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Relaxation of excited states of Tm^{3+} and $Tm^{3+}-Eu^{3+}$ energy transfer in YVO_4 crystal

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ABSTRACT $Tm^{3+}-Eu^{3+}$ energy transfer processes and relaxation dynamics of the $^3H_4$ and $^3F_4$ excited states of Tm^{3+} ions in 1 at. % Tm^{3+}, 5 at. % Eu^{3+}:YVO_4 single crystal were studied. Contribution of $Tm^{3+}-Eu^{3+}$ energy transfer reduces effectively the lifetime of terminal level in a potential $^3H_4-^3F_4$ laser transition at around 1.48 μm. Adverse quenching of the $^3H_4$ emission by Eu^{3+} ions is found to be less efficient than that reported for Tm^{3+} + Tb^{3+} system in YVO_4. The classical Inokuti–Hirayama model accounts well for an experimental decay curve of the $^3H_4$ emission recorded for co-doped crystal. Stimulated emission cross section for $^3H_4-^3F_4$ transition of Tm^{3+} at around 1.48 μm was analyzed taking into account the anisotropy of YVO_4 crystal.

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1 Introduction

YVO_4 crystal doped with neodymium has been a well-known laser material for last forty years [1]. Laser operation in YVO_4 containing 5 at. % of Tm^{3+} for transition $^3F_4-^3H_6$ was demonstrated later [2]. YVO_4:Tm system emitting near 1.8 μm is of interest as a source of light in the near infrared, considerably less dangerous for human eye than neodymium-doped materials. The laser performance of crystals and glasses doped with trivalent thulium was evaluated extensively [3]. An inconvenience of laser action associated with the $^3F_4-^3H_6$ transition of thulium is related to its quasi three level scheme involving re-absorption losses [3].

Structure of energy levels of Tm^{3+} offers also a possibility of obtaining potentially more efficient four-level laser operation associated with the $^3H_4-^3F_4$ transition near 1.45 μm. The spectroscopic and laser properties of thulium in this spectral range, which is advantageous for telecommunication purposes, were studied in the fluoride crystals $LiYF_4$ [4–6] and $BaYb_2F_8$ [7] as well as in the oxide material $SrGdGa_3O_7$ [8]. In all these crystalline materials, the lifetime of the $^3F_4$ terminal laser level is longer than that of the $^3H_4$ initial level what makes laser operation self-terminated. A forced simultaneous oscillation of the $^3H_4-^3F_4$ and $^3F_4-^3H_6$ transitions is one of the methods that may overcome the shortcoming [9]. Another method used to overcome the problem may consist of additional doping with Tb^{3+} [4] or Eu^{3+} ions [6]. It was found that Tb^{3+} ions actually shorten the $^3F_4$ lifetime but they quench adversely the $^3H_4$ emission [8]. The potential generation channel that makes use of the $^3H_4-^3F_4$ transition near 1.45 μm in YVO_4:Tm, Tb has been examined by Ermeneux et al. [10].

In this paper we examine the co-doping of YVO_4:Tm with europium ions because their level structure is less favourable for the depletion of the $^3H_4$ level by Tm-Eu energy transfer.

2 Experimental details

Single crystal of YVO_4 grown by the Czochralski technique containing 1 at. % of Tm^{3+} and 5 at. % of Eu^{3+} has been investigated. The content of thulium and europium ions in the crystal was checked by inductively coupled plasma (ICP) method. Concentrations of Tm^{3+} and Eu^{3+} measured were 0.98 at. % and 4.77 at. % respectively. Absorption spectra were recorded with a Varian 5E UV-VIS-IR spectrophotometer. Polarised emission spectra in the near infrared were recorded using a set-up consisting of Dongwoo Optron DM 711 monochromator equipped with a photomultiplier or InGaAs detector and a PC computer. A krypton ion laser provided cw excitation in the red light range. To record luminescence decay curves in the infrared region (1100–2100 nm) a SPM 2 monochromator equipped with a cooled EG&G InSb detector was used. Luminescence decay curves in the visible and IR range were recorded with a Tektronix Model TDS 3052 digital oscilloscope following the short pulse excitation by Continuum Surelite I optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser.

3 Results and discussion

A survey absorption spectrum of Tm^{3+} and Eu^{3+} in YVO_4 recorded at room temperature with unpolarized light is shown in Fig. 1. The spectrum in the 3000–14 000 cm^{-1} spectral region consists of three bands corresponding to transitions from the ground $^3H_6$ multiplet to the $^3F_4$, $^3H_5$ and $^3H_4$ multiplets of thulium and at longer wavelength from the ground multiplet $^7F_0$ to the $^7F_{4-6}$ levels of europium. Corresponding energy level scheme is shown in Fig. 2. For the purpose of optical pumping the band situated

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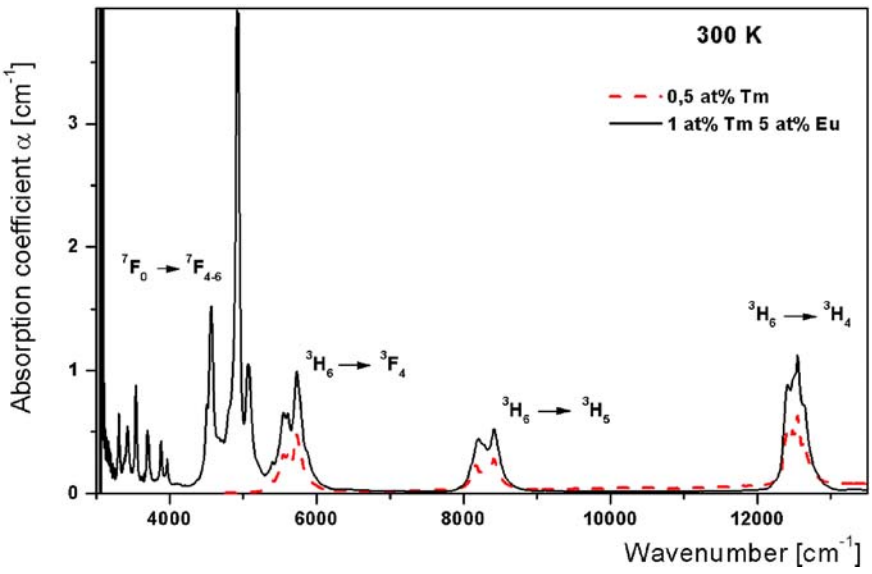

FIGURE 1 Unpolarized absorption spectrum for Tm^{3+}, Eu^{3+} in the YVO_4 at 300 K

between 12000 and 13 000 cm^{-1} (750–850 nm) is relevant, since it perfectly matches the emission wavelength of commercial high-power AlGaAs laser diodes. The intensity of this broad and unresolved band is advantageously high. The maximum peak value of the absorption cross-section σ_{abs} was found to be 2.87×10^{-20} cm^2 at 797.5 nm [11]. Incorporation of europium ions to selective transfer of energy from $^3F_4$ level of Tm^{3+} to the $^7F_6$ multiplet of Eu^{3+} is expected to provide a simple depopulation scheme for terminal $^3F_4$ level of thulium. It can be seen in Fig. 1 that the Eu^{3+} ions do not absorb at around 800 nm; thus, they will not reduce the pumping efficiency under laser diode excitation. It follows from Fig. 2 that there is an energy mismatch between $^7F_6$ level of Eu^{3+} and $^3F_4$ of Tm^{3+} and energy transfer from both the $^3F_4$ and $^3H_4$ emitting levels of Tm^{3+} in YVO_4 to acceptor Eu^{3+} ions is supposed to be phonon-assisted. The excited ^7F_J multiplets of Eu^{3+}will decay very rapidly to the ground state via multiphonon relaxation thus Eu^{3+}–Tm^{3+} back transfer is hardly possible. Inspection of Tm^{3+} energy level scheme (see Fig. 2) leads to the conclusions that YVO_4:Tm^{3+}, Eu^{3+} system may be pumped into the $^3H_4$ level effectively because optical losses such as ESA of pump radiation around 800 nm are not likely to occur.

To obtain the interaction parameters characterizing the energy-transfer processes single and co-doped samples were examined. The decay curves from $^3F_4$ level in 0.5 at. % Tm^{3+}:YVO_4, 6 at. % Tm^{3+}:YVO_4 and 1 at. % Tm^{3+} + 5 at. % Eu^{3+}:YVO_4 samples were measured for the $^3F_4$–$^3H_6$ luminescence transitions at around 1.8 μm (see Fig. 3). In the crystal singly doped with thulium decay curves are clearly exponential for both 0.5 at. % Tm and 6 at. % Tm concentrations. However, concentration-dependent quenching process is evidenced by shortening of the $^3F_4$ lifetime from about 1.9 ms to 1.4 ms when Tm^{3+} concentration increases from 0.5 at. % to 6 at. %. The origin of this quenching is not clear. It might be caused by migration of accelerated energy transfer to traps of unknown nature. At a higher thulium concentration the $^3H_4$ excitation is transferred to the $^3F_4$ level by a cross relaxation process (see Fig. 2) and the laser operation associated with the $^3F_4$–$^3H_6$ transition becomes feasible. In contrast to laser operation near 1800 nm the generation around 1480 nm associated with the $^3H_4$–$^3F_4$ transition requires low doping level to reduce the cross-relaxation losses. The $^3F_4$ lumines-

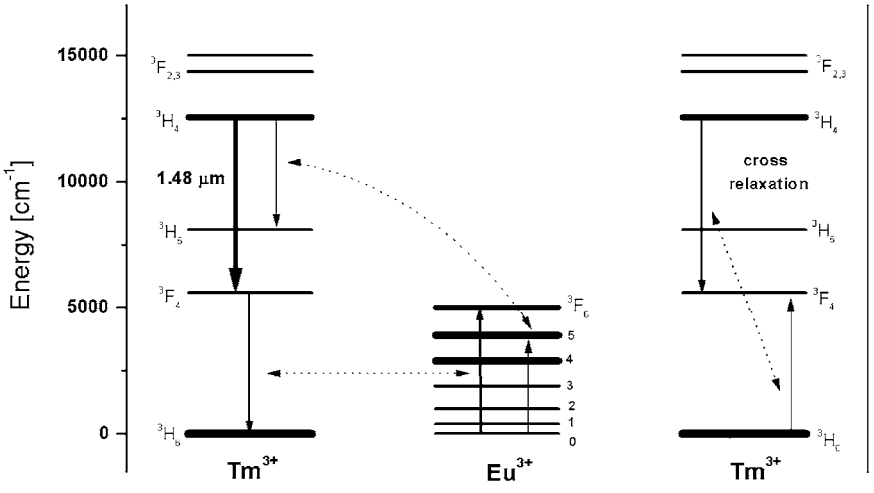

FIGURE 2 The energy level diagram of Tm^{3+}, Eu^{3+} ions in the YVO_4 crystal and energy transfer as well as cross-relaxation processes among activator ions

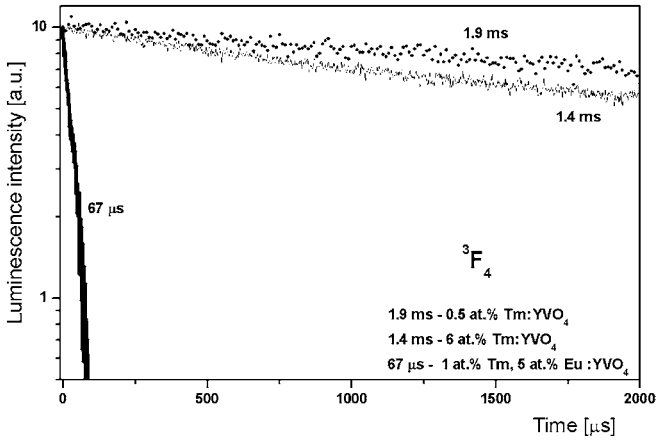

FIGURE 3 Decay curves of the $^3F_4$ luminescence for samples containing 0.5 at. % Tm^{3+}; 6 at. % Tm^{3+} and 1 at. % Tm^{3+}, 5 at. % Eu^{3+} recorded at room temperature

cence lifetime of Tm^{3+} in a sample co-doped with Eu^{3+} ions is advantageously short and amounts to 67 μs. The direct energy transfer from $^3F_4$ level of Tm^{3+} to unexcited Eu^{3+} ions proceeds according to the scheme:

$$^3F_4(Tm^{3+}) + {}^7F_0(Eu^{3+}) \rightarrow {}^3H_6(Tm^{3+}) + {}^7F_6(Eu^{3+})$$

Efficiency η of energy transfer defined as $\eta = 1 - (\tau/\tau_0)$ where τ_0 is an intrinsic lifetime of donor is close to 0.95.

Using room temperature unpolarized absorption spectra corresponding to $^3H_6$–$^3F_4$ transition, we have calculated the stimulated emission cross sections $\sigma_{em}(\lambda)$ according to the formula:

$$\sigma_{em}(\lambda) = \frac{Z_{low}}{Z_{up}} \sigma_a(\lambda) \exp\left(\frac{Z_{ZL} - E(\lambda)}{k_B T}\right) \quad (1)$$

Where $\sigma_a(\lambda)$ is an absorption cross section and Z_{low} , Z_{up} are partition functions for lower and upper states respectively, defined as:

$$Z_{low} = \sum_{i=1}^{n} g_i \exp\left(\frac{-E_i}{k_B T}\right)$$
$$Z_{up} = \sum_{j=1}^{n} g_j \exp\left(\frac{-\left(E_j - E(\lambda)\right)}{k_B T}\right) \quad (2)$$

where $g_i(g_j)$ are the degeneracies of crystal field levels, $E_i(E_j)$ are energies of crystal field levels, E_{ZL} is the energy separation between the lowest crystal field levels of upper and lower states, and k_B is the Boltzmann constant. For this calculation energies of the crystal field levels of the two multiplets were taken from [12]. Measured unpolarized absorption cross sections for transitions $^3H_6$–$^3F_4$ of Tm^{3+} and $^7F_0$–$^7F_6$ of Eu^{3+} as well as derived stimulated emission cross sections for transitions $^3F_4$–$^3H_6$ are shown in Fig. 4. The critical radius R_{DA} for energy transfer can be estimated from the overlap integral of the absorption and emission spectra of the donor and acceptor ions by using the formula [6]:

$$R_{DA}^6 = \frac{3c\tau_R}{8\pi^4 n^2} \int \sigma_{em}^D(\lambda)\, \sigma_{abs}^A(\lambda)\, d\lambda \quad (3)$$

where n is the refractive index of the material, τ_R is the radiative lifetime of the donor, σ_{em}^D is the stimulated emission cross section of the donor, and σ_{abs}^A is the absorption cross section of the acceptor. In the case of dipole–dipole transfer mechanism the energy transfer microparameters C_{DA} and the energy transfer probability P_{DA} are defined by [6]:

$$C_{DA} = \left(\frac{1}{\tau_R}\right)(R_{DA})^6 \qquad P_{DA} = C_{DA} R_{DA}^{-6} \quad (4)$$

The critical radius R_{DA} for energy transfer from $^3F_4$ of Tm^{3+} in YVO_4 calculated using the integral σ_{em}^D (Tm^{3+}) and σ_{abs}^A (Eu^{3+}) derived from the spectra shown in Fig. 4 amounts to R_{DA} = 5.95 Å and resulting microparameter $C_{DA} = 2.21 \times 10^{-41}\,cm^6 s^{-1}$. In this calculation the $^3F_4$ luminescence lifetime measured for a singly doped sample containing 0.5 at. % of Tm^{3+} was assumed to be equal to the $^3F_4$ radiative lifetime. The derived parameters are significantly smaller than the $R_{DA} = 14.84$ Å and $C_{DA} = 7.58 \times 10^{-40}\,cm^6 s^{-1}$ reported for energy transfer from the $^3F_4$ in $LiYF_4$:Tm^{3+}, Eu^{3+} [5]. This is due to the fact that the Tm^{3+}–Eu^{3+} energy transfer is not resonant and is supposed phonon-assisted. In consequence the overlap integral derived from the absorption and emission spectra associated with electronic transitions is very small. In the calculation of overlap integral for the $LiYF_4$:Tm^{3+}, Eu^{3+} system the contribution of phonon sidebands has been included by constructing the phonon sidebands for each transitions, according to exponential laws proposed by Auzel [13]. In our calculation the phonon sidebands were not considered; therefore, the derived overlap integral appears to be underestimated.

In contrast to the $^3F_4$ relaxation the decay curve of luminescence originating from the $^3H_4$ level in 1 at. % Tm^{3+}, 5 at. % Eu^{3+}:YVO_4 was non exponential (see Fig. 5). To receive information about non-radiative energy transfer processes the analysis of luminescence decay curves of donors may be performed using theoretical models proposed by Yokota–Tanimoto [14] and Inokuti–Hirayama [15]. The former model takes into account the excitation energy migration over donor system. The latter model applies when the donor concentration is sufficiently low to neglect the donor–donor interaction. According to Inokuti–Hirayama, the time depen-

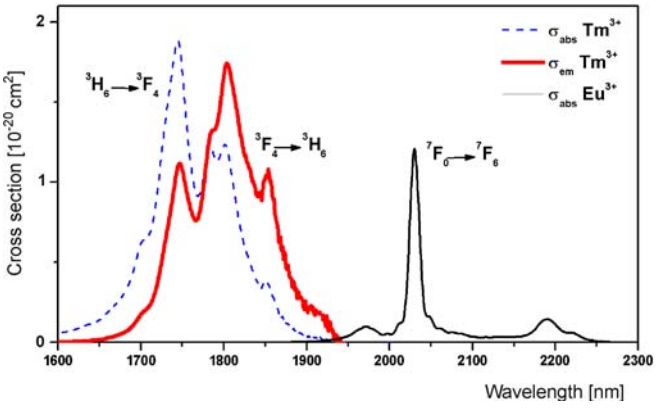

FIGURE 4 Emission cross section for transition $^3F_4$–$^3H_6$ of Tm^{3+} and absorption cross section for transitions $^3H_6$–$^3F_4$ of Tm^{3+} and $^7F_0$–$^7F_6$ of Eu^{3+} in YVO_4

dence of donor luminescence $\Phi(t)$ in the presence of acceptors is expressed by:

$$\Phi(t) = A \exp\left[-\frac{t}{\tau_0} - \alpha\left(\frac{t}{\tau_0}\right)^{\frac{3}{k}}\right] \quad (5)$$

where A is a constant, Φ(t) is emission intensity after pulse excitation, $k = 6$ for dipole–dipole interactions between ions, τ_0^{-1} is the intrinsic decay probability of donor ions involved in the energy transfer process in the absence of acceptors and α is the parameter described as:

$$\alpha = \frac{4}{3}\pi\Gamma\left(1 - 3/k\right) C_A\, R_{\mathrm{DA}}^3 \quad (6)$$

In (6) $k = 6$, thus $\Gamma(1 - 3/k) = \Gamma(1/2) = 1.77$ where Γ is the Euler function, C_A is the concentration of acceptor ions and R_{DA} is the critical transfer distance defined as the separation at which the probability of energy transfer between a donor–acceptor pair equals to inherent probability of donor decay.

Figure 5 compares decay curves of the $^3H_4$ luminescence recorded for YVO_4:0.5 at. % Tm^{3+} and for YVO_4:1 at. % Tm^{3+}, 5 at. % Eu^{3+}. The measured decay curve of the $^3H_4$ level of Tm^{3+} in the former crystal is exponential with estimated lifetime of 176 µs. The radiative lifetime calculated according to the Judd–Ofelt theory is equal to 224 µs [16]. In fluoride matrices at low thulium concentration the quantum efficiency of the $^3H_4$ level of Tm^{3+} is close to unity. However, oxide materials are characterized by higher phonon frequencies (around 900 cm^{-1} in YVO_4 [17]) than in fluoride crystals. Consequently, the $^3H_4$ quantum efficiency is reduced owing to considerably higher nonradiative relaxation probability from $^3H_4$ emitting level down to the $^3H_5$ level [6]. Experimental decay curve recorded with co-doped crystal fits well the time dependence predicted by the Inokuti–Hirayama expression (5–6) with parameter $\alpha = 3.37$. Evaluated values of $R_{\mathrm{DA}} = 15.4$ Å and $C_{\mathrm{DA}} = 7.58 \times 10^{-38}\,\mathrm{cm^6 s^{-1}}$ are considerably higher than those values reported for $LiYF_4$:Tm, Eu [5] corresponding $R_{\mathrm{DA}} = 8.89$ Å and $C_{\mathrm{DA}} = 2,47 \times 10^{-40}\,\mathrm{cm^6 s^{-1}}$. The measured decay curve of the $^3H_4$ level of Tm^{3+} in YVO_4:1 at. %Tm^{3+}, 5 at. %Eu^{3+} crystal is non-exponential and therefore a mean lifetime τ_{m} defined as:

$$\tau_{\mathrm{m}} = \frac{\int I\,(t)\,\mathrm{d}t}{I_0} \quad (7)$$

where I_0 is the initial intensity seems to be more convenient to characterize the decay. Thus, mean lifetime of the $^3H_4$ level of Tm^{3+} in the presence of Eu^{3+} ions is evaluated to be $\tau_{\mathrm{m}} = 37$ µs.

With this result and the $^3H_4$ radiative lifetime $\tau_0 = 224$ µs [15], the quantum efficiency defined as $\eta_{\mathrm{f}} = \tau_{\mathrm{m}}/\tau_0$ for the $^3H_4$ level of Tm^{3+} in 1 at. % Tm^{3+}, 5 at. % Eu^{3+}:YVO_4 is found to be 0.16, a value slightly higher than 0.15 reported for 1 at. % Tm^{3+}, 3 at. % Eu^{3+}:$LiYF_4$ [5]. The energy transfer rate from Tm^{3+} to Eu^{3+} ions $W_{\mathrm{Tm\text{-}Eu}}$, can be calculated from the Tm^{3+} decay times obtained for samples with and without Eu^{3+} ions:

$$W_{\mathrm{Tm-Eu}} = \frac{1}{\tau_{\mathrm{Tm,Eu}}} - \frac{1}{\tau_{\mathrm{Tm}}} \quad (8)$$

where τ_{Tm} and $\tau_{\mathrm{Tm,Eu}}$ are the emission decay times of the Tm^{3+}- states without and with the presence of Eu^{3+} ions in the YVO_4 crystals, respectively. With the lifetime values mentioned above the energy-transfer rates from Tm^{3+} to Eu^{3+} for YVO_4:1 at. %Tm^{3+}, 5 at. % Eu^{3+} are $\sim 17\,027\,\mathrm{s^{-1}}$ for $^3H_4$ and $14\,400\,\mathrm{s^{-1}}$ for $^3F_4$ levels of thulium.

Emission cross-section spectra associated with the $^3H_4$–$^3F_4$ transition of Tm^{3+} for σ and π polarization in 1 at. % Tm^{3+}, 5 at. % Eu^{3+}:YVO_4 are shown in Fig. 6. The spectra were excited by a cw radiation at 641.7 nm emitted by krypton ion laser and calculated using the so-called Fuchtbauer–Ladenburg method [18]. It can be seen that most remarkable feature presented by the stimulated emission spectra is presence of two intense lines centered at 1466 and 1480 nm for both σ and π polarization. Four-level laser channel associated with the $^3H_4$–$^3F_4$ transition is advantageous because

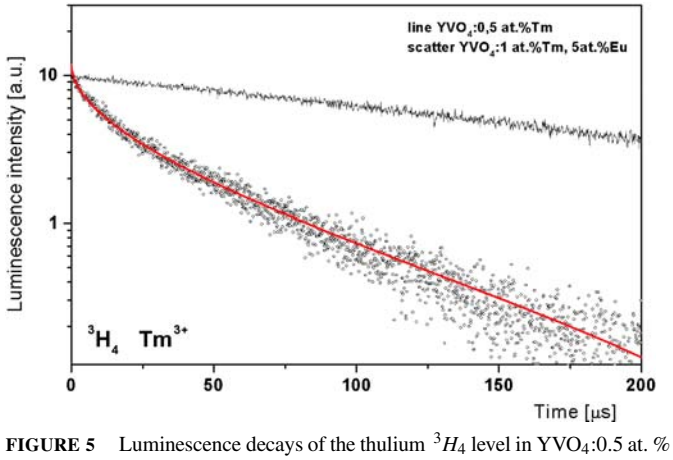

FIGURE 5 Luminescence decays of the thulium $^3H_4$ level in YVO_4:0.5 at. % Tm and in the YVO_4:1 at. % Tm:5 at. % Eu crystals measured at 300 K. The solid line presents the fitted curve (Inokuti–Hirayama model)

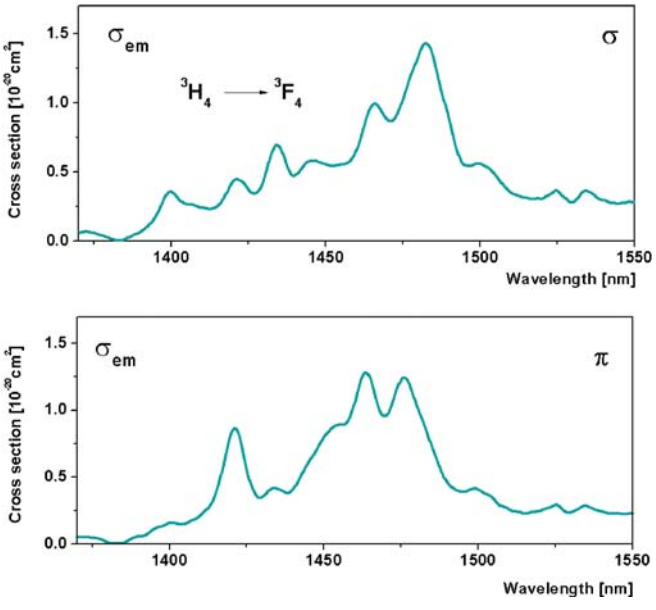

FIGURE 6 π and σ emission cross-section spectrum of Tm^{3+} in 1 at. % Tm^{3+}, 5 at. % Eu^{3+}:YVO_4 at around 1.5 µm

in contrast to the laser operation associated with the $^3F_4$–$^3H_6$ transition the terminal level is not the ground multiplet whose crystal field splitting of 360 cm^{-1} in YVO_4 is relatively small [11]. The maximum value of σ_{em} for σ polarization at around 1500 nm is considerably higher than that calculated for thulium-doped $LiYF_4$ crystal [5].

4 Conclusions

The energy transfet processes and relaxation dynamics of excited states were analysed for $Tm^{3+}-Eu^{3+}$ system in YVO_4 crystal. The europium ions shorten effectively the $^3F_4$ lifetime and simultaneously enhance nonradiative relaxation of the $^3H_4$ level of Tm^{3+}. Inokuti–Hirayama classical energy transfer model was applied successfully to describe the time dependence of luminescence decay from the potential upper laser level $^3H_4$ of Tm^{3+}. The quantum efficiency of the $^3H_4$ level of Tm^{3+} in YVO_4 is sufficiently high to justify the consideration of laser operation associated with $^3H_4$–$^3F_4$ transition. The distribution of emission band intensity and relatively high value of emission cross section at near 1480 nm are favorable for infrared laser emission in the YVO_4:Tm, Eu system. Intensity of a broad pump band associated with the $^3H_6$–$^3H_4$ transition of Tm^{3+} at around 800 nm is also advantageous for laser operation. Evaluated C_{DA} microparameters characterizing the processes of ion–ion interaction may be useful in assessment of optimal concentrations of Tm^{3+} and Eu^{3+} ions in the investigated material.

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REFERENCES

1 I.R. O'Connor, Appl. Phys. Lett. **9**, 407 (1966)
2 K. Ohta, H. Saito, M. Obara, N. Djeu, Jpn. J. Appl. Phys. **32**, 1651 (1993)
3 A.A Kaminskii, Phys. Stat. Solidi A **200**, 215 (2003)
4 R.C. Stoneman, L. Esterowitz, Opt. Lett. **6**, 232 (1991)
5 A. Braud, S. Girard, J.L. Doualan, R. Moncorge, IEEE J. Quantum Electron. **QE-34**, 2246 (1998)
6 J.T. Vega-Durãn, L.A. Diãz-Torres, M.A. Meneses-Nava, J.L. Maldonado-Rivera, O. Barbosa-Garcia, J. Phys. D Appl. Phys. **34**, 3203 (2001)
7 B.M. Antipenko, R.V. Dumbbravyanu, Y.E. Perlin, O.B. Rabu, L.K. Sukhareva, Opt. Spectrosc. **59**, 377 (1985)
8 W. Ryba-Romanowski, M. Berkowski, B. Viana, P. Aschehoug, Appl. Phys. B **64**, 525 (1997)
9 R.M. Percival, D. Szebesta, S.T. Davey, Electron. Lett. **28**, 1866 (1992)
10 F.S. Ermeneux, C. Goutaudier, R. Moncorge, M.T. Cohen-Adad, M. Bettinelli, E. Cavalli, Opt. Mater. **8**, 83 (1997)
11 R. Lisiecki, W. Ryba-Romanowski, T. Łukaszewicz, H. Mond, K. Petermann, Laser Phys. **15**, 306 (2005)
12 K.D. Knoll, Phys. Stat. Solidi B **45**, 553 (1971)
13 F. Auzel, Phys. Rev. B **13**, 2809 (1976)
14 M. Yokota, J. Tanimoto, J. Phys. Soc. Jpn. **22**, 779 (1967)
15 M. Inokuti, F. Hirayama, J. Chem. Phys. **43**, 1978 (1965)
16 C. Xueyuan, L. Zundu, J. Phys.: Condens. Matter **9**, 7981 (1997)
17 E.D. Reed, H.W. Moos, Phys. Rev. B **8**, 980 (1973)
18 Y. Gujot, H. Manaa, J.Y. Rivoire, R. Moncorge, N. Garnier, E. Descoix, M. Bon, P. Laporte, Phys. Rev. B **51**, 784 (1995)