Emission properties of Tb$_3$Sc$_2$Al$_3$O$_{12}$-TbScO$_3$ eutectic with self-organized rodlike microstructure

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Abstract

An investigation of spectroscopic properties of Tb$^{3+}$ ions in terbium-scandium-aluminum garnet - terbium-scandium perovskite Tb$_3$Sc$_2$Al$_3$O$_{12}$ - TbScO$_3$ (TSAG-TSP) eutectic and, for comparison, in bulk Tb$_3$Sc$_2$Al$_3$O$_{12}$ (TSAG) and TbScO$_3$ (TSP) crystals is presented. The emission and fluorescence decays from the $^5$D$_4$ level of Tb$^{3+}$ ion after pulsed, one-photon excitation are characterized as a temperature function from 10 to 300 K. Spectrally selected groups of Tb$^{3+}$ ions located in particular phases of eutectic were characterized using a time–resolved spectroscopy. The cross-relaxation process leading to the quenching of luminescence from the $^5$D$_4$ excited state of Tb$^{3+}$ ions in all investigated materials was observed and analyzed. The presented eutectic materials have a high potential for photonic applications.

PACS: 78.47.-p, 78.47.Cd, 78.66.Nk, 78.66.Sq

Keywords: eutectic, Tb$_3$Sc$_2$Al$_3$O$_{12}$, TbScO$_3$, terbium, Tb$^{3+}$, luminescence quenching

doi:10.1016/j.phpro.2009.07.024
1. Introduction

In recent years in the field of photonics, concepts of new materials appeared such as photonic crystals [1-3] and metamaterials [4-5]. There are many sophisticated techniques for manufacturing of photonic crystals and metamaterials. One of the ways could be also self-organization. Another kind of self-organized materials which could find application in the field of photonics (photonic crystals, metamaterials), and which are not widely investigated are eutectics.[6] The directional solidification of eutectics is a promising approach for growth of self-organized micro- and nanostructures.[7-9] Eutectics are interesting because they are in the same time a monolith and multiphase material [10]. The great advantage of eutectics is that different component materials (isolators, semiconductors, metals) and different kind of structuring (rod-like, spiral, lamellar, globular, percolated and others) can be obtained. Eutectics can have two kinds of properties: the additive properties, which arise from the properties of component phases and the product properties which can exist only in the eutectic.

In this paper emission properties of a Tb₃Sc₂Al₃O₁₂-TbScO₃ eutectic with a rodlike microstructure are investigated, as well as the single crystals of Tb₃Sc₂Al₃O₁₂ and TbScO₃ for comparison.[7, 11, 12] The interesting fact is that Tb₃Sc₂Al₃O₁₂ shows the Faraday effect [13] which may be enhanced in the photonic crystals. The careful study of luminescence properties in eutectics were only rarely performed e.g. in ref. [14].

The emission spectrum of trivalent terbium (Tb³⁺) is dominated by transitions from the ⁵D₃ and ⁵D₄ exited states located at about 26000 and 20500 cm⁻¹ respectively. Due to the large energy gaps below, i.e. 5500 and 15000 cm⁻¹ respectively, the probability of multiphonon relaxations from these levels is negligible. Thus for low density of active ions only radiative transitions from ⁵D₃ and ⁵D₄ exited states takes place. The strongest emission is observed in the green part of the spectrum around 540 nm, corresponding to the ⁵D₄ → ⁷F₅ transition.

Up to now information on terbium laser systems is limited to only a few works. The first terbium laser emitting at 547 nm was reported by Bjorklund et al. already in 1967 [15]. Terbium was in liquid form pumped with a flash lamp. Another lasing action at 544.5 nm was observed in highly doped (10%) LiYF₄:Ta₅⁺,Gd³⁺ crystal excited with a xenon flash lamp [16]. In this system the initial laser level (⁵D₄) was populated by strong cross-relaxation process from the higher ⁵D₃ excited state.

2. Material and experiment

The self-organized rodlike microstructure of terbium-scandium-aluminum garnet - terbium-scandium perovskite Tb₃Sc₂Al₃O₁₂-TbScO₃ (TSAG-TSP) eutectic was grown using the micro-pulling down method (m-PD) in the Institute of Electronic Materials.
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Technology (ITME) in Warsaw. High purity oxide powders (99.995%), Tb4O7, Sc2O3, Al2O3 were used as starting materials. The oxides were mixed with ethanol in alumina mortar and then dried. The investigated eutectic was grown with a volume ratio of \( V_{\text{TSAG}}:V_{\text{TSP}} = 2 \), and with 0.45 mm/min pulling rate under nitrogen atmosphere. The rodlike structure consisting of the TSP microfibers with 1.8 \( \mu \text{m} \) diameter submerged with TSAG phase has been obtained. The crystal grown was seeded with a \(<111>\) \( Y_3\text{Al}_5\text{O}_{12} \) single crystal. A picture presenting the cross-section (\( \perp \) the crystal growth direction) and longitudinal section (\( \parallel \) the crystal growth direction) of the eutectic is given in Fig. 1. Details of fabrication of obtained microstructures have been previously reported \([7, 11, 12]\). Bulk TSAG and TSP crystals were also grown using m-PD method. \( \text{Ts}_2\text{Sc}_2\text{Al}_3\text{O}_{12} \) is a garnet, with a cubic system and a typical garnet, \( \text{IA}^3\text{d} \), space group. The structure is the same as for \( Y_3\text{Al}_5\text{O}_{12} \) (YAG lattice constant = 12.0003(14)) \([17]\), however the lattice constant is much bigger, 12.286 \( \text{Å} \) \([18]\), due to bigger cations in comparison with YAG (\( \text{Tb}^{3+} \) and \( \text{Sc}^{3+} \) instead of \( \text{Y}^{3+} \) and \( \text{Al}^{3+} \)). In TSAG, \( \text{Tb}^{3+} \) ions are located in the dodecahedral sites. \( \text{TbScO}_3 \) crystallizes with distorted perovskite structure of orthorhombic system and Pbnn space group, with lattice constants of \( a=5.466, b=5.727, c=7.915 \) \([19]\). It crystallizes in the same space group as \( \text{YAlO}_3 \) (\( a=5.1671(6), b=5.3148(8), c=7.3538(9) \)) \([20]\), but with bigger lattice constants due to bigger cations.

Luminescence was excited by a frequency-tripled radiation (355 nm) of pulsed YAG:Nd laser (Continuum Surelite II). The emission signal from the samples was dispersed by CVI DK480 monochromator and detected by the cooled EMI C1034-02 GaAs photomultiplier. For emission spectra data acquisition was performed using Stanford SR 400 photon-counting system controlled by a PC. Luminescence lifetimes measurements were carried out using Stanford SR 430 multichannel analyzer. The samples were cooled by the Displex Model CSW-202 closed cycle cryogenic system to about 10 K. Presented results of time-resolved measurements were recorded with two different settings of SR 400 photon counter:

1. \( t_1 \) – gate width 7 \( \mu \text{s} \), gate delay 0 \( \mu \text{s} \),
2. \( t_2 \) – gate width 100 \( \mu \text{s} \), gate delay 30 \( \mu \text{s} \).

3. Results and discussions

3.1 Room temperature emission properties

Several emission lines in the visible part of a spectrum, at 490, 550, 590, 620, 660, 680 and 690 nm wavelength, corresponding to the the \( 4f^8 - 4f^8 \) transitions starting from \( ^2\text{D}_4 \) excited state of terbium, were observed in all investigated hosts. Example spectrum with all observed emission lines recorded for TSAG is presented in Fig. 2. An absence of UV emissions (between 350 and 450 nm) indicates that strong quenching of luminescence from the higher lying \( ^3\text{D}_3 \) energy level takes place.
The initial level of observed optical transitions (5D₄) was excited by strong cross-relaxation process from 5D₃ state populated by fast multiphonon relaxations from directly pumped level. Based on the energy level structure of Tb³⁺ determined in other similar hosts [21] the scheme of pumping and relaxation paths is proposed and presented in Fig. 3. Indicated cross-relaxation paths X₁ and X₂ are in good agreement with the ones proposed for other solid-state hosts [22-26].

Due to different values of luminescence decay constants for different hosts spectral selection of Tb³⁺ ions located in individual phases of eutectic was possible. Using a time-resolved technique of measurement the emission characteristics of TSAG-TSP were carried out. Results compared with spectra recorded for bulk TSAG and TSP crystals are presented in Fig. 4. As could be seen the emission spectra for TSAG-TSP eutectic measured with short (t₁) and wide (t₂) gate of SR 430 counter are almost the same as for bulk TSP and TSAG crystals respectively. It indicates that terbium ions both in particular phases of eutectic and in corresponding bulk crystals have very similar emission properties.

3.2 Luminescence dynamic

Measured decay profile of the 5D₄ excited state of Tb³⁺ in TSAG-TSP eutectic consists of two considerable different parts corresponding to the emission from TSP phase (ETSP) and from TSAG phase (ETSAG) what is shown in Fig. 5. Decay curves of 5D₄ luminescence were measured as a temperature function, from about 10 to 300 K, for both eutectic and bulk TSAG and TSP crystals. The comparison between measured lifetimes of 5D₄ excited state of Tb³⁺ in all investigated materials is presented in Fig. 6. Obtained results show considerable differences of measured lifetimes in individual phases of eutectic and in bulk crystals with the same crystal structure. Decay constants for garnet in eutectic (ETSAG) and in bulk (TSAG) crystals have very similar values for low temperature range, below about 50 K. Above this temperature decay constants in eutectic become distinctly longer than in bulk crystal, approximately 1.8 times longer. In the case of TSP and ETSP decays the most differences of luminescence constants, about 8 times, are observed in low temperature, below 50 K.

3.3 5D₄ luminescence quenching

Observed strong dependence of luminescence constants on temperature indicates strong cross-relaxation process involving the 5D₄ excited state of Tb³⁺ taking place in all investigated hosts. This phenomenon has already been observed in other terbium-doped systems [23, 27-31] but the essence of this mechanism has not been clearly explained. Relying on the energy level structure of Tb³⁺ [21] it is not possible to find cross-relaxation paths assuming two- or three-ions interactions. In respect of the energy matching the most probable scheme of this process can be described as (5D₄, 3F₆) → (7F₃, 3F₂).
In this case energy from the $^5D_4$ excited state is non-radiatively transmitted to three nearest terbium neighbours immediately, exciting them from $^7F_6$ ground state to higher $^5F_2$ level. Such multi-ions mechanism seems to be possible due to very high density of terbium (100 % at.) in studied materials. From the data presented in Fig. 6 it could be seen that strength of the luminescence quenching strongly depends on the temperature, especially below 50 K. It indicates that transitions responsible for cross-relaxation process initiate not from the lowest but from higher lying Stark sublevels of the $^5D_4$ or $^7F_6$ ground state which are coupled by the Boltzmann statistic, so a thermal activation energy is needed.

The energy transfer rate $X$ could be define as:

$$X = \frac{1}{\tau_{\text{exp}}} - \frac{1}{\tau_0},$$  

(1)

where $\tau_{\text{exp}}$ is the measured lifetime and $\tau_0$ represents the lifetime in the absence of any Tb$^{3+}$-Tb$^{3+}$ interactions. Due to the very large energy gap between $^5D_4$ and lower lying state of Tb$^{3+}$, $\tau_0$ is equal to a radiative lifetime of $^5D_4$ level. The temperature dependence of the cross-relaxation rate can be described by following expression:

$$X(T) = X_{\text{max}} \exp\left(-\frac{\Delta E}{kT}\right),$$  

(2)

where $k$ is a Boltzmann constant, $X_{\text{max}}$ is the transfer rate for $T \to \infty$ and $\Delta E$ is the activation energy. Obtained cross-relaxation rates plotted as a $1/T$ function in semi-logarithmic scale for all investigated materials is given in Fig. 7. For the appropriate choice of $\tau_0$ the plot gives a straight line in agreement with Eq. (2). The maximal transfer rates $X_{\text{max}}$ and activation energies $\Delta E$ were found as a result of the best fitting of experimental points by Eq. (2). Comparison of obtained values for eutectic and corresponding bulk crystals are presented in Tab. 1. Determined radiative lifetime of $^5D_4$ excited state of Tb$^{3+}$ in TSAG bulk crystal is comparable to measured in YAG powdered phosphors with low density of Tb$^{3+}$ [23, 24].

4. Summary

Spectroscopic properties of Tb$_3$Sc$_2$Al$_3$O$_{12}$-TbScO$_3$ eutectic with self-organized rodlike microstructure and Tb$_3$Sc$_2$Al$_3$O$_{12}$ and TbScO$_3$ bulk crystals have been studied. Time-resolved emission spectra and lifetime of $^5D_4$ excited state of Tb$^{3+}$ ions in all investigated hosts have been measured and compared. Energy transfer between terbium ions leading to quenching of luminescence from $^3D_4$ excited state of Tb$^{3+}$ have been discussed. The TSAG-TSP eutectic is interesting optically active material in which both radiative and measured lifetimes of $^5D_4$ manifold of Tb$^{3+}$ ions are longer than in bulk TSAG and TSP crystals.

Acknowledgment

This work is supported by the Ministry of Science and Higher Education of Poland, grant no. N N515 421034.
References


Figure captions

Fig. 1. Microstructure of Tb₃Sc₂Al₃O₁₂-TbScO₃ eutectic: a) longitudinal-section, b) cross-section. Grey colour stands for TbScO₃ phase and black colour stands for Tb₃Sc₂Al₃O₁₂ phase, SEM images.

Fig. 2. Measured emission spectrum of TSAG:Tb³⁺ crystal exhibiting optical transitions from the ⁵D₄ excited state of Tb³⁺ to the lower lying ⁷F₁ levels.

Fig. 3. Partially energy level diagram of Tb³⁺ ion. Colored arrows – observed radiative transitions, black arrows – non-radiative transitions. X₁ and X₂ denote (⁵D₃, ⁷F₆) → (⁵D₄, ⁷F₁) and (⁵D₃, ⁷F₆) → (⁷F₀, ⁵D₄) cross-relaxation paths, respectively.

Fig. 4. Comparison of time-resolved emission spectra for TSAG-TSP eutectic and for a) TSP and b) TSAG bulk crystals. t₁ – gate width 7 μs, delay 0 μs, t₂ – gate width 100 μs, delay 30 μs.

Fig. 5. Decay profile of the ⁵D₄ luminescence in TSAG-TSP eutectic.

Fig. 6. Measured lifetimes of the ⁵D₄ excited state of Tb³⁺ in TSAG-TSP eutectic and in TSAG and TSP bulk crystals as a function of temperature. ETSAG and ETSP denote TSAG and TSP phase in TSAG-TSP eutectic respectively.

Fig. 7. Coefficients of cross-relaxation from ⁵D₄ level of Tb³⁺ ions X as a function of inverse temperature for a) bulk TSP and TSP phase of eutectic (ETSP), and b) bulk TSAG and TSAG phase of eutectic (ETSAG). ℏ₀ – radiative lifetime of the ⁵D₄ excited state of Tb³⁺, ΔE – activation energy of the cross-relaxation process, Xₘₐₓ – rate of the cross-relaxation process for T → ∞.
Tables

Tab. 1. Parameters obtained for individual phases of TSAG-TSP eutectic (ETSAG, ETSP) and for TSAG and TSP bulk crystals. $\tau_0$ – radiative lifetime of the $^5D_4$ excited state of Tb$^{3+}$, $\Delta E$ – activation energy of the cross-relaxation process from $^5D_4$ level of Tb$^{3+}$, $X_{\text{max}}$ – rate of the cross-relaxation process from $^5D_4$ level of Tb$^{3+}$ for $T \to \infty$.

<table>
<thead>
<tr>
<th></th>
<th>TSAG</th>
<th>TSP</th>
<th>ETSAG</th>
<th>ETSP</th>
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<td>$\tau_0$ [ms]</td>
<td>4</td>
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<td>10</td>
<td>0.4</td>
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<tr>
<td>$\Delta E$ [cm$^{-1}$]</td>
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<td>23</td>
<td>31</td>
<td>37</td>
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<tr>
<td>$X_{\text{max}}$ [$\mu$s$^{-1}$]</td>
<td>0.016</td>
<td>0.55</td>
<td>0.009</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Figures

Fig. 1
Fig. 2

Tb₃Sc₂Al₃O₁₂
T=300K

Intensity
λ [nm]
Fig. 3

![Energy diagram with levels and transitions](image-url)
Fig. 4

a) TSAG/TSP (t₁)

Intensity

λ [nm]

b) TSAG/TSP (t₂)

Intensity

λ [nm]

Fig. 5.

TSAG-TSP

$T = 300\text{K}$ em. 540 nm

Intensity [a. u.]

Time [$\mu$s]
Fig. 6

The figure shows a plot of the $\delta D_4$ lifetime [s] against Temperature [K]. The data points are categorized into different categories: TSAG, TSP, ETSAG, and ETSP. The graph displays a trend where the $\delta D_4$ lifetime decreases as the temperature increases.
Fig. 7

a) TSP
- $\tau_0 = 200 \mu s$
- $\Delta E = 23 \text{ cm}^{-1}$
- $X_{\text{max}} = 0.55 \mu \text{s}^{-1}$

ETSP
- $\tau_0 = 400 \mu s$
- $\Delta E = 37 \text{ cm}^{-1}$
- $X_{\text{max}} = 0.16 \mu \text{s}^{-1}$

b) TSAG
- $\tilde{\tau}_0 = 4 \text{ ms}$
- $\Delta E = 40 \text{ cm}^{-1}$
- $X_{\text{max}} = 0.016 \mu \text{s}^{-1}$

ETSAG
- $\tilde{\tau}_0 = 10 \text{ ms}$
- $\Delta E = 31 \text{ cm}^{-1}$
- $X_{\text{max}} = 0.009 \mu \text{s}^{-1}$