Luminescence of Mn^{2+} ions in $\text{Tb}_3\text{Al}_5\text{O}_{12}$ garnet

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ABSTRACT

The paper is dedicated to investigation of the Mn^{2+} luminescence in $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (TbAG) garnet, as well as the processes of excitation energy transfer between host cations (Tb^{3+} ions) and activators (Mn^{2+} and Mn^{2+} – Ce^{3+} pair ions) in single crystalline films of TbAG:Mn and TbAG:Mn,Ce garnets which can be considered as promising luminescent materials for conversion of LED's radiation. Due to the effective energy transfer between TbAG host and activator, Mn^{2+} ions in TbAG possess the bright orange luminescence in the bands peaked at 595 nm with a lifetime of 0.64 ms which are caused by the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ radiative transitions. The simultaneous process of energy transfer is realized in TbAG:Mn,Ce: (i) from Tb^{3+} to Mn^{2+} ions; (ii) from Tb^{3+} cations to Ce^{3+} ions and then partly to Mn^{2+} ions through Tb^{3+} ion sublattice and Ce–Mn dipole–dipole interaction.

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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^{4+} ($3d^3$) ions which are isoelectronic to Cr^{3+} was investigated in detail for $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) garnet [5]. The luminescence spectrum of Mn^{4+} ions in RT range consists of the sharp R-lines peaked around 645–675 nm, which are caused mainly by the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transitions and partly by the ${}^2\text{T}_1 \rightarrow {}^4\text{A}_2$ transitions [5]. This luminescence is excited in the band peaked around 460–480 nm, which are attributed to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Mn^{4+} ions in the octahedral position of garnet host [2].

The luminescence of Mn^{3+} in the octahedral sites of Al- and Ga- garnets has been investigated in detail in [4] and elsewhere [2,5,6]. Mn^{3+} ions in the (a)-sites of the garnet lattice usually possess the intensive luminescence caused by the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ or ${}^1\text{T}_2 \rightarrow {}^5\text{E}$ transition in the orange-red and infra-red spectral ranges,

respectively [2,4]. The relative intensity of the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ or ${}^1\text{T}_2 \rightarrow {}^5\text{E}$ 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 ${}^5\text{E} \rightarrow {}^5\text{T}_2$ transition of Mn^{3+} ions.

The luminescence of Mn^{2+} ($3d^5$) ions in Al- and Ga-garnets has been investigated in detail in $(\text{Ca}-\text{Cd})\text{Al}_2\text{Ge}_3\text{O}_{12}$ [7] and has been briefly reported for $\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ and YAG [2,4]. The typical emission with the maxima around 590 nm, attributed to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transitions of Mn^{2+} ions, was observed in all the mentioned garnets. The luminescence of Mn^{2+} ions can be excited in several bands in the 400–520 nm range related to the ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1$, ${}^4\text{E}$, ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ and ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ transitions.

Due to such a position of the emission and absorption/excitation bands, the Mn^{4+} , Mn^{3+} and Mn^{2+} doped garnets, in principle, can be considered also as promising materials for luminescent converters of blue LEDs. For these reasons, the Mn^{3+} luminescence and the influence of Ce^{3+} co-doping in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Mn}$ (YAG:Mn) powder phosphor were studied in [6].

Along with YAG, $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (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^{3+} ions [9–12] and simultaneously to Ce^{3+} and Eu^{3+} ions [10,11] via the Tb^{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

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luminescence properties of TbAG:Mn in the context of the Tanabe-Sugano diagram of Mn^{3+} ($3d^4$) and Mn^{2+} ($3d^5$) 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 $PbO-B_2O_3$ flux. The main characteristics of the MS, growth regimes and thicknesses of the obtained SCF are listed in Table 1. The concentrations of MnO_2 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 cm² 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 $Tb_3Al_{4.986}Mn_{0.014}O_{12}$ and $Tb_{2.992}Ce_{0.008}Al_{4.986}Mn_{0.0135}O_{12}$, 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 values of segregation coefficients, the concentrations of Mn ions in TbAG:Mn1 and TbAG:Mn2 SCF (0.019 and 0.07 at%, respectively) and Ce ions in TbAG:Mn2,Ce1 and TbAG:Mn2,Ce2 SCF (0.004 and 0.041 at%, respectively) were established as well (Table 1). Rather low segregation coefficients of these ions at crystallization of TbAG-based SCF by LPE is due to considerable difference in the ionic radii of Mn ions in the different charge states and Ce^{3+} ions (1.143 Å) with respect to the ionic radius of Al^{3+} (0.53 Å) and Tb^{3+} (1.04 Å) cations in the octahedral and dodecahedral sites of the garnet lattice, respectively [13].

Taking into account the multiplicity of the valence state of manganese, we also can expect the existence of different ions (specifically, Mn^{3+} , Mn^{2+} and Mn^{4+}) in the different crystal-

lographic positions of garnet host in TbAG:Mn SCF. Due to relative proximity of the ionic radius (0.645 Å) of Mn^{3+} to that of Al^{3+} cations in the six-fold (0.53 Å) coordination [13], Mn^{3+} ions are localized preferably in the octahedral (a)-sites of garnet lattice [2,4]. The Mn^{4+} ions with ionic radii of 0.39 Å and 0.53 Å in the six-fold and four-fold coordinations, respectively, can substitute both the octahedral and tetrahedral sites of Al^{3+} cations. The relatively large Mn^{2+} ions (0.96 and 0.83 Å in the eight-fold and six-fold coordinations, respectively) can substitute both the dodecahedral and octahedral sites of the garnet lattice.

It is worth to note that Mn^{3+} ions are isovalent to cations of TbAG host but in the case of Mn^{2+} and Mn^{4+} states the charge compensation is required. It is important to note that the Mn^{2+} state can be preferably realized in TbAG SCF at low concentration of Mn ions due to the presence of the part of Tb cations in Tb^{4+} valence state as a result of using the typical Tb_4O_7 oxide for the charge preparation. Similar behavior is also observed in single crystals of $TbAlO_3$ perovskite grown from the melt-solution in air atmosphere [14]. In TbAG:Mn SCF, the charge compensation of Mn^{2+} and Mn^{4+} ions can also be partly done by the creation of the $Mn^{2+}-Mn^{4+}$ pairs or by Pb^{2+} (from flux) and Pt^{4+} (from crucible) trace impurities. The concentration of Pb^{2+} and Pt^{4+} ions in SCF can be changed in the tens–hundreds ppm ranges depending on the temperature of SCF crystallization [15].

For structural characterization of TbAG:Mn SCF we use the X-ray ($Cu_{K\alpha}$) diffraction investigation of TbAG:Mn1 SCF in comparison with the YAG substrate. The well separated reflection peaks from (211), (422) and (633) planes were obtained for both samples. The calculated values of the lattice constants of TbAG:Mn SCF and YAG substrate are equal to 12.0755 Å and 12.0115 Å, respectively, e.g., the relative difference in the lattice constants is +0.064 Å (0.53%).

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). The mechanism of formation of such TL during crystallization of SCF of the $R_3Al_5O_{12}$ ($R=Lu, Yb, Tb, Eu-Y$) garnets was considered in detail by us in the previous papers [11,12]. Here, we mention only the fact that in the case of TbAG, TbAG:Mn and TbAG:Mn,Ce SCF growth we also observed the formation of TL with a thickness of 1.5–1.9 μm on the TbAG-based SCF/YAG substrate borders using the scanning electron microscope (SEM) JEOL JSM-6420 (Fig. 1), in which an

Table 1

Conditions of growth of TbAG-based SCF by LPE onto YAG substrates. Concentrations of Mn and Ce in the corresponding SCF series are indicated in brackets.

Molar ratios, mole/mole	TbAG	TbAG:Mn	TbAG:Mn,Ce
$R_1 = [PbO]/[B_2O_3]$	11.64	12.8–13.4	14–14.5
$R_2 = \Sigma R_2O_3/[PbO+B_2O_3]$	0.026	0.024	0.023–0.0275
$R_3 = [Tb_4O_7]/[Al_2O_3]$	0.113	0.113	0.133
$R_4 = [MnO_2]/[\Sigma R_2O_3]$	–	0.0095 (0.019 at%)	–
		0.035 (0.07 at%)	
		0.035 (0.07 at%)	
$R_5 = [CeO_2]/[\Sigma R_2O_3]$	–		0.0044 (0.004 at%)
			0.041 (0.041 at%)
Temperature of growth (°C)	980–1000	970–1000	970–990
Speed of substrate rotation (rpm)	100	100	100
SCF growth rate ($\mu m/min$)	1.05–1.6	0.63–2.0	0.35–1.73
Thickness of SCF (μm)	7–74	14–64	20–78

Fig. 1. Cathodoluminescence (CL) image of cleavage between TbAG SCF (a) and TbAG:Mn,Ce SCF (b) with a thickness of 7.3 μm (a) and 20 μm (b) and YAG substrates with a multiplication of 10,000 (a) and 3000 (b), respectively. TL (grey or bright streaks in the middle of the picture with a thickness of 1.5–1.9 μm) exists between YAG substrate (bottom of the pictures) and TbAG:Ce SCF (a) and TbAG:Ce,Mn (b) SCF (top of the pictures).

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 multi-channel 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

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 Ce^{3+} 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 Ce^{3+} concentration. In particular, for TbAG:Mn2,Ce2 SCF, where the Ce^{3+} concentrations are close to 0.041 at%, the LY of RL amounts to 36.9–44.2% of the LY of TbAG:Ce SCF with the Ce^{3+} 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 concentration of Ce^{3+} ions. This result provides the evidence that: (i) Mn^{2+} ions do not widely quench the Ce^{3+} luminescence in TbAG and (ii) the excitation energy in TbAG host is transferred simultaneously both to Mn^{2+} and Ce^{3+} ions.

The LY of PL of TbAG:Mn1 SCF under excitation in the vicinity of the f–d transition of Tb^{3+} 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 Ce^{3+} ions (Table 2). Next increase of the Ce concentration to 0.041 at% leads to significant increase in the LY of PL to 62.5% in TbAG:Mn2,Ce2 SCF (Table 2).

Table 2

Relative LY of radioluminescence (RL) and PL of Mn- and Mn–Ce-doped TbAG SCF under excitation correspondingly by α -particles of a Pu239 (5.15 MeV) source in comparison with standard YAG:Ce SCF samples with an LY of 12,200 Ph/MeV and by light at a wavelength of 326 nm.

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

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 ($E_4^1 \rightarrow E_2^1$), 222–232 nm ($E_3^1 \rightarrow E_2^1$), 259–275 nm ($E_2^1 \rightarrow E_2^3$) and 325 nm (E_1) belong to the spin-allowed ($E_4 \rightarrow E_2$) and spin-forbidden (E_1) transitions of Tb^{3+} cations, respectively [10,11]. The structure of the $E_2 \rightarrow E_4$ absorption bands is caused by the presence of two types of the $4f^8(^7F_j) \rightarrow 4f^75d^1$ transitions between the 7F_j ground state and 7E and 9E states of the 5d-shell (see [10] for details). Due to the existence of the part of cations in Tb^{4+} 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 Tb^{4+} ions. The position of this band coincides well with the position of analogues band in TbAlO_4 perovskite host [14].

The absorption spectra of TbAG, 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 Tb^{3+} cations, the group of lines in the 355–360 and 371–379 nm ranges, related correspondingly to the $^7F_6 \rightarrow ^5D_2$, 5D_3 transitions of Tb^{3+} 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 $^7F_6 \rightarrow ^5D_4$ transition of Tb^{3+} cations, strongly overlaps with the Mn- 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 Mn^{2+} ions the sharp-line absorption bands peaked at 410 nm related to the $^6A_1 \rightarrow ^4A_1$, 4E transitions and two wide bands with the maxima approximately at 440 and 522 nm which can be related correspondingly to $^6A_1 \rightarrow ^4T_2$, 4T_1 transitions of Mn^{2+} ions [16,17]. It should be noted that all mentioned Mn^{2+} -related absorption bands have very weak intensity due to the spin-forbidden origin of transitions which are slightly allowed by spin–orbit interaction [16,17]. Apart from the Mn^{2+} 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 $4f(^2F_{5/2}) \rightarrow 5d^1$ transitions of Ce^{3+} 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 $^4A_2 \rightarrow ^4T_2$

Fig. 3. Normalized (by maximum of intensity) CL (a) and PL (b) spectra under excitation at a wavelength of 326 nm in the f–d absorption bands of Tb^{3+} cations of TbAG:Mn1 (1), TbAG:Mn2,Ce1 (2), TbAG:Mn2,Ce2 (3) and TbAG:Ce SCF (4) at 300 K in comparison with CL (a) and PL (b) spectrum of YAG:Ce SCF (5) under excitation at a wavelength of 340 nm. Relative intensity of PL for different SCF is presented in Table 2.

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 $^7\text{F}_6 \rightarrow ^5\text{D}_4$ 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 $4f(^2\text{F}_{5/2}) \rightarrow 5d^1$ transitions. It should be noted that: (i) the absorption bands of Ce^{3+} ions matches well with the $\text{E}_1(\text{sf})$ and 4f–4f absorption bands of the Tb^{3+} cations [10–12], (ii) the absorption bands related to the radiative $\text{F}_6 \rightarrow ^5\text{D}_3$, $^5\text{D}_4$ transition of Tb^{3+} cations is located above the corresponding $^6\text{A}_1 \rightarrow ^4\text{A}_1$, ^4E and $^6\text{A}_1 \rightarrow ^4\text{T}_1$ 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 $^6\text{A}_1 \rightarrow ^4\text{T}_1$ absorption band 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^{4+} 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^{3+} luminescence; e.g., the excitation energy cannot be transferred to Mn^{3+} 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 $5d^1 \rightarrow 4f(^2\text{F}_{5/2,7/2})$ 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 weak absorption bands peaked at 410–415, 440 and 521 nm related correspondingly to the $^6\text{A}_1 \rightarrow ^4\text{A}_1$, ^4E , $^4\text{T}_2$, and $^4\text{T}_2$ transition of Mn^{2+} ions and the band peaked 463 nm related to the $4f(^2\text{F}_{5/2}) \rightarrow 5d$ transition of Ce^{3+} trace impurity. The excitation bands peaked at 487 and 376 nm are related correspondingly to the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ and $^5\text{D}_3$ 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–4f transition of Tb^{3+} cations (Fig. 4b, curve 1). The peak at $E_{\text{ex}} = 7.14$ eV in the TbAG exciton 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

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.

Fig. 5. (a) Decay kinetics of the Mn^{2+} emission in TbAG:Mn(1) SCF at 600 nm; (b) decay kinetics of the host luminescence at 540 nm in TbAG (1), TbAG:Mn(1) (2) and TbAG:Mn(2) (3) SCF under excitation by an eximer laser at 308 nm at 300 K.

TbAG:Mn SCF in the high-energy region (Fig. 4b, curve 1) are similar in the whole to the excitation spectra of the $\text{Mn}^{2+} + \text{Ce}^{3+}$ 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 $(\text{Ca}-\text{Cd})\text{Al}_2\text{Ge}_3\text{O}_{12}$ 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+} ions on the decay kinetics of the TbAG host luminescence is shown in Fig. 5b under excitation at 308 nm in the E_1 absorption band of Tb^{3+} cations. As we can see from this figure, due to the presence of Mn^{2+} the decay kinetics of TbAG host emission is strongly accelerated. Specifically, the lifetime of the TbAG host luminescence significantly decreases with increasing the content of Mn ions from 8.87 μs for TbAG SCF (curve 1) to 5.09 μs for TbAG:Mn1 (0.019 at%) (curve 2) and 1.05 μs for TbAG:Mn2 (0.07 at%) (curve 3). This also clearly confirms the existence of the energy transfer from TbAG host to Mn^{2+} ions.

Fig. 6. Initial part of decay kinetics of Ce^{3+} luminescence at 540 nm in TbAG:Mn2,Ce1 (2) and TbAG:Mn2,Ce2 SCF (3) in comparison with TbAG:Ce SCF (1) under excitation at 308 nm in the vicinity of d–f absorption band of Tb^{3+} cations by eximer laser at 300 K.

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 μs 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 $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ 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 $\text{Tb}^{3+} \rightarrow \text{Mn}^{2+}$ and $\text{Tb}^{3+} \rightarrow \text{Mn}^{2+} - \text{Ce}^{3+}$ energy transfer in the TbAG

host. Under high-energy excitation the excitation energy from host can transfer from $5d^{14}f^7$ states through 5D_3 and 5D_4 4f-states of Tb^{3+} cations to 4A_1 , 4E and 4T_1 states of Mn^{2+} ions as well as through 5D_0 (or $5d^{14}f^7$) and 5D_3 states of Tb^{3+} cations to 5d states of Ce^{3+} ions [10]. Excitation of the 5d states of Ce^{3+} ions also occurs by means of the optical transitions of these ions or due to the energy transfer from Tb^{3+} cations (Fig. 4a); afterwards a part of the excitation energy can transfer to the 5D_4 state of Tb^{3+} cations [9,11] and 4T_1 state of Mn^{2+} ions due to partial overlapping of the emission spectra of Ce^{3+} ions (Fig. 3) and excitation spectra of Tb^{3+} cations and Mn^{2+} ions in the range of 460–550 nm (Fig. 4a). In turn, the $^5D_4 \rightarrow ^7F_j$ radiative transitions of Tb^{3+} cations also can cause the additional excitation of the 4T_1 states of Mn^{2+} ions (Fig. 4a). Besides, we also cannot exclude the existence of the dipole–dipole interaction between Ce^{3+} and Mn^{2+} ions. Specifically, notable decrease of the average lifetime of the fast components of the Ce^{3+} luminescence with increasing the Mn^{2+} ions content in TbAG:Mn,Ce SCF under excitation in the vicinity of the d–f absorption band of Tb^{3+} cations (Fig. 6) support this conclusion. Finally, the $^4T_1 \rightarrow ^6A_1$ and $5d^1 \rightarrow 4f(^2F_{5/2}, ^7/2)$ radiative transitions of Mn^{2+} and Ce^{3+} 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 $PbO-B_2O_3$ flux onto YAG substrate without any additional doping for reducing the significant mismatch ($\Delta a = +0.064 \text{ \AA}$) 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 SEM 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 Mn^{2+} charge state in the dodecahedral positions of the garnet lattice due to the existence of the part of Tb^{3+} cations in the Tb^{4+} charge state. The segregation coefficient of Mn ions in TbAG SCF grown by LPE onto YAG substrate is about of 0.02.

The effective energy transfer from the TbAG host to Mn^{2+} ions takes place in TbAG:Mn SCF and results in the intensive Mn^{2+} emission in the bands peaked at 595 nm with a lifetime of 0.64 ms which are caused by the $^4T_1 \rightarrow ^6A_1$ radiative transitions. The excitation energy from the TbAG host to Mn^{2+} ions transfers both

from the d–f and f–f states of Tb^{3+} cations via the radiative transition from 5D_3 and 5D_4 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 Tb^{3+} cations to Ce^{3+} and Mn^{2+} ions is realized. The energy transfer in the $Ce^{3+} \rightarrow Mn^{2+}$ and $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Mn^{2+}$ pairs can cause additional channels for excitation of the Mn^{2+} luminescence. Due to the existence of the Mn^{2+} 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.

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