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Abstract: The absorption, cathodoluminescence, excitation spectra of photoluminescence (PL) and PL decay kinetics were studied at 300 K for the double Bi3+-Ce3+ doped and separately Bi3+ and Ce3+ doped Y3Al5O12 (YAG) and Lu3Al5O12 (LuAG) single crystalline film phosphors grown by liquid phase epitaxy method. The emission bands in UV range arising from the intrinsic radiative transition of Bi3+-based centers, and emission bands in visible range, related to luminescence of excitons localized around Bi-based centers, were identified both Bi-Ce and Bi-doped YAG and LuAG SCF. The processes of energy transfer from the host lattice to Bi3+ and Ce3+ ions and from Bi3+ to Ce3+ ions were investigated. Competition between Bi3+ and Ce3+ ions in the processes of energy transfer from the YAG and LuAG hosts was evidenced. The strong decrease of the intensity of Ce3+ luminescence both in YAG:Ce and LuAG:Ce SCF phosphors, grown from Bi2O3 flux, is observed due to the quenching influence of Bi3+ flux related impurity. Due to overlap of the visible emission band of Bi3+ centers with the absorption band of Ce3+ ions takes place, resulting in the appearance of slower component in the Ce3+ luminescence decay kinetics.

**Cover Letter** 

Dear Editors, Please considered for publication our new paper With best wishes, Yuriy Zorenko, corresponding author

# Highlights

- Bi and Ce doped single crystalline film phosphor grown by liquid phase epitaxy method from Bi<sub>2</sub>O<sub>3</sub> flux
  Energy transfer from Bi<sup>3+</sup> to Ce<sup>3+</sup> ions
  Strong quenching of the Ce<sup>3+</sup> luminescence by Bi<sup>3+</sup> co-dopant

# Abstract

The absorption, cathodoluminescence, excitation spectra of photoluminescence (PL) and PL decay kinetics were studied at 300 K for the double  $Bi^{3+}-Ce^{3+}$  doped and separately  $Bi^{3+}$  and  $Ce^{3+}$  doped  $Y_3Al_5O_{12}$  (YAG) and  $Lu_3Al_5O_{12}$  (LuAG) single crystalline film phosphors grown by liquid phase epitaxy method. The emission bands in UV range arising from the intrinsic radiative transition of  $Bi^{3+}$ -based centers, and emission bands in visible range, related to luminescence of excitons localized around Bi-based centers, were identified both Bi-Ce and Bi-doped YAG and LuAG SCF. The processes of energy transfer from the host lattice to  $Bi^{3+}$  and  $Ce^{3+}$  ions and from  $Bi^{3+}$  to  $Ce^{3+}$  ions were investigated. Competition between  $Bi^{3+}$  and  $Ce^{3+}$  ions in the processes of energy transfer from the YAG hosts was evidenced. The strong decrease of the intensity of  $Ce^{3+}$  luminescence both in YAG:Ce and LuAG:Ce SCF phosphors, grown from  $Bi_2O_3$  flux, is observed due to the quenching influence of  $Bi^{3+}$  flux related impurity. Due to overlap of the visible emission band of  $Bi^{3+}$  centers with the absorption band of  $Ce^{3+}$  ions to  $Ce^{3+}$  ions takes place, resulting in the appearance of slower component in the  $Ce^{3+}$  luminescence decay kinetics.

# Bi<sup>3+</sup>-Ce<sup>3+</sup> energy transfer processes and luminescence properties of LuAG:Bi,Ce and YAG:Bi,Ce single crystalline films

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#### Abstract

The absorption, cathodoluminescence, excitation spectra of photoluminescence (PL) and PL decay kinetics were studied at 300 K for the double  $Bi^{3+}-Ce^{3+}$  doped and separately  $Bi^{3+}$  and  $Ce^{3+}$  doped  $Y_3Al_5O_{12}$  (YAG) and  $Lu_3Al_5O_{12}$  (LuAG) single crystalline film phosphors grown by liquid phase epitaxy method. The emission bands in UV range arising from the intrinsic radiative transition of  $Bi^{3+}$ -based centers, and emission bands in visible range, related to luminescence of excitons localized around Bi-based centers, were identified both Bi-Ce and Bi-doped YAG and LuAG SCF. The processes of energy transfer from the host lattice to  $Bi^{3+}$  and  $Ce^{3+}$  ions and from  $Bi^{3+}$  to  $Ce^{3+}$  ions were investigated. Competition between  $Bi^{3+}$  and  $Ce^{3+}$  ions in the processes of energy transfer from the host lattice to  $Bi_{2}O_{3}$  flux, is observed due to the quenching influence of  $Bi_{3}^{3+}$  flux related impurity. Due to overlap of the visible emission band of  $Bi_{3}^{3+}$  centers with the absorption band of  $Ce_{3}^{3+}$  ions takes place, resulting in the appearance of slower component in the  $Ce_{3}^{3+}$  luminescence decay kinetics.

*Keywords*: luminescence; energy transfer; garnets; single crystalline films, Bi<sup>2+</sup> and Ce<sup>3+</sup> ions *PACS*: 78.55.Hx; 78.47.+p; 71.55.-i

## 1. Introduction

The Ce<sup>3+</sup> doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG) garnets posses an intense and fast emission in the visible (515-530 nm) range due to 5d-4f radiative transition of Ce<sup>3+</sup> ions and have been considered now for different scintillator applications [1-4]. The Ce-doped YAG and LuAG–based scintillators can be prepared both in the form of bulk single crystals (SC) by the Czochralski or Bridgman methods [1-4] as well as in the form of single crystalline films (SCF) by the Liquid Phase Epitaxy (LPE) method with the typical thickness of 2-60  $\mu$ m [5-7]. Apart the traditional scintillation applications for environmental radiation monitoring [7] they can be employed also for imaging screens with high spatial resolution [8-10] with some advantages with respect to typical powder phosphorbased screens [11-13].

Under excitation in the range of band-to-band transition of YAG and LuAG host, an intense complex slow intrinsic luminescence arrises in the melt-grown undoped and Ce<sup>3+</sup> doped YAG and LuAG SCs in the UV spectral range [11, 12, 14]. This emission was related to the luminescence of exciton localized near the  $Y_{AI}$  and Lu<sub>AI</sub> antisite defects (AD) and emission of the  $Y_{AI}$  and Lu<sub>AI</sub> ADs itself [14]. The emission of AD-related centers is overlapped with the Ce<sup>3+</sup> absorption bands, which influences timing characteristics of YAG:Ce and LuAG:Ce SC scintillators [11, 12]. The  $Y_{AI}$  and Lu<sub>AI</sub> ADs in YAG:Ce and LuAG:Ce SC play also role the shallow electron traps, which are responsible for intensige thermoluminescence peaks within 120-200 K [13, 15] and can be thus another reason for considerable amount of very slow decay components in the scintillation response of YAG:Ce and LuAG:Ce bulk SC scintillators [12, 13].

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In our previous works [11-15] we found that the formation of  $Y_{Al}$  and  $Lu_{Al}$  ADs is completely suppressed in SCF grown by the Liquid Phase Epitaxy (LPE) method. As the result of ADs elimination, the YAG:Ce and LuAG:Ce SCF phosphors show considerably better timing characteristics under excitation in the range of interband transition with respect to their bulk SC analogues [11, 12]. At the same time, at the preparation of SCF by LPE method usually from PbO-based fluxes, lead ions are also introduced into the garnet lattice [16, 17] and can influenced on the luminescent and scintillation properties of rare-earth doped SCF phosphors. Namely, the influence of Pb-related centers on the luminescence of Ce<sup>3+</sup> and Pr<sup>3+</sup> ions in YAG and LuAG SCF, grown from PbO-based flux, were investigated in details in our previous works [17-20].

Recently we show that the Bi<sub>2</sub>O<sub>3</sub> flux also can be successfully applied for producing SCF phosphors based on garnets compounds, specifically YAG:Bi and LuAG:Bi SCFs [21, 22]. Some aspects of absorption and luminescence of the Bi-containing centers in YAG and LuAG SCF have been investigated by us in [23-25]. In particular, the absorption/excitation bands in 265-280 nm and 210-200 nm ranges was ascribed to the  ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$  and  ${}^{1}S_{0} \rightarrow {}^{1}P_{1}$  transition of Bi<sup>3+</sup> in YAG and LuAG hosts [21, 22]. Excitation of YAG:Bi and LuAG:Bi SCF in the range of interband transitions results in the appearance of two Bi-related emission bands in the UV and visible (VIS) spectral ranges [21, 22]. The luminescence in the UV and VIS bands is characterized by substantially different excitation spectra and emission decay what points to different nature and excitation mechanisms of Bi-related centers in the UV and VIS ranges [23-25]. Specifically, the nature of UV luminescence in YAG:Bi and LuAG:Bi we attribute to the intrinsic radiative  ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$  transition of Bi<sup>3+</sup>-based centers, when the emission bands in VIS range we related to the luminescence of excitons localized around Bi-based centers [23-25]. At very large Bi concentration (above 0.15-0.2 at. %), the intensity of the UV band decreases but the intensity VIS band increases with increasing concentration of Bi ions in the SCF due to formation of Bi<sup>3+</sup> dimer centers [21, 22]. The energy structure of single and dimer centers was also investigated by us in YAG:Bi and LuAG:Bi SCF under excitation by synchrotron radiation with energy 3.7-25 eV [25].

However, the influence of the Bi-related centers on  $Ce^{3+}$  luminescence characteristics in YAG and LuAG SCF phosphors has not been studied in the literature yet. Therefore, the aim of this work to study the phenomena related to the influence of the Bi<sup>3+</sup> ions on the luminescence properties of YAG and LuAG-based SCF phosphors, namely: (i) to identify the spectral bands arising from the Bi-related centers in YAG:Ce and LuAG:Ce SCF; (ii) to study energy transfer processes from the YAG and LuAG hosts both to the Bi<sup>3+</sup> and Ce<sup>3+</sup> ions; (iii) to clarify the influence of the Bi<sup>3+</sup>-based centers on the luminescence characteristics of Ce<sup>3+</sup> ions in YAG:Ce and LuAG:Ce SCF phosphors.

#### 2. SCF growth and experimental technique

The sets of YAG:Bi,Ce and LuAG:Ce,Bi SCF with dimensions of about  $1\times1$  cm<sup>2</sup> and thickness between 12 and 60 µm were grown on (110) oriented YAG substrates at LOM, Lviv University, using the LPE method from super-cooled melt-solution based on Bi<sub>2</sub>O<sub>3</sub> oxide flux. We did not use any codoping to reduce a significant mismatch between the lattice constants of LuAG SCF (11.884 Å) and YAG substrate (11.999 Å). The concentration of crystal forming components with respect to the total content of melt-solution was 6.7 mol % and 5.6 mol %, respectively. These values determine the different temperatures of saturation of respective melt-solutions T<sub>S</sub> ~1080 °C and ~1025 °C and as well as the ranges of SCF growth temperature T<sub>g</sub>= 1015-1050 °C and 965-995 °C, respectively, see Table 1. The relative concentration of Bi<sup>3+</sup> and Ce<sup>3+</sup> ions in all samples of series of LuAG:Bi and YAG:Bi

The relative concentration of  $\text{Bi}^{3+}$  and  $\text{Ce}^{3+}$  ions in all samples of series of LuAG:Bi and YAG:Bi SCFs varied as ~ 1/T<sub>g</sub>, see Table 1. The content of bismuth and cerium in YAG:Bi and LuAG:Bi SCF was determined using JEOL JXA-733 electron microprobe analyzer and was found within 0.05-1 at. % and 0.04-0.275 at.% ranges, respectively, see Table 1. Due to the large ionic radius of Bi<sup>3+</sup> and Ce<sup>3+</sup> (1.17 and 1.14 Å for the coordination 8 [26]), Bi<sup>3+</sup> and Ce<sup>3+</sup> ions are localized exclusively in the dodecahedral {c}-sites replacing Y<sup>3+</sup> or Lu<sup>3+</sup> cations in the garnet lattice.

We have fund the strong competition between  $Bi^{3+}$  and  $Ce^{3+}$  ions in the energy transfer processes in YAG:Ce,Bi and LuAG:Ce,Bi SCF phosphors under high-energy excitation by e-beam or  $\alpha$ -particles  $Pu^{239}$  source (5.15 eV). This competition leads to the strong decreasing of the scintillating light yield

SCF	No of		T ⁰C	հ սա	Ph at %	Ri at %	Ce at %	LV %
sample	samples	Flux	Ig, C	π, μπ	1 D, at. 70	DI, at. 70	Ce, al. 70	L1, 70
YAG:Bi,Ce	8-13-3	Bi <sub>2</sub> O <sub>3</sub>	1050	36		0.096	0.016	10
LuAG:Bi,Ce	8-11-4	$Bi_2O_3$	965	19		0.98	0.275	13
YAG:Bi	7-5-2	$Bi_2O_3$	993	17		0.15	-	
LuAG:Bi	7-8-2	Bi <sub>2</sub> O <sub>3</sub>	1050	21		0.05	-	
YAG:Ce	42-7	PbO	1005	58	>0.01	-	0.04	100
LuAG:Ce	LL1	PbO	1021	22.6	>0.01	-	0.04	120

Table 1. Growth conditions and dopant content in (Y-Lu)AG:Bi,Ce, (Y-Lu)AG:Bi and (Y-Lu)AG:Ce SCFs grown prepared by LPE method from the  $Bi_2O_3$  and PbO-based flux onto YAG substrates.  $T_g$  – temperature of growth, h – SCF thickness

(LY) of YAG:Ce and LuAG:Ce SCF phosphors, grown from the  $Bi_2O_3$  based fluxes, in comparison with the SCF analogues of these garnets, prepared from PbO-based fluxes (see Table 1). Lower LY of YAG:Ce and LuAG:Ce SCF, grown by LPE from  $Bi_2O_3$  flux even at relatively high (above 1000°C) temperatures, is caused by the substantially large  $Bi^{3+}$  content in these phosphors (in the range of several hundredth-tenth at. %) in comparison with the typical Pb<sup>2+</sup> contamination (usually less then 0.01 at. %) in mentioned SCF, grown from the PbO-based flux at relatively same growth conditions (see Table 1). The reasons for such differences in the concentration of flux-related impurities in mentioned SCF is higher segregation coefficient of  $Bi^{3+}$  ions at LPE growth of YAG and LuAG SCF from  $Bi_2O_2$  flux, in comparison with the segregation coefficient  $Pb^{2+}$  ions at LPE crystallization of these SCFs from PbO-based flux due to the significant differences in their ionic radii [25].

The luminescent properties of chosen two samples YAG:Bi,Ce and LuAG:Ce,Bi SCF were compared with the properties of two respective samples of YAG:Bi and LuAG:Bi SCF from our previous work [22] as well as with the properties of two samples YAG:Ce and LuAG:Ce SCF, grown from PbO-based flux (see Table 1).

The absorption spectra of Bi-doped LuAG and YAG SCFs were measured using UV/VIS/NIR absorption spectrophotometer Shimadzu UV-310 PC in the wavelength range 190-1200 nm at 300 K.

The cathodoluminescent (CL) spectra of YAG:Bi SCF were studied at 300 K with a set-up based on a DMR-4A monochromator and a PMT FEU-106 under pulsed e-beam excitation (duration of pulse of 2  $\mu$ s and frequency of 30-3 Hz) with an energy of electrons of 9 keV and a beam current of 100  $\mu$ A. The CL spectra were corrected for the sensitivity of detection part of the set-up.

The excitation spectra of Bi<sup>3+</sup> and Ce<sup>3+</sup> luminescence in 3.7-25 eV range in YAG:Bi,Ce, YAG:Bi and LuAG:Ce,Bi, LuAG:Bi SCFs was investigated at 300 K at the Superlumi station at HASYLAB under excitation by synchrotron radiation (SR) with an energy of 3.7-25 eV. The excitation spectra were corrected for the spectral dependence of transmittance of Al-grating and intensity of SR beam.

The decay kinetics of the Bi<sup>3+</sup> and Ce<sup>3+</sup> luminescence at 300 K was measured with a modified Spectrofluorometer 199S (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flashlamp using single grating monochromators. The detection was performed with an TBX-04 photomultiplier module (IBH Scotland) using the method of time-correlated single photon counting. A deconvolution procedure (SpectraSolve software package) was applied to extract true decay times using the multiexponential approximation.

#### 3. Experimental results

**3.1.** Absorption spectra. Absorption spectra of YAG:Bi,Ce and LuAG:Bi,Ce SCF in comparison with the absorption spectra of YAG:Ce and LuAG:Ce SCF, grown from the traditional PbO flux, are shown in Fig.1 a and Fig.1 b, curves 1 and 2, respectively.

The absorption spectra of YAG:Bi,Ce and LuAG:Bi,Ce SCF consists two strong absorption bands peaked at 273-274 nm and ~200 nm, related to  ${}^{1}S_{0}\rightarrow{}^{3}P_{1}$  and  ${}^{1}S_{0}\rightarrow{}^{1}P_{1}$  transition of Bi<sup>3+</sup> ions (A and C bands, respectively). Apart these bands, the absorption spectra of Ce<sup>3+</sup> doped YAG and LuAG-based SCFs also contains the two bands, peaked at 341 and 459 nm (YAG) and 346 and 449 nm (LuAG), assigned to 4f ( ${}^{2}F_{5/2}$ ) $\rightarrow$ 5d<sub>1,2</sub> transition of Ce<sup>3+</sup> ions. The difference in the position of absorption bands of



Fig.1. (a) - absorption (1, 2) and CL spectra of YAG:Bi,Ce (1, 3), YAG:Ce (2), YAG:Bi (4) SCF grown from the  $Bi_2O_3$  (1-3) and PbO-based (2) fluxes; (b) - absorption (1, 2) and CL spectra (3, 4) of LuAG:Bi,Ce (1, 3), LuAG:Ce (2) and LuAG:Bi (4) SCF grown from the  $Bi_2O_3$  (1-3) and PbO-based (2) fluxes. For better presentation absorption spectra are shown in the logarithmic scale.

 $Ce^{3+}$  and  $Bi^{3+}$  ions, related to above mentioned transitions in YAG and LuAG hosts, are caused by the difference in the crystal field strength in the dodecahedral position of garnet lattices, where the large  $Bi^{3+}$  and  $Ce^{3+}$  ions (1.143 and 1.17 Å, respectively, in 8-fold coordination) are localized.

**3.2. Cathodoluminescence (CL) spectra.** The CL spectra of YAG:Bi,Ce and LuAG:Bi,Ce SCF in comparison with the CL spectra of YAG:Bi and LuAG:Bi SCF, grown from the Bi<sub>2</sub>O<sub>3</sub> flux, are shown in Fig.1 a and Fig.1 b, curves 3 and 4, respectively. The CL spectra of YAG:Bi,Ce and LuAG:Bi,Ce SCF at 300 K (Fig.1, curves 3) show the Ce<sup>3+</sup> luminescence in the visible range in the double bands peaked at 540 and 571 nm (YAG) and 513 and 554 nm (LuAG) caused by the allowed  $5d_{1,2}\rightarrow 4f$  (<sup>2</sup>F<sub>5/2</sub>) transition of Ce<sup>3+</sup> ions. The different positions of these bands of YAG and LuAG host well correlated with respective changes in the position of Ce<sup>3+</sup> absorption bands in YAG and LuAG host (Fig.1a and 1b, respectively, curves 1), Specifically, the high-energy shift of the emission spectrum and decrease of energy distant between absorption bands of Ce<sup>3+</sup> ions occurs for LuAG:Bi,Ce SCF in comparison with the position of this bands in YAG:Bi,Ce SCF which are caused by the smaller crystal fields strength in the dodecahedral position of garnet lattices.

The CL spectra of YAG:Bi, YAG:Bi,Ce, LuAG:Bi and LuAG:Bi,Ce SCF show the intensive UV luminescence in the bands peaked at 303 and 296 nm, respectively, related to  ${}^{3}P_{1}\rightarrow{}^{1}S_{0}$  transitions of Bi<sup>3+</sup> ions. In the visible range the CL spectra of YAG:Bi and LuAG:Bi SCFs also consists the complex emission bands caused by the superposition of luminescence of excitons localized at Bi<sup>3+</sup> *single* and *dimer* centers in the bands peaked at 486 and 422 nm (YAG) and 468 and 417 nm (LuAG), respectively (Fig.1, curves 4). It is important to noted that the both VIS emission bands related to exciton emission in YAG:Bi and LuAG:Bi SCF (Fig.1, curves 4) are strongly overlapped with the 4f-5d<sub>2</sub> absorption bands of Ce<sup>3+</sup> ions peaked at 459 and 449 nm, respectively. That results in the existence of the some kinds "deeps" in the emission spectra of YAG:Bi,Ce and LuAG:Bi,Ce SCF just in the places where are located the mentioned absorption bands of Ce<sup>3+</sup> ions. Such reabsorption of the emission of exciton localized at Bi<sup>3+</sup> *single* and *dimer* centers by the absorption bands of Ce<sup>3+</sup> ions leads to Bi<sup>3+</sup>  $\rightarrow$ Ce<sup>3+</sup> energy transfer resulted in the Ce<sup>3+</sup> luminescence in the VIS range.

**3.3. Excitation spectra.** Excitation spectra of  $Ce^{3+}$  luminescence at 300 K in YAG:Bi,Ce and LuAG:Bi,Ce SCFs at 530 and 515 nm, respectively (curves 1) are shown in Fig.2 in comparison with the excitation spectra of Bi<sup>3+</sup> luminescence in UV bands at 303-296 nm (curves 2) and VIS bands at 460 nm (curves 3) in YAG:Bi and LuAG:Bi SCFs. Apart the excitation bands peaked at 3.63 and 3.58



Fig.2. Excitation spectra of  $Ce^{3+}$  luminescence (curves 1) in YAG:Bi,Ce SCF at 530 nm (a) and LuAG:Bi,Ce SCF at 515 nm (b) and Bi<sup>3+</sup> luminescence in UV bands at 303-296 nm (curves 2) and VIS bands at 460 nm (curves 3) in YAG:Bi (a) and LuAG:Bi (b) SCFs at 300 K.

eV, which coincide with absorption band of  $Ce^{3+}$  ions around 2.70-2.76 eV, the excitation spectra of  $Ce^{3+}$  luminescence in YAG:Bi,Ce and LuAG:Bi,Ce SCFs contain also the several bands related to the excitation of Bi<sup>3+</sup> ions luminescence. Namely, the bands peaked at 4.735 and 4.78 eV (A-bands) and 5.62 and 5.78 eV (C band) as well as at 4.26 and 4.315 eV (labeled as A' bands) and 6.15 and 6.08 eV (labeled as C' bands) corresponds to the  ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$  (A, A') and  ${}^{1}S_{0} \rightarrow {}^{1}P_{1}$  (C, C') transition in Bi<sup>3+</sup> single and *dimer* centers, respectively. It is necessary to noted that the position of A and A' can not be determined here with good accuracy due to the very large absorption of YAG:Bi and LuAG:Bi based SCF in 255-290 nm range (OD >1, see Fig 1.). The bands peaked at 5.26 and 6.55 eV (YAG:Bi) and 5.29 and 6.6 eV (LuAG:Bi) can be assigned to the charge transfer transition (CTT) between the oxygen ligands and Bi<sup>3+</sup> ions (O<sup>2-</sup>→Bi<sup>3+</sup> CTT) and Bi<sup>3+</sup> ions and bottom of conductive bands (Bi<sup>3+</sup>→Bi<sup>2+</sup>+e CTT), respectively. The band peaked at 7.55 eV and 7.15 eV in the range of fundamental absorption edge of YAG and LuAG hosts corresponds to formation of excitons bound with the Bi<sup>3+</sup> and Ce<sup>3+</sup> respectively.

The presence of Bi<sup>3+</sup> related bands in the excitation spectrum of Ce<sup>3+</sup> luminescence confirm the existence of the efficient Bi<sup>3+</sup> $\rightarrow$ Ce<sup>3+</sup> energy transfer in YAG:Bi and LuAG:Bi SCFs. It is important to noted that the shape of excitation spectra of Ce<sup>3+</sup> luminescence is very close to excitation spectra of the VIS emission of Bi<sup>3+</sup> single and dimer centers in YAG:Bi and LuAG:Bi SCF; e.g., the energy from Bi<sup>3+</sup> to Ce<sup>3+</sup> ions is mainly transferred via reabsorption of Bi<sup>3+</sup> VIS emission by the Ce<sup>3+</sup> absorption bands.

**3.4. Decay kinetic of Ce^{3+} and Bi^{3+} luminescence.** The presence of effective energy transfer between the  $Bi^{3+}$  ions and  $Ce^{3+}$  ions in YAG and LuAG host is strongly supported by the decay kinetic of  $Ce^{3+}$  luminescence in YAG:Bi,Ce and LuAG:Bi,Ce SCFs (Fig.3). This figures presents the decay kinetic of  $Ce^{3+}$  emission at 300 K in YAG:Bi,Ce and LuAG:Bi,Ce SCF under excitation in A-absorption band of  $Bi^{3+}$  ions at 260 nm in comparison with the decay kinetic of  $Ce^{3+}$  luminescence in YAG:Ce SCF under excitation at 340 nm in 4f-5d band of  $Ce^{3+}$  ions.

The decay kinetic of  $Ce^{3+}$  luminescence in mentioned YAG:Ce and LuAG:Ce SCFs under excitation in 4f-5d absorption bands of  $Ce^{3+}$  ions at 340 nm is close to exponential course with the decay time of main components of 55 and 50 ns, respectively (Fig.3 a, b, curves 2). The second low-intensity component in the decay of  $Ce^{3+}$  luminescence with decay time in range of hundred ns are arises from the Pb<sup>2+</sup> ions presence in these SCFs and their influence on the decay kinetic of  $Ce^{3+}$  luminescence [18-20]. The decay kinetic of  $Ce^{3+}$  ions in YAG:Bi,Ce and LuAG:Bi,Ce SCF under excitation bands of Bi<sup>3+</sup> becomes more slower (Fig.3 a, b, curves 1). Apart the fast components with decay time of 66 and 56 ns,



Fig.3. Decay kinetic of Ce<sup>3+</sup> luminescence at 515 nm in YAG:Bi,Ce SCF (a) and LuAG:Bi,Ce SCF (b) under excitation in A- absorption band of Bi<sup>3+</sup> ions at 260 nm (1) in comparison with decay kinetic of Ce<sup>3+</sup> luminescence in YAG:Ce SCF (a) and LuAG:Ce SCF (b) under excitation in 4f-5d band of Ce<sup>3+</sup> ions (2) at 340 nm; T=300 K. The corresponding two-component approximations of the decay curves I(t) = A<sub>i</sub> exp(-t/ $\tau_i$ ) are shown be the solid line.

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#### Conclusions

The room-temperature absorption, cathodoluminescence, excitation spectra of photoluminescence and decay kinetics of photoluminescence were studied for  $Bi^{3+}$  and  $Bi^{3+}$ - $Ce^{3+}$ -doped  $Y_3Al_5O_{12}$  (YAG) and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG) single crystalline film (SCF) phosphors grown by liquid phase epitaxy method from the Bi<sub>2</sub>O<sub>3</sub>-based flux. Apart Ce<sup>3+</sup> related emission bands in the visible (530-515 nm range), the luminescence bands in UV range at 296 and 303 nm arising from the intrinsic radiative transition of Bi<sup>3+</sup>centers, and emission bands in visible range at 486 and 468 nm, related to the luminescence of excitons localized around Bi-based centers, were identified in both Bi-doped YAG and LuAG based SCFs.

We have evidenced the competition between  $Bi^{3+}$  and  $Ce^{3+}$  ions in the processes of energy transfer from the YAG and LuAG hosts to these ions under band-to-band excitation. This competition leads to the strong decreasing of the scintillating light yield of YAG:Ce and LuAG:Ce SCF phosphors, grown from the Bi<sub>2</sub>O<sub>3</sub> based fluxes, in comparison with the SCF analogues of these garnets, prepared from PbO-based fluxes. The reason for such LY decrease is the higher segregation of Bi<sup>3+</sup> ions in comparison with the segregation of Pb<sup>2+</sup> ions at crystallization of garnet SCFs from mentioned fluxes due to the significant differences in their ionic radii (1.17 and 1.29 Å, respectively). As a result of such differences, the substantially large Bi<sup>3+</sup> content (even in range several tens at. %) can be realized in YAG:Ce and LuAG:Ce SCF phosphors grown by LPE onto YAG substrates at relatively high (above 1000°C) temperatures, in comparison with the typical Pb<sup>2+</sup> contamination in mentioned SCF, grown from the PbO-based flux at same growth conditions (usually less then 0.01 at. %).

The processes of energy transfer from the host lattice to  $Bi^{3+}$  and  $Ce^{3+}$  ions and from  $Bi^{3+}$  to  $Ce^{3+}$ ions were investigated Bi<sup>3+</sup>-Ce<sup>3+</sup>-doped YAG and LuAG SCF under excitation by synchrotron radiation with energy in 3.7-10 eV range. Due to overlap of the visible emission band of Bi<sup>3+</sup> centers with the absorption band of Ce<sup>3+</sup> centers at 459-449 nm range, an effective non-radiative energy transfer from Bi<sup>3+</sup> ions to Ce<sup>3+</sup> ions takes place in mentioned films, resulting in the appearance of slower component in hundred ns range in the luminescence decay kinetics of  $Ce^{3+}$  ions.

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