Luminescence of Mn\textsuperscript{2+} ions in Tb\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} garnet

Yu Zorenko\textsuperscript{a,}, V. Gorbenko\textsuperscript{a}, T. Voznyak\textsuperscript{a}, M. Batentschuk\textsuperscript{b}, A. Osvet\textsuperscript{b}, A. Winnacker\textsuperscript{b}

\textsuperscript{a} Laboratory of Optoelectronic Materials, Electronics Department, Ivan Franko National University of Lviv, Gen. Tarnavskyj Str. 107, 79017 Lviv, Ukraine

\textsuperscript{b} Department of Materials Sciences 6, University of Erlangen-Nürnberg, Martensstrasse 7, D-91058 Erlangen, Germany

1. Introduction

Manganese ion in oxides is a well-known activator used mainly for producing tunable solid-state laser media, holographic recording and optical data storage as well as thermo-luminescent detectors [1–3]. A peculiarity of doping by manganese is creation of different charge states of Mn ions (2+, 3+ and 4+) depending on the condition of crystallization, content of growth atmosphere and post-growth treatment, as well as the charge state of co-dopants [2].

The luminescence of different states of Mn ions in garnets was studied in the works [1–7]. The luminescence of Mn\textsuperscript{4+} (3d\textsuperscript{5}) ions which are isoelectronic to Cr\textsuperscript{3+} was investigated in detail for Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (YAG) garnet [5]. The luminescence spectrum of Mn\textsuperscript{4+} ions in RT range consists of the sharp R-lines peaked around 645–675 nm, which are caused mainly by the \(5T_2 \rightarrow 5E\) transition of Mn\textsuperscript{3+} ions. This luminescence is excited in the broad absorption band in the 450–600 nm range caused by the \(5E \rightarrow 4T_2\) transition of Mn\textsuperscript{3+} ions.

The luminescence of Mn\textsuperscript{3+} (3d\textsuperscript{4}) ions in Al- and Ga-garnets has been investigated in detail [4] and elsewhere [2,5,6]. Mn\textsuperscript{3+} ions in the (a)-sites of the garnet lattice usually possess the intensive luminescence caused by the \(4A_2 \rightarrow 4T_2\) or \(4A_2 \rightarrow 4E\) transition in the orange-red and infra-red spectral ranges, respectively [2,4]. The relative intensity of the \(5T_2 \rightarrow 5E\) or \(4T_2 \rightarrow 4E\) transitions strongly depends on the crystal field strength in the (a)-sites of garnet lattice and temperature [4]. This luminescence is excited in the broad absorption band in the 450–600 nm range caused by the \(4E \rightarrow 3T_2\) transition of Mn\textsuperscript{3+} ions.

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The luminescence of Mn\textsuperscript{2+} ions can be excited in several bands in the 400–520 nm range related to the \(4A_2 \rightarrow 4A_1\), \(4E\), \(6A_1 \rightarrow 4T_1\) and \(6A_1 \rightarrow 4T_2\) transitions. Due to such a position of the emission and absorption/excitation bands, the Mn\textsuperscript{3+}, Mn\textsuperscript{2+} and Mn\textsuperscript{2+} doped garnets, in principle, can be considered also as promising materials for luminescent converters of blue LEDs. For these reasons, the Mn\textsuperscript{3+} luminescence and the influence of Ce\textsuperscript{3+} co-doping in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Mn (YAG: Mn) powder phosphor were studied in [6].

Along with YAG, Tb\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (TbAG) garnet is considered as a promising host for creation of luminescent material for conversion of blue LED's radiation [8]. For example, effective processes of the energy transfer are realized in TbAG host to Ce\textsuperscript{3+} ions [9–12] and simultaneously to Ce\textsuperscript{3+} and Eu\textsuperscript{3+} ions [10,11] via the Tb\textsuperscript{3+} cation sublattice. In this work, we present for the first time the results of investigation of the manganese luminescence in TbAG host.

TbAG refers to the garnets with large crystal field strength [9,10]. It is also interesting to analyze from this point of view the
The luminescence properties of TbAG:Mn in the context of the Tanabe-Sugano diagram of Mn$^{3+}$ (3d$^4$) and Mn$^{4+}$ (3d$^5$) ions in comparison with the YAG:Mn with the weaker crystal field strength [4].

The investigations have been carried out on the specially grown single crystalline objects—single crystalline films (SCF) of TbAG:Mn garnets grown by Liquid-Phase Epitaxy (LPE) on substrates from undoped YAG single crystal (see for details [11,12]). For consideration of the manganese luminescence and analysis of the energy transfer processes in TbAG:Mn phosphors we investigated the luminescent properties of TbAG:Mn SCF depending on the concentration of Mn ranging from 0.019 to 0.07 at%. The influence of Ce$^{3+}$ co-doping on the TbAG:Mn luminescence was studied as well.

2. Growth of TbAG:Mn and TbAG:Mn,Ce SCF

A series of structurally perfect and optically transparent undoped TbAG, TbAG:Mn and TbAG:Mn,Ce SCF was grown by LPE onto YAG substrates from melt-solutions (MS) based on PbO–B$_2$O$_3$ flux. The main characteristics of the MS, growth regimes and thicknesses of the obtained SCF are listed in Table 1. The concentrations of Mn$_2$O$_3$ and CeO$_2$ activators in the MS were equal to 0.87 and 2.45 mol% and 0.43 and 4.0 mol%, respectively. Below, the SCF samples, corresponding to these contents, will be denoted as TbAG:Mn1, TbAG:Mn2, TbAG:Mn2,Ce1 and TbAG:Mn2,Ce2, respectively.

The perfect-quality SCF samples with an area of 1.5–2 cm$^2$ and a thickness of 14–35 μm were selected from the TbAG:Mn1, TbAG:Mn2, TbAG:Mn2,Ce1 and TbAG:Mn2,Ce2 SCF series for further studies. Multiple X-ray microanalysis of the selected TbAG:Mn2 and TbAG:Mn2,Ce2 SCF samples has shown that their content is close to Tb$_3$Al$_{4.98}$Mn$_{0.014}$O$_{12}$ and Tb$_3$Ce$_{0.0066}$Al$_{4.981}$Mn$_{0.0135}$O$_{12}$, respectively. This allows us to calculate the segregation coefficients of Mn and Ce ions at crystallization of these SCF that amount to 0.02 and 0.01, respectively. Taking into account these low segregation coefficients of these ions at crystallization of TbAG:Mn SCF and YAG substrate are equal to 12.0755 ˚A and 12.0115 ˚A, respectively, e.g., the relative difference in the lattice constants of the SCF–substrate interface (Fig. 1). The mechanism of formation of the transition layers (TL) at the temperature of SCF crystallization [15].

Such a large mismatch between the lattice constants of the SCF and YAG substrate is the main problem in obtaining the perfect TbAG-based SCF by LPE [11,12]. It is important to note, that we did not use any additional doping to reduce such a difference in the lattice constants of the SCF and the substrate [12]. The possibility of obtaining the perfect optically transparent SCF based on TbAG with a thickness up to ~80 μm by LPE on YAG substrates (Table 1) is achieved by means of formation of the transition layers (TL) at the SCF–substrate interface (Fig. 1).

Table 1

<table>
<thead>
<tr>
<th>Molar ratios, mole/mole</th>
<th>TbAG</th>
<th>TbAG:Mn</th>
<th>TbAG:Mn,Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_1$=[PbO]/[B$_2$O$_3$]</td>
<td>11.64</td>
<td>12.8–13.4</td>
<td>14–14.5</td>
</tr>
<tr>
<td>R$_2$=[Σ R$_6$O$_3$]/[PbO+B$_2$O$_3$]</td>
<td>0.026</td>
<td>0.024</td>
<td>0.023–0.0275</td>
</tr>
<tr>
<td>R$_3$=[Tb$_2$O$_3$]/[Σ [Al$_2$O$_3$]</td>
<td>0.113</td>
<td>0.113</td>
<td>0.133</td>
</tr>
<tr>
<td>R$_4$=[MnO$_2$]/[2 Σ R$_6$O$_3$]</td>
<td>–</td>
<td>0.0095 (0.019 at%)</td>
<td>–</td>
</tr>
<tr>
<td>R$_5$=[CeO$_2$]/[Σ R$_6$O$_3$]</td>
<td>–</td>
<td>0.035 (0.07 at%)</td>
<td>0.0044 (0.004 at%)</td>
</tr>
<tr>
<td>Temperature of growth (°C)</td>
<td>980–1000</td>
<td>970–1000</td>
<td>970–990</td>
</tr>
<tr>
<td>Speed of substrate rotation (rpm)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>SCF growth rate (μm/min)</td>
<td>1.05–1.6</td>
<td>0.63–2.0</td>
<td>0.35–1.73</td>
</tr>
<tr>
<td>Thickness of SCF (μm)</td>
<td>7–74</td>
<td>14–64</td>
<td>20–78</td>
</tr>
</tbody>
</table>
equalization of the difference between the lattice constants of these two garnets takes place during the SCF growth [11,12].

3. Experimental technique

The absorption of TbAG-based SCF was measured using a Perkin-Elmer spectrophotometer at RT. The cathodoluminescence (CL) spectra of the TbAG:Mn and TbAG:Mn,Ce SCF in comparison with the CL spectra of TbAG:Ce SCF from our previous paper [11] were recorded using a SEM JSM-6420 and a front-side illuminated Jobin-Yvon CCD-3500V as recording devices. Low-resolution excitation and photoluminescence (PL) spectra were measured by a J+M-Tidas FL 3095 spectrometer system. The emission spectra were not corrected for the sensitivity of a Si-detection array. Excitation spectra in the 330–550 nm range were corrected for the energy distribution of a UV-lamp and a quartz fiber. Excitation spectra in the UV–VUV range (3.7–9 eV) at 10 K were measured under excitation by synchrotron radiation at Superlumi experimental station (HASYLAB, DESY, Hamburg).

The photoluminescence decay measurements were carried out at RT at excitation wavelengths of 308 nm using an XeCl excimer laser with the pulse duration being equal to 25 ns. Detection was realized with a set-up consisting of monochromator, photomultiplier and digital storage oscilloscope.

Due to different thickness in all series of SCF samples the correct comparative study of the relative light yield (LY) of TbAG:Mn, TbAG:Mn,Ce and TbAG:Ce SCF depending on the concentration of Mn and Ce ions were performed under high-energy steady-state excitation by α-particles of Pu$^{239}$ sources (5.15 MeV) with a penetration length in the material of about 10 μm using a detector based on FEU-110 PMT and a multichannel single-photon counting system within a time interval of 0.5 μs Fig. 2.

4. Results and discussion

4.1. LY measurements

The LY of radioluminescence (RL) of the series of TbAG:Mn, TbAG:Mn,Ce and TbAG:Ce SCF in comparison with a standard sample of YAG:Ce SCF with the known LY of RL 12,200 Photons/MeV under excitation by α-particles of Pu$^{239}$ sources are presented in Table 2. It is worth noting that under such high-energy excitation the contribution of the luminescence of Tb$^{3+}$ cations in the total LY of all TbAG-based SCF is insignificant at RT due to the concentration quenching [10,11]. The luminescence TbAG:Mn1 and Mn2 SCF is mainly determined by the orange luminescence of Mn$^{2+}$ ions in the band peaked at 595 nm (Fig. 3a) without any significant contribution of other valence state of Mn.
ions. The LY of TbAG: Mn1 SCF was equal to 5.1% with respect to LY of the YAG:Ce SCF. The LY of TbAG: Mn2 SCF is increased to 6.1% with increasing the concentration of Mn ions from 0.019 to 0.07 at% (Table 2).

As seen from Table 2, the Ce3+ co-doping even in a small amount of 0.004 at% leads to a notable increase in the LY of the RL of TbAG:Mn2, Ce1 SCF and LY rapidly rises up at increasing the Ce3+ concentration. In particular, for TbAG: Mn2, Ce2 SCF, where the Ce3+ concentrations are close to 0.04 at%, the LY of RL amounts to 36.9–44.2% of the LY of TbAG: Ce SCF with the Ce3+ concentration of 0.13 at%. Thus, we can expect rather comparable LY of the RL in TbAG: Mn, Ce and TbAG: Ce SCF at close concentrations of Mn2+ ions. This result provides the evidence that: (i) Mn2+ ions do not widely quench the Ce3+ luminescence in TbAG and (ii) the excitation energy in TbAG host is transferred simultaneously both to Mn2+ and Ce3+ ions.

The LY of PL of TbAG: Mn1 SCF under excitation in the vicinity of the f–d transition of Tb3+ cation at 326 nm [9–12] is about 12.5% of LY of TbAG: Ce SCF and increases to 15% for TbAG: Mn2 SCF at rising the Mn concentration to 0.07 at%. The LY of PL of TbAG: Mn2, Ce1 SCF widely rises up at low-concentration (0.004 at%) co-doping by Ce3+ ions (Table 2). Next increase of the Ce concentration to 0.04 at% leads to significant increase in the LY of PL to 62.5% in TbAG: Mn2, Ce2 SCF (Table 2).

### Table 2

<table>
<thead>
<tr>
<th>SCF content</th>
<th>Mn content (at%)</th>
<th>Ce content (at%)</th>
<th>LY of RL* (%)</th>
<th>LY of PL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbAG: Mn1</td>
<td>0.019</td>
<td></td>
<td>5.1</td>
<td>12.5</td>
</tr>
<tr>
<td>TbAG: Mn2</td>
<td>0.07</td>
<td></td>
<td>6.1</td>
<td>15</td>
</tr>
<tr>
<td>TbAG: Mn2, Ce1</td>
<td>0.07</td>
<td>0.004</td>
<td>6.2–9.1</td>
<td>22.5</td>
</tr>
<tr>
<td>TbAG: Mn2, Ce2</td>
<td>0.07</td>
<td>0.041</td>
<td>23–35</td>
<td>62.5</td>
</tr>
<tr>
<td>TbAG: Ce</td>
<td>0.13</td>
<td></td>
<td>62.3–71.0</td>
<td>100</td>
</tr>
<tr>
<td>YAG: Ce SCF</td>
<td></td>
<td>0.073</td>
<td>100</td>
<td>–</td>
</tr>
</tbody>
</table>

The differences in the values of LY for TbAG: Mn and TbAG: Mn SCFs under α-particles and PL excitation are partly caused by the difference in the time interval for the luminescence registration which in the case of the PL was significantly larger than that at the RL measurement (0.5 μs).

### 4.2. Absorption spectra

The absorption spectra of TbAG and TbAG: Mn SCF in the 190–750 nm range are shown in Fig. 2a. In the presented spectra the dominant absorption bands with the maxima in ranges of 198–203 nm (E1–2), 222–232 nm (E1–2), 259–275 nm (E1–3) and 325 nm (E1) belong to the spin-allowed (E4–E2) and spin-forbidden (E4) transitions of Tb3+ cations, respectively [10,11]. The structure of the E2–E4 absorption bands is caused by the presence of two types of the 4F7/2–5D1 transitions between the 7Fj ground state and 5E and 7E states of the 5d-shell (see [10] for details). Due to the existence of the part of cations in Tb4+ charge state, the absorption spectra of some undoped TbAG SCF (Fig. 2a, curve 1) also consist of the wide band peaked at 430 nm, which is most probably caused by the charge-transfer transition between oxygen ligands and Tb4+ ions. The position of this band coincides well with the position of analogues band in TbAlO4 perovskite host [14].

The absorption spectra of TbAG: Mn, TbAG: Mn, Ce SCFs in the 300–750 nm range, which is important from the point of view of the luminescence excitation of these SCF, are shown in Fig. 2b and c. Besides the above-mentioned 4F–5d absorption bands of Tb3+ cations, the group of lines in the 355–360 and 371–379 nm ranges, related correspondingly to the 7F6–5D4 transitions of Tb3+ ions are seen in the spectra of all TbAG-based SCF. Another group of absorption lines peaked at 487 nm, which is caused by the 7F6–5D4 transition of Tb3+ cations, strongly overlaps with the Mn2+ and Ce-related absorption bands.

The absorption of TbAG: Mn1, Mn2 SCF (Fig. 2b, curves 2, 3 and 2c, curve 3) also consists the characteristic for Mn2+ ions the sharp-line absorption bands peaked at 410 nm related to the 4A2–6A1, 4A2–4E transitions and two wide bands with the maxima approximately at 440 and 522 nm which can be related correspondingly to 4A2–6F5/2, 4A2–4T1 transitions of Mn2+ ions [16,17]. It should be noted that all mentioned Mn2+–related absorption bands have very week intensity due to the spin-forbidden origin of transitions which are slightly allowed by spin–orbit interaction [16,17]. Apart from the Mn2+ absorption bands, other wide absorption band peaked at 462 nm is present in the absorption spectra of TbAG: Mn SCF. The nature of this absorption band is caused both by the 4F2–5D1 transitions of Ce3+ ions as the trace impurity in substrate and SCF located just in this spectral range (Fig. 2c, curves 4 and 5) as well as and the 4A2–4T1 transitions of Tb3+ cations.
transition of Mn$^{4+}$ ions, because under excitation in this band the low-intensity luminescence of Ce$^{3+}$ and Mn$^{4+}$ ions is observed in the bands peaked at 540 nm and 673 and 708 nm, respectively. The short-wavelength tail of the 462 nm absorption band also significantly overlaps with the 4f–4f absorption bands of the Tb$^{3+}$ cations peaked at 487 nm related to the radiative $^7F_6\rightarrow^5D_4$ transitions of Tb$^{3+}$ cations.

The absorption of Ce$^{3+}$ ions in TbAG:Mn, Ce SCF (Fig. 2c, curves 4 and 5) is manifested in two bands with the maxima at 464 and 338 nm which are caused by the 4f$^2(2P_{3/2,1/2})$–4d$^5$ transitions. It should be noted that: (i) the absorption bands of Ce$^{3+}$ ions matches with the $E_1$(sf) and 4f–4f absorption bands of the Tb$^{3+}$ cations [10–12], (ii) the absorption bands related to the radiative $F_6\rightarrow^5D_3$, $^5D_4$ transition of Tb$^{3+}$ cations is located above the corresponding $^6A_1\rightarrow^4A_1$, $^4E$ and $^6A_1\rightarrow^4T_1$ absorption bands of Mn$^{2+}$ ions and (iii) the absorption band peaked at 464 nm related to the transitions in the lowest radiative 5d$^1$ state of Ce$^{3+}$ ions are located above the $^6A_1\rightarrow^4T_1$ absorption bands of Mn$^{2+}$ ions. This can be important condition for the simultaneous energy transfer both to Mn$^{2+}$ and Ce$^{3+}$ ions in the TbAG host/or for the energy transfer between the Ce$^{3+}$ and Mn$^{2+}$ ions.

### 4.3. Emission spectra

The CL (Fig. 3a) and PL (Fig. 3b) spectra of TbAG:Mn SCF under excitation at 326 nm in the vicinity of the f–d absorption bands of Tb$^{3+}$ cations (Fig. 3b) show the bright orange Mn$^{2+}$ luminescence in the band peaked at 595 nm (2.08 eV) at 300 K with a half width of 0.123 eV and Stocks shifts of 0.29 eV. The later high-pressure spectroscopy investigations of TbAG:Mn SCF confirms the relation of this emission exactly to Mn$^{2+}$ luminescence. Specifically, the red shift of this emission with increasing the pressure was observed in agreement with the Tanabe–Sugano diagram for d$^5$ ions [17]. In comparison with the position of the Mn$^{2+}$ luminescence band in YAG:Mn at 590 nm [4], the corresponding emission bands in TbAG:Mn SCF are slightly shifted to the long-wavelength range due to increasing the crystal field strength in the dodecahedral sites of TbAG host [10,12]. The large crystal field strength in the Mn$^{2+}$ ions positions also explains the relatively large (0.29 eV) Stocks shift of this emission. The two low-intensity shoulders around 673 and 708 nm in PL spectra of TbAG:Mn SCF are caused by the Mn$^{2+}$ ions luminescence [3,5].

The intensity of CL and PL of TbAG:Mn SCF rises up at increasing the Mn content in SCF (Table 2). Thus, the energy is well transferred in TbAG host to Mn$^{2+}$ ions both under high-energy excitation and excitation in the absorption band of Tb$^{3+}$ cations. It is interesting to note that the luminescence spectra of TbAG:Mn1 and TbAG:Mn2 SCF in RT range do not show the Mn$^{2+}$ luminescence; e.g., the excitation energy cannot be transferred to Mn$^{2+}$ ions via the Tb$^{3+}$ cation sublattice in TbAG host.

The Ce$^{3+}$ doping leads to significant increase of the LY of CL and PL of TbAG:Mn, Ce SCF (Table 2) in the complex band peaked at 564–574 nm range (Fig. 3, curves 2 and 3) due to the contribution of the Ce$^{3+}$ luminescence related to the $5d^1$–$4f(2P_{3/2,1/2})$ transition. In general, the luminescence spectra of TbAG:Mn, Ce SCF present the mixture of Ce$^{3+}$ and Mn$^{2+}$ luminescence with the prevailing contribution of the Ce$^{3+}$ emission. At the same time, even at large concentration of Ce$^{3+}$ ions 0.04 at% the PL and especially CL spectra of TbAG:Mn1, Ce2 SCF (curves 3) are notably shifted with respect to the spectra of TbAG:Ce and YAG:Ce SCF (curves 4 and 5) in the long-wavelength range due to contribution of the Mn$^{2+}$ emission. Thus, the simultaneous energy transfer both to the Ce$^{3+}$ and Mn$^{2+}$ ions is realized in the TbAG:Mn, Ce SCF.

### 4.4. Excitation spectra of Mn$^{2+}$ and Ce$^{3+}$ luminescence

The excitation spectra of the Mn$^{2+}$ luminescence in TbAG:Mn SCF in the 440–550 nm range (Fig. 4a, curve 1) consist of the broad band peaked at 467 nm, which is the superposition of the week absorption bands peaked at 410–415, 440 and 521 nm related correspondingly to the $^6A_1\rightarrow^4A_1$, $^4E$, $^4T_2$, and $^4T_2$ transition of Mn$^{2+}$ ions and the band peaked 463 nm related to the 4f$^2(2P_{3/2,1/2})$–5d transition of Ce$^{3+}$ trace impurity. The excitation bands peaked at 487 and 376 nm are related correspondingly to the $^7F_6\rightarrow^5D_4$ and $^5D_3$ transition of Tb$^{3+}$ cations. In the UV–VUV range the excitation spectra of the Mn$^{2+}$ luminescence in TbAG:Mn SCF also consist of several $E_1$–$E_5$ bands related to the 4f–4f5d transition of Tb$^{3+}$ cations (Fig. 4b, curve 1). The peak at $E_{ex}=7.14$ eV in the TbAG excitation range [10] (Fig. 4b, curve 1) corresponds to the energy of creation of excitons localized around Mn$^{2+}$ ions. It is important to note that the excitation spectra of the Mn$^{2+}$ luminescence in

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**Fig. 4.** Excitation spectra of luminescence at 590 nm in TbAG:Mn (1), TbAG:Mn, Ce (2) and TbAG:Ce (3) SCF in comparison with YAG:Ce SCF (4) in the 330–550 nm range at 300 K (a) and the 330–120 nm range at 10 K under excitation by synchrotron radiation (b). Intensity of curve 1 is multiplied by 20.
TbAG:Mn SCF in the high-energy region (Fig. 4b, curve 1) are similar in the whole to the excitation spectra of the Mn$^{2+}$ + Ce$^{3+}$ and Ce$^{3+}$ luminescence in TbAG:Mn,Ce and TbAG:Ce SCF (Fig. 4b, curves 2 and 3, respectively). This is an evidence of the effective energy transfer both to the Mn$^{2+}$ and Ce$^{3+}$ ions in TbAG host.

The excitation spectra of TbAG:Ce,Mn SCF (Fig. 4a, curve 2) present superposition of the excitation spectra of Mn$^{2+}$ and Ce$^{3+}$ luminescence (Fig. 4a, curve 1 and 3, respectively) due to the efficient simultaneous energy transfer to Mn$^{2+}$ and Ce$^{3+}$ ions in TbAG:Mn,Ce SCF. At the same time, the contribution of the Ce$^{3+}$-related bands peaked at 339.5 and 468 nm to the total intensity of the emission at 590 nm in TbAG:Ce,Mn SCF strongly increases with rising the Ce$^{3+}$ content in these SCF (Fig. 4a, curve 2 and 3, respectively).

4.5. Decay kinetics

The decay kinetics of the Mn$^{2+}$ luminescence registered at a wavelength of 600 nm in TbAG:Mn1 SCF at 300 K is shown in Fig. 5a under excitation at 308 nm in the vicinity of the d–f E$_1$ absorption band of Tb$^{3+}$ cations. The main component of Mn$^{2+}$ emission decay with the lifetime $\tau=0.64$ ms at 300 K. In comparison with the lifetime of Mn$^{2+}$ luminescence at 570 nm in (Ca–Cd)Al$_2$Ge$_3$O$_{12}$ garnet (12 ms) the decay time of Mn$^{2+}$ luminescence in TbAG host is about 20 times lower. At the same time, the decay time of the Mn$^{2+}$ luminescence in TbAG:Mn SCF is the same order with the lifetime of the Mn$^{2+}$ luminescence in YAG [3]. Thus, short decay time of the Mn$^{2+}$ luminescence in TbAG:Mn SCF can be partly explained by extremely large crystal field strength in the dodecahedral sites of TbAG host. Next high-pressure investigation of the Mn$^{2+}$ luminescence in TbAG:Mn SCF [18] confirms the strong decrease of the decay time of Mn$^{2+}$ luminescence with increasing of crystal field strength. At the same time, it is not excluded the possible existence of additional deactivations channels for Mn$^{2+}$ luminescence.

The influence of Mn$^{2+}$ doping on the decay kinetics of Ce$^{3+}$ luminescence in TbAG:Ce,Mn SCF is shown in Fig. 6. It is necessary to note that after ending of short (25 ns) laser pulse all decay curves in Fig. 6 contain the 0.6–1.1 $\mu$s initial parts where rise of the Ce$^{3+}$ and Mn$^{2+}$ luminescence intensity occurs. This also confirms the existence of the energy transfer to these ions via the sublattice of Tb$^{3+}$ cations. As can be also seen from Fig. 6, the notable decrease of the average lifetime of the fast components of Ce$^{3+}$ emission occurs under excitation at 308 nm in vicinity of the d–f absorption band of Tb$^{3+}$ cations. Such decrease of the lifetime of the Ce$^{3+}$ luminescence can be explained by the Ce$^{3+}$ – Mn$^{2+}$ energy transfer via the dipole–dipole interaction [11]. At the same time, this assumption needs the additional experimental confirmation.

5 Discussion

Based on the above-mentioned properties of TbAG:Mn SCF, we can conclude that the effective energy transfer to Mn$^{2+}$ ions via the Tb$^{3+}$ sublattice takes place in TbAG host. For this reason TbAG:Mn phosphor, in principle, can be applied for conversion of LED’s radiation in the orange-red spectral range. This conclusion also can be extended to TbAG:Mn, Ce phosphor with higher efficiency of luminescence in the mentioned range with respect to YAG:Ce and TbAG:Ce phosphors (Fig. 4).

Let us briefly consider the complex cascade mechanism of the Tb$^{3+}$ – Mn$^{2+}$ and Tb$^{3+}$ – Mn$^{2+}$ – Ce$^{3+}$ energy transfer in the TbAG.
host. Under high-energy excitation the excitation energy from TbAG host can transfer from 5d–f states through 5D2 and 5D4 4f-states of Tb3+ cations to 5D3 and 5D4 4f-states of Tb3+ cations as well as through 7F0 (or 5d 14f7) and 5D3 states of Tb3+ cations to 5d states of Ce3+ ions [10]. Excitation of the 5d states of Ce3+ ions also occurs by means of the optical transitions of these ions or due to the energy transfer from Tb3+ cations (Fig. 4a); afterwards a part of the excitation energy can transfer to the 5D4 state of Tb3+ cations [9,11] and 4T1 state of Mn2+ ions due to partial overlapping of the emission spectra of Ce3+ ions (Fig. 3) and excitation spectra of Tb3+ cations and Mn2+ ions in the range of 460–550 nm (Fig. 4a). In turn, the 5D4→7F radiative transitions of Tb3+ cations also can cause the additional excitation of the 4T1 states of Mn2+ ions (Fig. 4a). Besides, we also cannot exclude the existence of the dipole–dipole interaction between Ce3+ and Mn2+ ions. Specifically, notable decrease of the average lifetime of the fast components of the Ce3+ luminescence with increasing the Mn2+ ions content in TbAG:Mn, Ce SCF under excitation in the vicinity of the d–f absorption band of Tb3+ cations (Fig. 6) support this conclusion. Finally, the 4T1→6A1 and 5d1→4F(5/2, 7/2) radiative transitions of Mn2+ and Ce3+ ions occur in TbAG:Mn, Ce SCF after the corresponding relaxation between the excited states of these ions.

6. Conclusion

The structurally and optically perfect TbAG, TbAG:Mn and TbAG:Mn, Ce single crystalline films (SCF) have been crystallized for the first time by liquid-phase epitaxy (LPE) method from PbO–B2O3 flux onto YAG substrate without any additional doping for reducing the significant mismatch (Δa = +0.064 Å) between the lattice constants of SCF and substrate. It has been confirmed that the possibility of obtaining TbAG-based SCF onto YAG substrates by LPE is achieved by means of formation of the transition layers (TL) between SCF and substrate in which an equalization of the difference between the lattice constants of these two garnets takes place during the SCF growth. The cathodoluminescence images of TL at the TbAG:Mn SCF/YAG substrate interface are presented for supporting such a model of TBAG SCF growth.

It has been shown that the manganese dopant introduces in the mentioned TbAG SCF during LPE growth preferably in the Mn2+ charge state in the dodecahedral positions of the garnet lattice due to the existence of the part of Tb3+ cations in the Tb4+ charge state. The segregation coefficient of Mn ions in TbAG SCF grown by LPE onto YAG substrate is about 0.02.

The effective energy transfer from the TbAG host to Mn2+ ions takes place in TbAG:Mn SCF and results in the intensive Mn2+ emission in the bands peaked at 595 nm with a lifetime of 0.64 ms which are caused by the 4T1→6A1 radiative transitions. The excitation energy from the TbAG host to Mn2+ ions transfers both from the d–f and f–f states of Tb3+ cations via the radiative transition from 5D2 and 5D4 levels in UV (375 nm) and visible (487 nm) ranges. For this reason, TbAG:Mn can be used, in principle, as a luminescent converter medium for radiation of UV and blue LEDs.

In TbAG:Mn, Ce, the simultaneous energy transfer from Tb3+ cations to Ce3+ and Mn2+ ions is realized. The energy transfer in the Ce3+ → Mn2+ and Ce3+ → Tb3+ → Mn2+ pairs can cause additional channels for excitation of the Mn2+ luminescence. Due to the existence of the Mn2+ emission, TbAG:Mn, Ce phosphor demonstrates the relatively higher contribution to the luminescence in the orange-red spectral range as compared with the YAG:Ce and TbAG:Ce phosphors.

Acknowledgement

The work was supported by the DFG project Wi 323/23/1. The authors also express their gratitude to Prof. Dr. G. Zimmerer and Dr. M. Gryzhanuky for their assistance in carrying out experiments in HASYLAB at DESY in the frame of II-05-105 “Luminescence of oxide films” research project.

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