

## Concentration quenching of Tb<sup>3+</sup> luminescence in Tb<sub>x</sub>A<sub>3-x</sub>Al<sub>5</sub>O<sub>12</sub> (A=Yb, Y) single crystals

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Tb-doped Yb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystals were grown by the micropulling-down method in the form of rods of 2 mm diameter and a few cm in length. Emission spectra and decay times of Tb<sup>3+</sup> luminescent centers were measured for Tb concentrations in a Y(Yb) sublattice of (1-70) %. A noticeable decrease of the emission intensity and decay time was obtained for Tb concentrations above 15% and 30% for Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Yb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> hosts, respectively. Both effects are ascribed to the concentration quenching of Tb<sup>3+</sup> luminescence due to energy migration over the Tb<sup>3+</sup> subsystem and subsequent energy transfer to unspecified nonradiative traps. Energy migration process and structural aspects are discussed.

**Key words:** micropulling-down crystal growth, luminescence, rare earth ions, concentration quenching.

### Introduction

Rare earth (RE) ion-doped single crystals of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) garnet have been studied in many papers due to their extensive use for solid state lasers (Nd-doped [1]), scintillator (Ce-doped [2]) and other applications. For such applications usually dopant concentration up to a few percent is used to avoid unwanted effects arising in the case of high RE ion concentration like cross-relaxation, concentration quenching, etc. For RE ions similar in size to the Y cation, it is easy to prepare solid solutions of a mixed-cation garnet and/or to grow even the rare earth aluminium garnets, which are of the same structure, e.g. Tb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (TbAG) [3] or Yb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YbAG) [4]. Another mixed Tb<sub>3</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> garnet single crystal growth was reported recently mentioning its possible application as a Faraday rotator [5]. Tb<sup>3+</sup>-luminescence based on radiative transitions within the 4f-shell is well-known in many host materials [6] showing typically two emission multiplets related to the radiative transitions from the excited state <sup>5</sup>D<sub>4</sub> level (dominating lines at 486 nm, 542 nm, 580 nm and 620 nm) and <sup>5</sup>D<sub>3</sub> level (lines within 370-480 nm spectral region) to the <sup>7</sup>F<sub>x</sub> ground state manifold. The <sup>5</sup>D<sub>3</sub>→<sup>7</sup>F<sub>x</sub> radiative transitions are strongly suppressed in the emission spectra for Tb<sup>3+</sup> concentrations above a few percent due to cross-relaxation processes between two closely spaced Tb<sup>3+</sup> ions.

It is the aim of this paper to report the concentration

quenching effects in Tb<sup>3+</sup> luminescence, which occur in parallel to the above mentioned cross-relaxation process for higher Tb concentrations in YbAG and YAG hosts. While a cross-relaxation process does not result in the overall emission quenching (it is "just" an energy conversion from the <sup>5</sup>D<sub>3</sub> to <sup>5</sup>D<sub>4</sub> excited state), concentration quenching brings substantial emission intensity loss due to energy migration over the Tb-subsystem and its dumping in nonradiative traps.

### Experimental

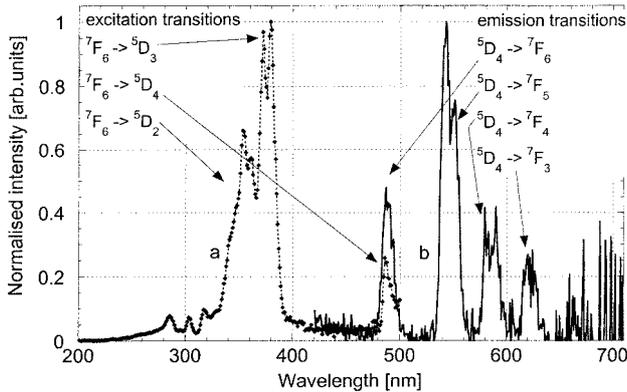
Single crystals of Tb<sub>x</sub>A<sub>3-x</sub>Al<sub>5</sub>O<sub>12</sub> (A=Y or Yb) with varying concentrations of Tb<sup>3+</sup> cations were grown in the form of rods (2 mm in diameter) and a few cm in length by the micropulling-down method. Rods were cut into 8 mm pieces and flattened to 0.8 mm thickness with optically polished surfaces.

The spectra and decay of Tb<sup>3+</sup> photoluminescence were measured at room temperature (RT) in a Spectrofluorometer 199S (Edinburgh Instruments) using a steady-state hydrogen or microsecond pulse xenon flashlamp (IBH Scotland), respectively, as an excitation source. Photoluminescence spectra were corrected for spectral distortions and the decays were approximated typically by a single exponential function to extract the decay times (DT).

### Experimental Results and Discussion

In the emission spectra of Tb-containing YbAG or YAG matrices a typical four-line spectrum peaking at about 488 nm, 542 nm, 584 nm and 621 nm was

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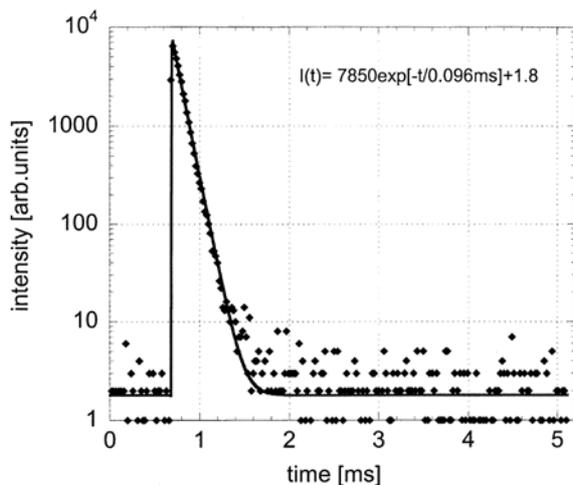
**Fig. 1.** Excitation (a) and emission (b) spectra of  $Tb^{3+}$  centers in YbAG:Tb (5%) at room temperature. (a)  $\text{em}=542$  nm; (b)  $\text{ex}=325$  nm.

obtained, which is ascribed to the radiative transition from the  $^5D_4$  excited state of  $Tb^{3+}$  to the ground  $^7F_{6,5,4,3}$  multiplet – Fig. 1. In the excitation spectrum of the 542 nm emission line in Fig. 1 the dominant peaks at about 488 nm, 372+379 nm and 354 nm can be ascribed to the upward transitions from the  $^7F_6$  ground state to the  $^5D_4$ ,  $^5D_3$  and  $^5D_2$  excited state levels, respectively. With an increasing concentration of  $Tb^{3+}$ , a considerable decrease of emission intensity and shortening of the emission decay time was obtained, see Fig. 2 for  $Tb_{2.2}Yb_{0.8}AG$ . Such behavior is typical, when the luminescence concentration quenching occurs, i.e. when the luminescence ions become so close that the excitation energy starts to migrate among them and becomes progressively lost at unspecified nonradiative traps (lattice defects) [7]. The concentration dependence of decay times of the  $Tb^{3+}$  542 nm emission line is shown in Fig. 3 for both YAG and YbAG matrices. It can be seen that the knee on the curves is obtained above 30% of  $Tb^{3+}$  in the case of the YbAG matrix, while a some-

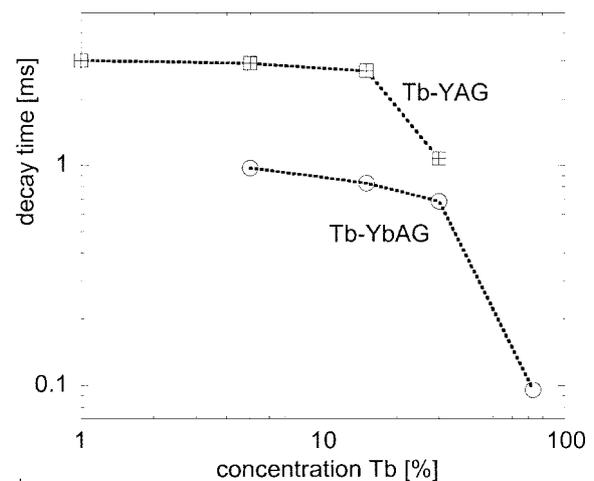
what lower concentration between 15-30% is enough to obtain noticeable DT shortening in the YAG matrix. Furthermore, a higher isolated  $Tb^{3+}$  DT (low concentration limit) of about 3 ms was obtained in YAG compared to about 1 ms in YbAG matrix.

Interestingly enough, the decay curves do not deviate from a single exponential course for any Tb concentration (example in Fig. 2), which is expected in the case of the multipolar interaction between the donor themselves ( $Tb^{3+}$  ion) and donor-acceptor (a nonradiative trap) pairs. Diffusion-limited energy transfer processes are theoretically described for multipolar interactions in generally accepted energy transfer models (e.g. Yokota-Tanimoto limited diffusion model [8], Ghosh-Hegarty-Huber model [9]), which show well-expressed non-exponentialities in the initial part of the decay curves. Due to the fact that the emission transition of  $Tb^{3+}$  occurs between the well-screened 4f-like levels and it is strongly forbidden (decay times of 1-3 ms), the interaction between  $Tb^{3+}$  ions and between  $Tb^{3+}$  and nonradiative traps could be considered to be of short-range exchange character and a relatively high  $Tb^{3+}$  concentration is thus necessary to achieve a significant concentration quenching effect. In the case of exchange interaction the energy transfer probability decreases exponentially with the Tb-Tb (Tb-trap) distance and above 6-10 Å it becomes negligibly small [10]. In such a case the number of donor ions in the sphere of the influence of an acceptor will always be very small (see also below) and the hopping model of Burshtein seems to be more appropriate [11], in which the above mentioned non-exponential decay features may become less significant. It follows from the above text that whatever is the nature of the acceptor nonradiative traps, their interaction with  $Tb^{3+}$  donor subsystems must be of very short (probably exchange) character.

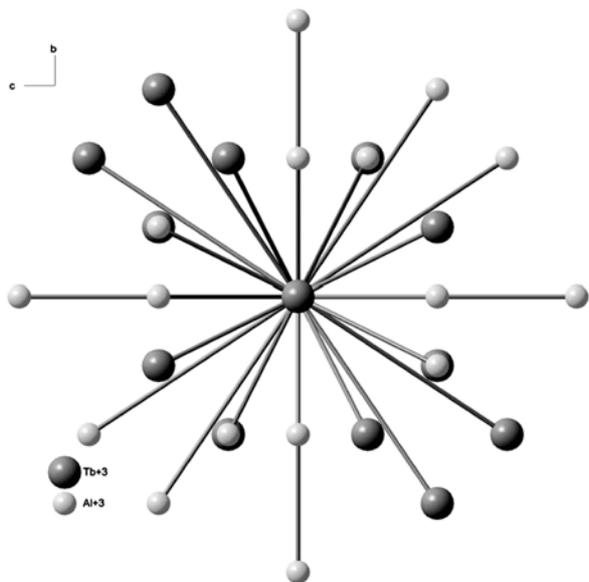
To provide more insight into structural features of



**Fig. 2.** Photoluminescence decay of  $Tb_{2.2}Yb_{0.8}Al_5O_{12}$  at room temperature.  $\text{Exc}=490$  nm,  $\text{em}=542$  nm. A single exponential approximation is given by the solid line. The decay time of 0.096 ms was calculated.



**Fig. 3.**  $Tb^{3+}$  concentration dependencies of the decay times related to the 542 nm emission line of the  $Tb^{3+}$  emission center in YbAG and YAG matrices measured under  $\text{exc}=490$  nm and room temperature.



**Fig. 4.** Sketch of TbAG structural arrangement along the b axis with a central  $Tb^{3+}$  ion (oxygen anions omitted).

(Tb-Yb)AG and related possibilities for the energy migration among  $Tb^{3+}$  ions, the number of Tb ions within a sphere of 10 Å from a central Tb ion is calculated together with from-central-Tb ion distances by considering TbAG structure [4]. A sketch of the cation spatial arrangement is given in Fig. 4. We obtain the result that from 51 Tb ions present in such a sphere, there are four ions at a distance of 3.67 Å, eight ions at a distance of 5.61 Å and two ions at a distance of 6.00 Å from the central Tb ion. As the exchange interaction probability between Tb-Tb pairs decreases exponentially with their mutual distance, the energy transfer probability will decrease 5-6 times, if transfer from the central  $Tb^{3+}$  ion over the 5.61 Å distance to the next-nearest  $Tb^{3+}$  ions is considered, with respect to the closest (3.67 Å)  $Tb^{3+}$  cations. An abrupt decrease in decay time in Fig. 3 for Tb concentrations above 15% (YAG) and 30% (YbAG) must be thus connected with the increased occurrence of  $Tb^{3+}$  ions at the nearest

neighbor (3.67 Å) positions to allow efficient energy migration over possibly many  $Tb^{3+}$  ions until a non-radiative trap has been reached. Deeper quantitative considerations are excluded, however, as the nature and concentration of the acceptor nonradiative traps are unknown.

Based on these simple considerations, it is however difficult to understand the reason for the earlier (lower Tb concentration) onset of the decay time shortening in the YAG matrix, where  $Y^{3+}$  cations are of even bigger size with respect to the  $Yb^{3+}$  ones. A bigger cation implies generally a bigger lattice constant for the structure, which could in principle make the diffusion over a  $Tb^{3+}$ -doped subsystem a little less efficient. This aspect thus needs further consideration. Furthermore, a significant difference in the low concentration limit of the  $Tb^{3+}$  decay times in YAG and YbAG matrices, which is probably related to different mixing  $Tb^{3+}$  4f states with the opposite parity states of the host, would deserve a deeper consideration as well.

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