer microparameters for migration ($C_{\text{MIG}}^{\text{thul}}$) and self-quenching ($C_{\text{SQ}}^{\text{thul}}$), we used formulae (3) and (7) from Ref. [3]. The calculated values of the 3H_4 term in Tm:YLF are listed in Table 3.

As is seen, the migration microparameter for the 3H_4 term of Tm:YLF is $3.24 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$, considerably exceeding the self-quenching microparameters

Table 2
Calculated (N^{3H_2}) and experimental ($N_{\text{exp}}^{3H_2}$) self-quenching rates of the 3H_4 term in Tm:YLF

Crystal	Tm concentration		$N_{\text{exp}}^{3H_2}$ (s^{-1})	N^{3H_2} (s^{-1})
	$(10^{18} \text{ cm}^{-3})$	(at.%)		
Tm:YLF	1.4	1	296	225
	2.8	2	1182	882
	4.2	3	2470	1908
	7	5	5418	7938
	14	10	20400	$> 10^4$

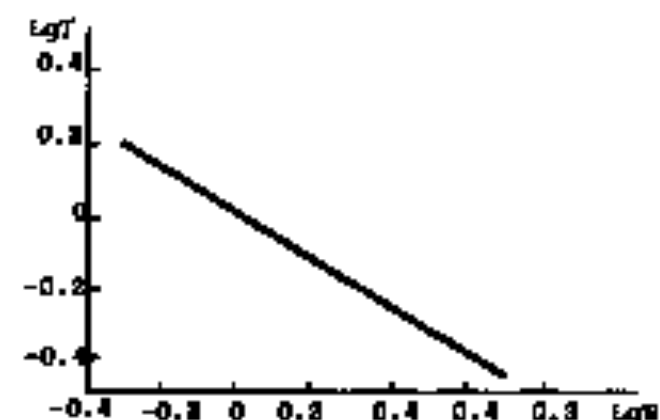


Fig. 3. Concentration dependence of the decay time of the 3H_4 level in Tm:YLF. $T = 300 \text{ K}$.

Table 3
Migration and self-quenching microparameters for Tm:YLF

No.	Process	Calc $C_{\text{MIG}} \times 10^{19}$ ($\text{cm}^3 \text{ s}^{-1}$)	Exp $C_{\text{SQ}} \times 10^{19}$ ($\text{cm}^3 \text{ s}^{-1}$)
(i)	Migration $(^3H_4 \rightarrow ^3H_4) + (^3H_4 \rightarrow ^3H_4)$	32.4	
	$(^3H_4 \rightarrow F_4) + (^3H_4 \rightarrow F_4)$	67.0	
(ii)	Self-quenching $(^3H_4 \rightarrow F_4) + (^3H_4 \rightarrow F_4) + 2h\nu$		0.59
(iii)	Self-quenching $(^3H_4 \rightarrow F_4) + (^3H_4 \rightarrow H_4) - h\nu$		0.591

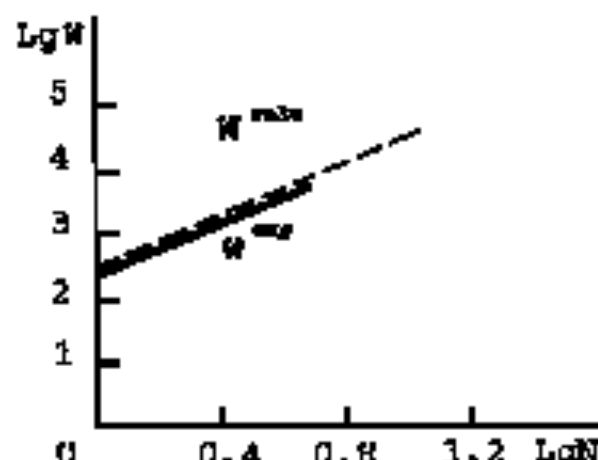


Fig. 4. Experimental (solid line) and calculated (dashed line) concentration dependences of the self-quenching rate N^{3H_4} of the 3H_4 term in Tm:YLF crystal, $T = 300 \text{ K}$.

for schemes (ii) and (iii), i.e. condition $C_{\text{MIG}} \gg C_{\text{SQ}}$ is fulfilled. Besides, the self-quenching is accompanied by generation of two phonons with energies more than 330 cm^{-1} in (ii), and by absorption of phonons 520 cm^{-1} in (iii), decreasing the probability of the latter is lower by more than an order of magnitude, $C_{\text{SQ}}^{\text{thul}}(\text{ii}) = 3.9 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ and $C_{\text{SQ}}^{\text{thul}}(\text{iii}) = 1.1 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$. Thus, the rate of self-quenching can be estimated by the hopping model [10]

$$N^{3H_4} = (49) \pi^2 (2s)^2 n^2 (C_{\text{MIG}} C_{\text{SQ}})^{1/2}$$

where the total rate $C_{\text{SQ}}^{\text{thul}}$ for processes (ii) and (iii) is $C_{\text{SQ}}^{\text{thul}} = 5.9 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$. The calculated self-quenching rates N^{3H_4} of the 3H_4 level for different thulium concentrations N are shown in Table 2. As is seen, the experimental self-quenching rates obtained from the luminescence decay curves and the calculated values are in good accord. Both experimental and calculated $N^{3H_4} = f(N_{\text{thul}})$ dependences are close to the quadratic law (Fig. 4), so that self-quenching of the 3H_4 level takes place together with migration. The rate of migration over the 3H_4 levels greatly exceeds that of self-quenching. The N^{3H_4} value is well described within the framework of the theory of self-quenching developed in Ref. [4,7].

An increase in thulium concentration in Tm:YLF will decrease the population of the 3H_4 level and increase that on the 3F_4 level via the $(^3H_4-^3F_4):(^3H_4-^3F_4)+2h\nu$ process, so that one absorbed pumping quantum will excite two thulium ions in the 3F_4 state, making this scheme promising for 1.88- μm Tm lasing and sensitizing of 2.0- μm Ho lasing in Tm,Ho:YLF crystals. The alternative processes to this case are sp-conversion and quenching by other impurities.

2.6. Up-conversion in Tm:YLF crystal

An increase in the pumped power density gives rise to the non-zero probability of non-linear processes related to the interaction of excited states. Here, we consider only sp-conversion from the 3F_4 level, since quenching of the 3H_4 state is very efficient in highly concentrated crystals and sp-conversion from this level can be neglected. We estimated the energy transfer via the $(^3F_4-^3H_4):(^3F_4-^3H_4)+2h\nu$ process under conditions Tm-Tm interaction. To estimate the effect and probability of sp-conversion, we once again use the model microcalculation method. Let us compare the calculated microparameter of migration and sp-conversion from the 3F_4 Tm level. The energy-transfer microparameter of the $(^3F_4-^3H_4):(^3H_4-^3F_4)$ migration is $C_{\text{TM}}^{\text{TM}} = 67 \times 10^{-21} \text{ cm}^2 \text{ s}^{-1}$, the calculated microparameter of $(^3F_4-^3H_4):(^3F_4-^3H_4)+2h\nu$ sp-conversion is $C_{\text{TM}}^{\text{TM}} = 8.5 \times 10^{-21} \text{ cm}^2 \text{ s}^{-1}$, thus $C_{\text{TM}}^{\text{TM}}/C_{\text{TM}}^{\text{TM}} = 79$, so that $C_{\text{TM}}^{\text{TM}} \gg C_{\text{TM}}^{\text{TM}}$. Therefore, limiting sp-conversion rate can be estimated by the hopping model using (1), $W_{\text{TM}}^{\text{TM}} = 7350 \text{ s}^{-1}$ at $N_{\text{TM}} = 10^{21} \text{ cm}^{-3}$.

Comparison with the $W_{\text{TM}}^{\text{TM}}$ values listed in Table 2 shows that self-quenching ($W_{\text{TM}}^{\text{TM}} = 79 \text{ s}^{-1}$) dominates, and excited 3H_4 level immediately quenches again to 3F_4 . Therefore, sp-conversion in Tm:YLF crystal should be taken into account only at very high rates of pumping.

3. Conclusion

The analysis of the crystal absorption spectra and the excitation of a GaAlAs laser diode shows the 3H_4 level to be most suitable for σ -polarized laser-diode pumping at 781 nm.

Migration and self-quenching processes were compared in detail for the 3H_4 level. The experimental and calculated self-quenching rates are in good accord, their dependences being close to the quadratic law. The rate of migration over the 3H_4 levels greatly exceeds that of self-quenching.

At high Tm concentrations, the pumped 3H_4 level is efficiently quenched to the 3F_4 one, so that one absorbed pump quantum excites two Tm ions in the 3F_4 state. This scheme is promising for 1.88- μm Tm lasing and sensitizing of 2.0- μm Ho lasing in Tm,Ho:YLF crystals.

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