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## **Radiation Measurements**

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# Novel UV-emitting single crystalline film phosphors grown by LPE method

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## ABSTRACT

This work reports the development of new types of UV-emitting phosphors based on single crystalline films (SCF) of aluminum garnet and perovskite compounds grown by the liquid phase epitaxy method. We consider peculiarities of the growth and the luminescent and scintillation properties of the following *four types* of UV SCF phosphors: i) Ce-doped SCF of Y–Lu–Al-perovskites with the Ce<sup>3+</sup> emission in the 300-450 nm range of the decay time of 16–17 ns; ii) Pr-doped SCF of Y–Lu–Al garnets and perovskites with the Pr<sup>3+</sup> emission in the 300–400 nm and 235–330 nm ranges with the decay time of 13–19 and 7–8 ns, respectively; iii) La<sup>3+</sup> or Sc<sup>3+</sup> doped SCF of Y–Lu–Al-garnets, emitting in the 280-400 nm range due to formation of the La<sub>Y,Lu</sub>, Sc<sub>Y,Lu</sub> and Sc<sub>Al</sub> centers with decay time of the order of several hundreds of nanoseconds; iv) Bi<sup>3+</sup> doped SCF of garnets with Bi<sup>3+</sup> emission in 275–350 nm with decay time of about 1.9  $\mu$ s.

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Radiation Measurements

## 1. Introduction

The liquid phase epitaxy (LPE) for the last three decades shows itself as a beneficial method for the development of phosphors based on single crystalline films (SCF) of oxide compounds (Robertson and van Tol, 1984; Ferrand, et al., 1999; Zorenko, et al., 1990, 2002, 2003, 2009a,b; Zorenko and Gorbenko, 2009; Kucera et al., 2008). The application fields of such SCF phosphors now include the  $\alpha$ - and  $\beta$ -scintillators, screens for visualization of X-ray images and cathodoluminescent (CL) screens, thermoluminescent media and luminescent converters of LED (Zorenko, et al., 2005).

In this work, we focus on creation of the UV-emitting SCF phosphors based on garnet and perovskite compounds. The reasons for the development of such phosphors are as follows:

1. Shift of the emission spectra of SCF scintillators into the UV range with respect to recently developed SCFs of 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, emitting in the visible range (Zorenko, et al., 2007a), in principle, can result in the faster emission decay, larger light yield (LY) and higher energy resolution. Namely, we try to extend the class of novel

\* Corresponding author. E-mail address: zorenko@electronics.wups.lviv.ua (Y. Zorenko). UV-emitting SCF scintillators with the Ce-doped YAlO<sub>3</sub> (YAP) and LuAlO<sub>3</sub> (LuAP) perovskites and  $Pr^{3+}$ -doped garnets and perovskites.

- 2. Future development of raster scanning optical microscopes equipped by electron-beam tubes with SCF screens as CL light sources (Hrytskiv, et al., 2007) requires the creation of SCF screens emitting in the selected ranges from 400 to 230 nm. Specificaly, using the UV-emitting CL-excited light sources gives the possibility for analysis of biological objects in such microscope under the UV light.
- 3. Microimaging techniques with X-ray or synchrotron radiation (SR) for applications in microtomography and industry demand for the fast detectors of X-ray images, based on the SCF scintillating screens and microscope optics, with spatial resolution in the µm-sub-µm range (Koch, et al., 1999; Martin and Koch, 2006). Future increase of the spatial resolution of such detectors according to the formula:  $0.61^*\lambda/NA$ , where  $\lambda$  is the emission wavelength and NA is the numerical aperture of the optics, requires creation of SCF screens emitting in the UV range. For visualization of X-ray images through the UV light we try to develop the novel SCF scintillating screens based on LuAG and LuAP compounds with significantly higher density ( $\rho = 6.67$  and  $8.34 \text{ g/cm}^3$ ) and effective atomic number ( $Z_{\text{eff}} = 59$  and 62) (Zorenko et al., 2002) as compared to commonly used YAG ( $\rho = 4.6 \text{ g/cm}^3$ ,  $Z_{\text{eff}} = 29$ ) (Koch, et al., 1999). To obtain the



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intense UV scintillation, the  $Pr^{3+}$ ,  $La^{3+}$  and  $Sc^{3+}$  ions can be used as activators in LuAG SCF and  $Ce^{3+}$  and  $Pr^{3+}$  ions LuAP SCF.

In this work, we have briefly analyzed peculiarities of the growth and the luminescent and scintillation properties of several types of UV-emitting LPE-grown SCF phosphors.

#### 2. Growth of SCF phosphors and experimental techniques

The series of Pr, La, Sc and Bi-doped YAG and LuAG and Ce or Prdoped YAP and LuAP SCF phosphors were grown in University of Lviv by the LPE methods onto YAG and YAP substrates, respectively, with the melt-solution (MS) based on the PbO–B<sub>2</sub>O<sub>3</sub> flux at relatively low (950–1100 °C) temperatures as compared to Czochralskigrown single crystal (SC) analogues (~2000 °C). For the growth of YAP:Ce SCF onto YAP substrates we also used the novel lead-free BaO–BaF<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> flux. The Bi-doped YAG and LuAG SCF were grown on YAG substrates using the Bi<sub>2</sub>O<sub>3</sub> flux. The concentration of Bi<sup>3+</sup> ions in these SCFs was varied by the change of growth temperature in the 0.05–0.18 and 0.13–0.57 at. % ranges, respectively. The thickness of the SCF phosphors was in the 4.8–45 µm range.

The content of different dopants in SCF was determined using a JEOL JXA-8612 MX electron microscope and is presented in Table 1 for different series of SCF phosphors.

Lower growth temperature of SCFs of garnets and perovskites results in the absence of the  $Y_{AI}$  and  $Lu_{AI}$  antisite defects (AD) and decrease of the content of other type of defects in SCF in comparison with bulk SC analogues (Zorenko, et al., 2007a,b). On the other hand, flux components can be introduced in the SCF and can influence their emission and scintillation properties. We have shown recently that the YAG:Ce and LuAG:Ce SCFs grown from the PbO-based flux usually contain lead ion contamination preferably in the Pb<sup>2+</sup> charge state. It causes decrease of the LY and slowingdown the scintillation response (Babin, et al., 2007; 2009a,b). Therefore, LY of UV-emitting SCF phosphors can also strongly depend on the activator concentration and Pb<sup>2+</sup> contamination level.

Due to significant difference in the segregation coefficient of the La, Sc and Pr ions in YAG and LuAG SCF grown on YAG substrates and Ce and Pr ions in YAP and LuAP SCF, grown on YAP substrates (Zorenko, et al., 2003, 2009a), the content of Sc<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> oxides in MS was varied in the 2.25–6.7; 1.0–8.2, 3.1–8.6 mole % ranges, respectively, for SCF of garnets, and CeO<sub>2</sub> and Pr<sub>2</sub>O<sub>3</sub> oxides in 2.0–20 and 1.0–10.5 mole % ranges, respectively, for SCF of perovskites. The concentration of these dopants in the SCF depends not only on the content of activated oxides in MS, but is also strongly influenced by the SCF growth temperature. Usually the activators/Pb ratio increase with increasing the growth temperatures above 950 °C for the SCF growth.

The CL spectra of SCF phosphors were measured at 300 K with a set-up based on a DMR-4 monochromator and a FEU-106 PMT under pulsed e-beam excitation (9 KeV, 100  $\mu$ A) with pulse duration of 2  $\mu$ s and a frequency of 3–30 Hz.

The decay of luminescence was measured at 300 K in the time interval 0–200 ns under excitation by SR with pulse duration of 0.126 ns at Superlumi station (HASYLAB, DESY). Decay curves of Bi<sup>3+</sup> luminescence were measured by 199S Spectrofluorometer (Edinburgh Instrument) equipped by TBX-04 PMT detection modul (IBH Scotland) under the excitation by nanosecond coaxial hydrogen-filled flashlamp 5000F.

Relative LY of all the mentioned SCF phosphors was measured in comparison with that of the corresponding samples of YAG:Pr, LuAG:Pr, YAG:La, YAG:Sc, LuAG:Sc, YAP:Ce and Lu<sub>0.3</sub>Y<sub>0.7</sub>AG:Ce bulk SCs under the excitation by  $\alpha$ -particles of Am<sup>241</sup> (5.5 MeV) sources

#### Table 1

Dopant	Phosphors	A, at.%	$\lambda_{\rm max}$ , nm	<i>τ</i> , ns	LY,%
Ce	YAP:Ce SCF (PbO flux)	0.08	366	13.1	36.1
	YAP:Ce SCF (BaO flux)	0.053	373	16.1	33.7
	Y <sub>0.4</sub> Lu <sub>0.6</sub> AP:Ce SCF (PbO flux)	$\sim 0.04$	363	16.0	14.4
	LuAP:Ce SCF (PbO flux)	0.013	358	16.9	10.8
	YAP:Ce SC	~0.1	366	16.2	100
	Lu <sub>0.3</sub> Y <sub>0.7</sub> AG:Ce SC	~0.1	375	17.1	83.2
Pr	YAG:Pr SCF	0.085	323	12.5	33.7
	LuAG:Pr SCF	0.66	305		29.8
	YAG:Pr SC	0.19	327		75.4
	LuAG:Pr SC	0.31	308	18.6	59.3
	YAP:Pr SCF	~0.08	250	8.1	10
	LuAP:Pr SCF	~0.07	240	7.8	15
	YAP:Pr SC	~0.1	250	8.0	22.7
La	YAG:La SCF	0.045	297	290	13.6
	LuYAG:La SCF	0.04	282	170	15.9
	YAG:La SC	0.085	298	575	30.3
Sc	Y <sub>2.96</sub> Sc <sub>0.475</sub> Al <sub>4.555</sub> O <sub>12</sub> SCF	2.38	303;	~750	38.7
			329		
	Y <sub>2.84</sub> Lu <sub>0.14</sub> Sc <sub>0.37</sub> Al <sub>4.65</sub> O <sub>12</sub> SCF	1.85	298	~650	57.5
	Y <sub>2.76</sub> Lu <sub>0.18</sub> Sc <sub>0.715</sub> Ga <sub>0.09</sub> 5Al <sub>4.25</sub> O <sub>12</sub> SCF	3.60	325	~800	28.0
	Lu <sub>2.92</sub> Sc <sub>0.18</sub> Al <sub>4.9</sub> O <sub>12</sub> SCF	0.9	292	245;	48.5
				415	
	Y <sub>2.995</sub> Sc <sub>0.077</sub> Al <sub>4.864</sub> O <sub>12</sub> SC	0.39	290	~580	69.3
	$Lu_{2.77}3Sc_{0.022}Al_{5.205}O_{12}\ SC$	0.11	275	1330	31.4
Bi	YAG:Bi	0.13	303	1930	20.6
	LuAG:Bi	0.18	298	1840	15.1

using detector based on hybrid DEP PPO 475B PMT with the maximum sensitivity in the 200–400 nm range and multichannel analyzer working with shaping time of  $3 \mu s$ . The results of LY measurements are shown in Table 1.

#### 3. Luminescence spectra and LY of SCF phosphors

#### 3.1. Ce-doped perovskites

The CL spectra of YAP:Ce and LuAP:Ce SCF (Fig. 1) show the intensive emission band in the UV (320–450 nm) range related to the 5d  $\rightarrow$  4f transitions of Ce<sup>3+</sup> ions. The short-wavelength part of the Ce<sup>3+</sup> emission band in these SCFs grown from the PbO-based flux (labeled later as (Y,Lu)AP:Ce (PbO) SCFs) is strongly distorted by the UV emission band of Pb<sup>2+</sup> ions peaked at 340 nm (Babin, et al., 2009a,b) (Fig. 1). This caused a short-wavelength shift of the emission spectrum of YAP:Ce (PbO) SCF (Fig. 1, curve 2) with respect to the spectrum of the same SCF grown from the lead-free BaO-based flux (labeled later as YAP:Ce (BaO) SCF) (Fig. 1, curve 1).

The LY of best samples of YAP:Ce and LuAP:Ce SCF is significantly lower (by 3.9 and 7.6 times, respectively) than that of their YAP:Ce and (Y–Lu)AP:Ce SC analogues (Table 1). The main reason for such a low LY of these SCFs is the large incorporation of Pb<sup>2+</sup> ions in SCF of perovskites in comparison with SCF of garnets (Zorenko and Gorbenko, 2009;) due to larger volume of cuboctahedral position in perovskite lattice with respect to the dodecahedral sites of garnet host, where Pb<sup>2+</sup> ions are localized. We also note that the LY of (Y– Lu)AP:Ce SCF systematically decrease with rising the Lu content up to a value of 10.8% for LuAP:Ce SCF as compared to that of YAP:Ce SC. This effect is caused by the large content of Pb<sup>2+</sup> ions in LuAPbased SCF with respect to YAP SCF due to preferable Lu–Pb pair incorporation in comparison with Y–Pb pair in the case of SCF growth of both types of perovskites on YAP substrates (Zorenko and Gorbenko, 2009).



**Fig. 1.** CL spectra (normalized) of YAP:Ce (1, 2) and LuAP:Ce (3) SCF at 300 K grown from the BaO (1) and PbO (2, 3) based fluxes; insert – decay kinetics of  $Ce^{3+}$  luminescence in YAP:Ce (BaO) (1) and YAP (PbO) (2) SCF under excitation in  $Ce^{3+}$  absorption band at 300 nm.

The decay curve of Ce<sup>3+</sup> emission in YAP:Ce (PbO) SCF is strongly non-exponential (inset of Fig. 1, curve 2) and is characterized by the mean decay time of 13.1 ns (Table 1). Such a shortening the decay time of the Ce<sup>3+</sup> emission in YAP:Ce (PbO) SCF, can be caused by energy transfer from the  $Ce^{3+}$  ions to  $Pb^{2+}$ -related centers with the excitation bands in the 350-370 nm range which overlap with the Ce<sup>3+</sup> emission band (Babin, et al., 2009a,b). From the calculation of the integral of the normalized decay curves for YAP:Ce (PbO) and YAP:Ce (BaO) SCFs (inset of Fig. 1), we estimate that in the former SCF the losses of more than 50% of energy take place due to energy transfer from the Ce<sup>3+</sup> ions to Pb<sup>2+</sup>-based centers. Such large losses can partly explain very low LY of YAP:Ce (PbO) and LuAG:Pr (PbO) SCF (Table 1). Contrary to these SCFs, the  $Ce^{3+}$  emission decay in YAP:Ce (BaO) SCF is single-exponential (inset of Fig. 1, curve 2) with the decay time of 16 ns which is close to the decay time of the  $Ce^{3+}$ emission in YAP:Ce SC (Table 1). That reflects the great application potential of BaO-based fluxes for growth of SCF phosphors. However, the main problem of using the BaO-based flux is its high viscosity and surface tension. Low SCF growth rate resulted in worse surface morphology and uniformity of SCF properties (Zorenko, et al., 2009a). We also did not succeed with the heteroepitaxial crystallization of LuAG and LuAP SCFs on cheaper YAG and YAP substrates using the BaO-based flux.

## 3.2. $Pr^{3+}$ -doped garnets and perovskites

The CL spectra of YAG:Pr and LuAG:Pr SCFs showed intensive and fast emission in the 290–450 nm range with the main maxima at 323 and 305 nm, with the decay time of about 13 and 19 ns, respectively, caused by the  $5d^{1}4f^{1} \rightarrow 4f^{2}({}^{3}H_{4}, {}^{3}H_{5}, {}^{3}H_{6}, {}^{3}F_{3(4)})$  transition of Pr<sup>3+</sup> ions (Fig. 2) (Pejchal, et al., 2009). The same transitions in YAP:Pr and LuAP:Pr SCFs yield even faster emission in the 235–325 nm range with the maximum at 240 and 250 nm, respectively, and decay time of about 8 ns for both SCF (Fig. 2b) (Zhuravleva, et al., 2007).

The detailed consideration of luminescent properties of  $Pr^{3+}$  doped (YLu)AG and (Y,Lu)AP SCF is given in (Gorbenko et al., in this issue). Here we mentione only that the LY of (Y,Lu)AG:Pr and (Y,Lu)AP:Pr SCFs is significantly lower (by 2.2–2.8 times) than that of their SC analogues (Table 1). The main reason for such low LY of the  $Pr^{3+}$ -doped. SCF of garnets and perovskites is the strong quenching influence of the  $Pb^{2+}$  flux impurity. From the results presented in Table 1, we conclude that significantly larger influence



**Fig. 2.** CL spectra and decay kinetics (inset) of  $Pr^{3+}$  luminescence in YAG:Pr (1), LuAG:Pr (2), YAP:Pr (3) and LuAP:Pr (4) SCF at 300 K.

of Pb<sup>2+</sup> ions on the UV emission of Pr<sup>3+</sup> ions takes place in (Y,Lu)AG:Pr and (Y,Lu)AP:Pr SCFs in comparison with the influence of such impurity on the Ce<sup>3+</sup> emission in the visible range in SCF of Ce-doped garnets (Zorenko, et al., 2007a). The mechanism of the Pb<sup>2+</sup>  $\rightarrow$  Pr<sup>3+</sup> energy transfer in Pr-doped SCF of garnets is considered by Gorbenko et al., 2009.

#### 3.3. La-doped garnets

The CL spectra of YAG:La and LuAG:La SCFs are shown in Fig. 3a. The intensive complex emission bands in the 250–450 nm range are caused by the La<sup>3+</sup> isoelectronic impurity and present superposition of two closely-lying bands peaked at 298, 305 nm and 267, 282 nm (curve 1 and 2, respectively), related to the luminescence of exciton localized around La<sub>Lu,Y</sub> centers and recombination luminescence of La<sub>Y</sub> and La<sub>Lu</sub> centers, respectively (Zorenko, 2006). In (Y,Lu)AG:La SCFs, grown from PbO-based flux, the UV emission band of Pb<sup>2+</sup> ions peaked at 350–360 nm is also observed (Fig. 3a).

The decay kinetics of the La<sub>Y</sub> and La<sub>Lu</sub> centers emission in YAG:La and LuAG:La SCFs under excitation in the exciton range with energy of 6.52 and 6.88 eV, respectively, is shown in Fig. 3c. The decay time of main components of La<sub>Y</sub> and La<sub>Lu</sub> centers luminescence is 560 and 170 ns, respectively.

The LY of YAG:La and LuAG:La SCF significantly depends on the La content but is not so strongly influenced by the  $Pb^{2+}$  flux



**Fig. 3.** a – CL spectra (a) and decay kinetic (b) of luminescence of  $La_Y(1)$  and  $La_{Lu}(2)$  centers at 290 and 285 nm in YAG:La (1) and LuAG:La (2) SCFs under excitation by SR at 6.52 and 6.88 eV, respectively. T = 300 K.



**Fig. 4.** Normalize CL spectra of YAG:Sc (a) and LuAG:Sc (c) SCF with Sc content of 1.8 (1a), 4.13 (2a), 0.12 (1c), 1.94 (2c) and 4.08 (3c) at.%, respectively. Decomposition of spectrum 2 in Fig. 5a is given by dashed lines. (d) – dependence of integral intensity of CL on total scandium content in YAG:Sc (1) and LuAG:Sc (2) SCFs; (d) – decay kinetics of luminescence of Sc<sub>Lu</sub> (1) and Sc<sub>Al</sub> (2) centers at 280 (1) and 335 nm (2) in LuAG:Sc SCF under excitation by SR with an energy of 6.88 eV. T = 300 K.

impurity. Namely, the LY of (Y,Lu)AG:La SCFs with La content of 0.04–0.05 at. % is by 2–3 times lower in comparison with YAG:La (0.085 at.%) SC (Table 1). Also, the LY of these SCFs is significantly (by 2–4 times) lower than that of Sc-doped YLuAG and LuAG SCFs. Such a low LY of La-doped SCFs is mainly caused by very low (0.005) segregation coefficient of La<sup>3+</sup> ions at the LPE-growth of YAG:La and LuAG:La SCFs in comparison with that (0.14) for YAG:La SC. As a result, rather small (0.04–0.045 at.%) La<sup>3+</sup> concentration can be achieved in these SCFs (Table 1) even at large (above 8 mole %) content of La<sub>2</sub>O<sub>3</sub> dopant in MS in comparison with an optimum value of 0.4–0.9 at.% for Sc-doped SCF of these garnets (Table 1).

#### 3.4. Sc-doped garnets

In contrast to  $La^{3+}$  ions, the Sc<sup>3+</sup> isoelectronic impurity in YAG and LuAG SCFs has relatively high (0.8–0.55 and 0.4–0.2, respectively) segregation coefficient. This allows to readily achieving the optimum values of Sc doping in SCF of these garnets in the range 0.4–0.9 at. %, at which the highest LY of these SCFs is observed (Fig. 4b, Table 1).

The Sc<sup>3+</sup> ions in YAG and LuAG SCF substituted both the dodecahedral **{c}**- and octahedral **(a)**- sites of garnet lattice and formed the Sc<sub>Y,Lu</sub> and Sc<sub>Al</sub> emission centers, respectively (Zorenko, 2006). Such distribution of Sc<sup>3+</sup> ions over the **{c}**- and **(a)**-sites explains the dependence of the positions of emission bands of (Y,Lu)AG:Sc on the Sc content (Fig. 5b). At relatively small (x = 0.05–0.2 formula units (f.u.)) Sc content, the bands at 313 and 275 nm, respectively, dominates in the luminescence of YAG:Sc (Fig. 4a) and LuAG:Sc SCF (Fig. 4c). The bands at 353 and 323 nm, become



**Fig. 5.** a – CL spectra of LuAG:Bi and YAG:Bi SCF; b – decay kinetic of  $Bi^{3+}$  emission in UV (1) and visible (2) bands in LuAG:Bi SCF; T = 300 K.

dominant at larger (x > 0.2 f.u.) Sc content (Fig. 4a and c), which correlate with substantial increase of the LY of these SCF (Fig. 4b, Table 1). Maximum of the LY of YAG:Sc and LuAG:Sc SCF is reached at x = 0.3–0.4 f.u. (Fig. 4b). At the highest Sc content the decrease in the LY of SCs and SCFs (Fig. 4b) occurs due to the concentration quenching of the emission of Sc<sup>3+</sup>-related centers.

The luminescence decay kinetics of the  $Sc_{Y,Lu}$  and  $Sc_{Al}$  centers is shown in Fig. 4d on the example of LuAG:Sc SCF. Under excitation with energy of 6.88 eV in the exciton range the main components of the  $Sc_{Lu}$  and  $Sc_{Al}$  centers emission show the decay time of 245 and 415 ns (curve 1 and 2, respectively).

The LY of YAG:Sc and LuAG:Sc SCFs depends on the total Sc content and distribution of  $Sc^{3+}$  ions over the {c}- and (a)-sites of garnet host. The concentration of Sc<sub>YLu</sub> and Sc<sub>Al</sub> centers in these SCFs and their LY can be changed by substitution of host cations by other ions with smaller or larger dimensions. Namely, the Lu<sup>3+</sup> codoping in  $\{c\}$ -sites of  $Y^{3+}$  leads to increasing the LY of YAG:Sc SCF, whereas the  $Ga^{3+}$  co-doping in (a)-sites of  $Al^{3+}$  decrease the LY of these SCF (Table 1). The LY of (YLu)AG:Sc and LuAG:Sc SCFs at the optimal  $Sc^{3+}$  content 0.4–0.9 f.u. is comparable with their SC analogues and reaches values of 57.5 and 47.5%, respectively, of that for YAP:Ce SC (Table 1). This result shows that influence of Pb<sup>2+</sup> dopant on the UV luminescence of Sc3+-based centers is not so much significant than that on the Ce<sup>3+</sup> luminescence in SCF of perovskites and the Pr<sup>3+</sup> luminescence in SCF of garnets. This allows the usage of PbO-based flux for the growth of UV-emitting SCF phosphors with relatively high LY.

#### 3.5. Bi-doped garnets

For development of the UV-emitting SCF scintillators we also crystallized the  $Bi^{3+}$ -doped YAG and LuAG SCFs by LPE method on YAG substrates (Zorenko, et al., 2009b). The concentration of  $Bi^{3+}$  ions in these SCF was varied in the range of 0.05–0.18 at. % by changing the growth temperature.

The CL spectra of YAG:Bi and LuAG:Bi SCFs (Fig. 5a) show the dominant band in UV range peaked at 303 and 298 nm, respectively, related to  ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$  radiative transitions of Bi $^{3+}$  ions, and less intense visible one peaked in the 468–483 nm range caused by luminescence of localized excitons around Bi $^{3+}$  single and dimer centers (Babin, et al., 2009b). The ratio of UV/blue emission bands can be tuned by the Bi $^{3+}$  concentration: with increasing Bi $^{3+}$  content in (Y,Lu)AG:Bi SCF the reduction of the intensity of UV emission band and relative increase of the intensity of visible band are observed. Decay time of the UV emission of Bi $^{3+}$  ions in LuAG:Bi

and YAG:Bi SCF at 300 K is about of 1.9  $\mu$ s (Fig. 5c, curve 1). The decay of visible emission is slower and can be fitted by the sum of two components with decay times of 0.2–0.4 and 1.9–2.5  $\mu$ s, related to luminescence of localized excitons around the Bi<sup>3+</sup> single and dimer centers (Babin, et al., 2009b).

The LY of the LuAG:Bi and YAG:Bi SCFs reaches of about 15 and 21% of that of the YAP:Ce SC, respectively (Table 1). Therefore, these SCF can be proposed as scintillating screens for high-resolution X-ray imaging (Zorenko, et al., 2009b).

### 4. Conclusions

Development of four types of the UV-emitting single SCF phosphors grown by LPE methods is described in this work:

- i) Ce-doped SCF of Y–Lu–Al-perovskites with Ce<sup>3+</sup> emission in the 360–370 nm range with a decay time of 16–17 ns;
- ii) Pr-doped SCF of Y-Lu-Al garnets and perovskites with Pr<sup>3+</sup> emission in the 300-400 nm range with a decay time of 13-19 ns and ~8 ns, respectively;
- iii) La- and Sc-doped SCF of Y-Lu-Al-garnet compounds emitting in the 290–400 nm range due to formation of La<sub>Y,Lu</sub> or Sc<sub>Y,Lu</sub> and Sc<sub>Al</sub> emission centers with the decay time of the luminescence in the several hundred ns range.
- iv)  $Bi^{3+}$  doped SCF of garnets with  $Bi^{3+}$  emission in 275–350 nm with decay time of about 1.9 µs;

From all the above mentioned SCF phosphors the highest LY value is obtained at the (YLu)AG:Sc and LuAG:Sc SCF (45.5–57.5%), followed by YAG:Pr and LuAG:Pr SCF (30–34%) and YAP:Ce SCF (up to 36%) in comparison with the LY of YAP:Ce reference crystal.

The main problem in the development of UV-emitting SCF phosphors by LPE method from the traditional PbO-B<sub>2</sub>O<sub>3</sub> flux consists in significantly larger influence of Pb<sup>2+</sup> flux impurity on the UV luminescence of Ce<sup>3+</sup> ions in SCF of perovskites and Pr<sup>3+</sup> ions in SCF of garnets and perovskites with respect to recently developed YAG:Ce and LuAG:Ce SCF phosphors emitting in the visible range. This is the main reason for lower (by 2–3 times) LY of Pr-doped (Y–Lu)AG and (Y–Lu)AP SCFs and significantly lower (by 3.6–6 times) LY of Ce-doped YAP and LuAP SCFs in comparison with their SC analogues. Therefore, the future development of UV-emitting phosphors based on the Ce<sup>3+</sup> and Pr<sup>3+</sup> doped SCF of perovskites and Pr<sup>3+</sup> doped SCF of garnets *strongly demands the use of alternative lead-free fluxes* for their growth.

No such negative influence is observed in the Sc and La-doped SCF of Y–Lu-garnets which allow using the PbO-based flux for producing the UV-emitting SCF phosphors with high LY.

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