reprints

The luminescent and scintillation properties of YAlO_3 and $\text{YAlO}_3\text{:Ce}$ single crystalline films grown by liquid phase epitaxy from BaO-based flux

Y. Zorenko^{*1}, M. Nikl², J. A. Mares², V. Gorbenko¹, V. Savchyn¹, T. Voznyak¹, M. Kucera³, A. Beitlerova², R. Kucerkova², and A. Fedorov⁴

¹ Laboratory of Optoelectronics Material (LOM), Electronic Department Ivan Franko National University of Lviv, 107 Gen. Tarnawskogo str., 70017 Lviv, Ukraine

² Institute of Physics AS Czech Republic, 10 Cukrovarnicka str, 162 53 Prague, Czech Republic

³ Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, 12116 Prague 2, Czech Republic

⁴ Institute for Scintillation Materials NAS of Ukraine, 60 Lenina av., 61001 Kharkiv, Ukraine

Received 16 January 2009, revised 31 March 2009, accepted 5 June 2009

Published online 27 July 2009

PACS 71.55.Ht, 78.20.Ci, 78.55.Hx, 81.15.Lm

*Corresponding author: e-mail zorenko@electronics.wups.lviv.ua, Phone: +380322964205, Fax: +380322448585

Single crystalline films (SCFs) of undoped and Ce^{3+} -doped YAlO_3 (YAP) perovskite were crystallized by liquid-phase epitaxy method onto YAP substrates for the first time from the novel lead-free $\text{BaO-B}_2\text{O}_3\text{-BaF}_2$ fluxes. The absorption, luminescence, and scintillation properties of these films are

measured and compared with the films grown from the standard $\text{PbO-B}_2\text{O}_3$ flux. It appears that the films obtained from the BaO-based flux exhibit better luminescent and scintillation properties with respect to films grown from the PbO-based one.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction The liquid phase epitaxy (LPE) appears as a versatile tool for the manufacturing of single crystalline films (SCFs) of well-known oxide compounds [1–4]. The SCFs of Al garnets and perovskites doped by Ce^{3+} ions show intensive luminescence in the visible or near UV spectral ranges, respectively, fast scintillation response (20–70 ns), and high light yield (LY) [5, 6]. These SCF are used for 2D imaging screens for detection of X-ray, accelerated electrons, or synchrotron radiation [7–9]. The thickness of such scintillation screens should be preferably in the micrometer range due to necessity to obtain submicrometer spatial resolution of such detectors close to the diffraction limit [7–9].

In this work, we studied the growth and luminescent properties of YAP and YAP:Ce SCF prepared by an LPE method, which provides high optical quality and homogeneity of the films [1–6]. The SCF were grown from a supercooled melt-solution (MS) at relatively low temperatures (900–1100 °C) compared to Czochralski-grown single crystals (SCs) (~2000 °C). Lower growth temperature of SCF results in the absence of the antisite defects Y_{Al} and decrease concentration of other type of

defects in SCF in comparison with bulk SC analogs [10–12]. On the other hand, flux components can be introduced in the SCF that might have detrimental influence on the emission and scintillation properties of the SCF [2, 3, 13, 14]. The YAG- and YAP-based SCF are usually prepared from the $\text{PbO-B}_2\text{O}_3$ flux [1–3, 6, 13, 14]. Thus, these SCFs can contain lead ions preferably in the Pb^{2+} charge state. Since the PbO-based melt dissolves the platinum crucible, Pt^{4+} ions can also be introduced in the garnet or perovskite lattices. As a consequence, various locally non-compensated lattice defects can be created, for instance, the oxygen or cation vacancies [15, 16], which may result in the formation of the trap levels in the forbidden gap, the appearance of the slow component in the decay kinetics of luminescence of Ce^{3+} ions, and decrease of scintillation efficiency and LY [2, 5, 6, 13, 14].

This work reports the growth of Ce-doped YAP SCF with significantly higher purity as compared to SCF grown from a traditional PbO-based flux. We used the lead-free $\text{BaO-B}_2\text{O}_3\text{-BaF}_2$ flux which has been recently successfully adapted for SCF crystallization of YAG and LuAG garnets [17, 18]. For this flux the significantly lower (at least 20 times)

incorporation of Ba^{2+} flux dopant occurs in comparison with the incorporation of Pb^{2+} dopant at using $\text{PbO-B}_2\text{O}_3$ flux [19] due to the difference of ionic radii of Ba^{2+} (1.42 Å) and Pb^{2+} (1.29 Å) ions for eightfold coordination.

In the following sections, we present the results on the LPE growth of YAP and YAP:Ce SCF from MS based on the mentioned fluxes. The comparison of absorption, luminescence, and scintillation properties of YAP and YAP:Ce SCFs grown from the PbO and BaO-based fluxes is provided. It is shown that the SCFs obtained from the lead-free BaO-based flux provide better luminescent and scintillation properties with respect to those prepared from the PbO-based flux.

2 Growth, structure, and morphology of YAP and YAP:Ce SCF One set of the undoped YAP SCF and three sets of YAP:Ce SCF with the thickness of 2.5–9.0 μm were grown in LOM, Lviv University by LPE from MS based on $\text{BaF}_2\text{-BaCO}_3\text{-B}_2\text{O}_3$ (40:30:30 mol%) flux onto YAP substrates with (010) orientation with dimensions within $5 \times 5 \text{ mm}^2$ to $10 \times 10 \text{ mm}^2$ (labeled later as YAP (BaO) and YAP:Ce (BaO) SCF samples, respectively). Starting raw materials of 5N purity in the total weight of 100 g were used for the charge preparation and placed into Pt crucible with $40 \times 40 \text{ mm}^2$ dimension. The conditions of SCFs growth are summarized in Table 1. The concentration of crystal-forming components in MS was 18.8 mol%. The Y_2O_3 and Al_2O_3 oxides were chosen in the equal-molar ratio. The concentration of CeO_2 activator in MS was 0.5, 2.0, and 10 mol% with respect to the total content of crystal-formed components (Table 1). The temperature of saturation of MS was about of 1065–1067 °C. The temperature of SCF growth was in the range of 1015–1054 °C; e.g., the supercooling rate of MS was in the range of 9–52°. The substrate rotation in MS was $\omega = 80 \text{ rpm}$, and the rotation direction changed

every 10 s to achieve more homogenous MS during SCF crystallization.

After the growth the rest of the residual flux was removed in hot nitric acid. The thickness of SCF was achieved in the range of 2.5–11.0 μm and was determined by weighing method.

The absorption, luminescent, and scintillation properties of the above-mentioned SCF were compared with properties of one set of YAP SCF and two sets of YAP:Ce SCF with a thickness of 5–40 μm grown in LOM, Lviv University by LPE from MS based on $\text{PbO-B}_2\text{O}_3$ (12:1 mol mol⁻¹) flux using the same YAP substrates, initial raw crystal-forming materials, and Pt crucible (later YAP (PbO) and YAP:Ce (PbO) SCF samples, respectively). The total weight of charge was of about 300 g. The concentration of crystal-forming components with respect to the total content of MS was 2.6–2.9 mol%. The concentration of CeO_2 activator oxide in MS was 10 and 15 mol% of the total volume or the crystal-forming components (Table 1).

For structural characterization of YAP SCF we used X-ray ($\text{CuK}\alpha$) diffraction at YAP (PbO) SCF in comparison with YAP substrate. Well-separated reflection peaks from (110), (220), and (330) planes were obtained for both samples (Fig. 1). The calculated values of the lattice constants are equal to $a = 5.185 \text{ Å}$, $b = 5.314 \text{ Å}$, $c = 7.425 \text{ Å}$ for YAP SCF and $a = 5.180 \text{ Å}$, $b = 5.308 \text{ Å}$, $c = 7.363 \text{ Å}$ for YAP substrate. Larger value of the lattice constants for YAP SCF in comparison with YAP substrate can be caused by the Pb^{2+} ion incorporation in the Y^{3+} site of SCF due to its larger radius.

Using the BaO-based flux, at the same velocity of substrate rotation the SCF growth rate of $0.02\text{--}0.1 \mu\text{m min}^{-1}$ was significantly lower with respect to that of $0.48\text{--}1.33 \mu\text{m min}^{-1}$ achieved in the case of PbO-based flux (Table 1). We have studied the film surface

Table 1 Condition of crystallization and LY of YAP and YAP:Ce SCF grown from the MS based on BaO and PbO fluxes (T_g – temperature of growth, h – thickness SCF; f – SCF growth rate; LY with respect to YAP:Ce SC standard sample under excitation by α -particles of ^{241}Am (5.15 MeV).

SCF content	no. of samples	flux	CeO_2 content in MS (mol%)	Ce content in SCF (at.%)	$\kappa(\text{Ce})$	h (μm, μm min ⁻¹)	T_g (°C)	LY (%)
YAP	8.4.2	BaO				6.0/0.10	1043.5	
YAP	8.4.3	BaO				3.0/0.05	1038.5	
YAP	Ch-4	PbO				5.0/0.25	1019	
YAP	PCh-1	PbO				15/0.38	1018	
YAP:Ce	8.8.2	BaO	0.5			2.5/0.02	1027	4.8
YAP:Ce	8.8.3	BaO	0.5	0.0215	0.043	6.0/0.05	1008.5	4.5
YAP:Ce	8.4.6	BaO	2.0	0.035	0.018	8.5/0.09	1039.5	10.6
YAP:Ce	8.5.3	BaO	2.0	0.053	0.028	4.5/0.04	1018	23.8
YAP:Ce	8.5.4	BaO	2.0	0.038	0.019	7.4/0.05	1018.5	11.4
YAP:Ce	8.4.8	BaO	10	0.3	0.030	5.8/0.06	1054	9.2
YAP:Ce	8.4.10	BaO	10	0.11	0.011	11/0.12	1036	6.7
YAP:Ce	8.6.3	BaO	10	0.182	0.018	9.0/0.1	1015	8.6
YAP:Ce	Ch-6	PbO	15	0.084	0.006	40/1.33	1050	4.0
YAP:Ce	Ch-8	PbO	15	0.15	0.01	22/0.48	1035	2.4
YAP:Ce	PCh-4	PbO	10	0.0775	0.008	25/0.55	1038	9.1
YAP:Ce	PCh-5	PbO	10	0.091	0.009	33/1.0	1025	4.8

Figure 1 XRD pattern of (330) plane of YP (PbO) SCF grown by LPE onto YAP substrate.

morphology and surface profiles using the polarized optical microscopy in reflection and transmission modes and by means of interferometric surface profiler ZYGO. The YAP:Ce SCF grown from the PbO-based flux show very good structural and optical quality. The surface of the YAP:Ce SCF, grown from the BaO-based flux observed in optical microscope is shown in Fig. 2. Several types of surface defects are observed in the films grown from this flux. The surface pits are the most frequent ones that are well visible in transmission mode. They are rather deep, ranging from several hundreds of nanometers up to several microns and they can also penetrate through all the films up to the substrate. In the latter case the pits can originate from the defects existing in the substrate, e.g., from structure imperfections like dislocations, point mechanical defects in substrate surface, or contamination of the substrate surface before the growth. Another frequent defect, which we have observed in YAP:Ce (BaO) film, are tiny crystallites on the film surface. They are of several microns of lateral dimensions. These crystallites are randomly distributed over the film and their concentration strongly changes from place to place. Isolated crystallites are observed in the reflection mode as light or dark aggregates. They have presumably perovskite structure.

High concentration of the growth defects in the YAP:Ce films grown from the BaO-based flux (compared to films grown from the standard PbO flux) results mostly from the

Figure 3 (online color at: www.pss-a.com) Surface profile of YAP:Ce (BaO) SCF 8.5.3 measured by means of interferometric surface profiler ZYGO.

high viscosity and high surface tension of this flux. The flow of the BaO melt in the crucible is consequently very limited, which results in non-uniform film growth. Another important source of defects is the after-growth, when the BaO-based flux cannot be completely removed from the film surface at the end of the growth process, when the sample is removed from the melt. The growth can thus continue under undefined conditions from the rests of the melt on the sample surface. The non-uniform, rough, and undulating surface of the film (Fig. 3) originates mostly from these particular after-growth processes.

Reported concentrations of Ce and other impurities in the garnet lattice depend not only on the content of MS, but are also strongly influenced by the growth temperature. The most important is that the concentrations of Ce^{3+} ions as well as Pb^{2+} and Pt^{4+} trace impurities increase with decreasing growth temperature and *vice versa* [1–3]. For these reasons we have used relatively high growth temperatures above 1000°C (Table 1).

The Ce content in YAP:Ce SCF was determined using JEOL JXA-8612 MX electron microscope. For the YAP:Ce (PbO) SCFs grown from MS with CeO_2 content 10 and 15 mol% the Ce concentration in SCF was 0.077–0.091 and 0.084–0.15 at.%, respectively (Table 1). Thus, the segregation coefficient of Ce ions (i.e., ratio of concentration of Ce in the SCF and MS) is about 0.06–0.01 (Table 1). The same method was used to detect the Pb and Pt ion contamination, but their concentration appeared below the detection limit of the apparatus in most cases.

The Ce content in YAP:Ce (BaO) SCF grown from MS with CeO_2 content 0.5–10 mol% was in the range of

Figure 2 (online color at: www.pss-a.com) Optical microscope image with magnification $40\times$ of surface of YAP:Ce (BaO) SCF No. 8.5.3 with thickness of $4.5\ \mu\text{m}$ in the transmission (left) and reflection (right) regime.

0.02–0.3 at.% (Table 1), so that the segregation coefficient of Ce^{3+} ions in case of BaO-based flux, calculated within 0.011–0.043, is larger than in case using the PbO-based flux. However, the increase of CeO_2 content in MS up to 10 mol% leads to significant worsening of the condition of SCF growth as well as to decreasing the structural and morphological quality and light output of YAP:Ce (BaO) SCF (Table 1). The absorption spectra of these samples also show strong parasitic absorption around 330 nm (Fig. 1, curve 4). The above-mentioned results allow to conclude that the optimal CeO_2 content in BaO-based MS for growth of YAP:Ce SCF can be about 4–5 mol%.

3 Optical and luminescence properties of YAP and YAP:Ce SCF grown from BaO- and PbO-based fluxes

Absorption spectra of SCF were measured in wavelength range 190–600 nm at 300 K using UV/VIS/NIR Shimadzu absorption spectrophotometer UV-310 PC. The cathode-luminescence (CL) spectra were measured at 300 and 80 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 μs and frequency of 30.3 Hz) with an energy of electrons of 9 keV and a beam current of 100 μA .

The decay kinetics of Ce^{3+} luminescence was measured using time-correlated single photon counting method at Spectrofluorometer 199S equipped with the excitation and emission single grating monochromators. Excitation was provided by the nanosecond coaxial hydrogen-filled flashlamp. The detection was performed by IBH-04 photomultiplier modul. Deconvolution procedure was applied to extract true decay times from the experimental decay curves (SpectraSolve software package, LASTEK).

The photoelectron LY N_{phels} was measured using HPMT (DEP PPO 475B type) with maximum sensitivity in the 200–400 nm range under the excitation by ^{241}Am radioisotope (5.4857 MeV α -particles) with the shaping interval of 0.5 μs (see Ref. [20] for details).

3.1 Optical absorption The absorption spectra of YAP (BaO) SCF are completely different from spectra of YAP (PbO) SCF (Fig. 4a). Specifically, the spectra of undoped SCF do not contain any resolved band in the UV

range. Sharp increase of absorbance below 200 nm is most probably caused by YAP intrinsic absorption edge. On the contrary, the spectra of YAP (PbO) SCF show two bands peaked at 260 nm and below 220 nm. These bands are caused by the Pb^{2+} trace impurity in SCF and connected with the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition of Pb^{2+} ions and $\text{Pb}^{2+} \rightarrow \text{Pb}^{3+} + e$ charge-transfer transition (CTT), respectively [21, 22].

The absorption spectra of selected YAP:Ce (BaO) and YAP:Ce (PbO) SCF samples are shown in Fig. 4b. In addition to mentioned absorption of the undoped SCF, the spectra of YAP:Ce (PbO) SCFs contain the complex band in 260–320 nm range with components peaking at 272, 291, and 305 nm, respectively. This band is caused by $4f^1(^2\text{F}_{5/2}) \rightarrow 5d$ transitions of Ce^{3+} ions [6, 22]. It is necessary to note that amplitude of Ce^{3+} absorption bands in YAP:Ce (BaO) SCF is significantly lower due to their low thickness (Fig. 1, curves 2 and 3, respectively). Additionally to Ce^{3+} absorption bands, the spectra of YAP:Ce (BaO) SCFs also contain wide absorption band around 340 nm. The nature of this band is not clear: it might be related to the O^- based color centers formation both in substrate and SCF during SCF growth processes [23, 24]. The intensity of this band increases with increasing the Ce^{3+} content in SCF samples (Fig. 4b, curves 1 and 2, respectively). We note that intensity of this band is significantly lower in YAP:Ce (PbO) SCFs (Fig. 4b, curves 3 and 4).

3.2 Cathodoluminescence (CL) spectra The CL spectra of undoped YAP (BaO) SCF are presented in Fig. 5a. In comparison with the spectra of YAP (PbO) SCF (Fig. 5b) the spectra of YAP (BaO) SCF (Fig. 2a) shows low intensity luminescence in UV and visible ranges with bands peaked around 360 and 605 nm. Most probably these bands are connected with the Ce^{3+} trace impurity and YAP host defect emission centers, respectively [25, 26].

The emission of undoped YAP (PbO) SCF (Fig. 5b) in UV range consists of the luminescence of localized excitons (LE) around Pb^{2+} ions (at 290 nm) [27], luminescence of single Pb^{2+} centers (at 341 nm) arising due to the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ transition [13], and luminescence of the Pb-based dimer centers (at 365 nm) [27]. Furthermore, in the visible range the luminescence of YAP (PbO) SCF the bands peaking at 550–560 nm was ascribed to the Pb^{2+} -based more complex

Figure 4 Absorption spectra of YAP (PbO) SCF (1a) and YAP:Ce (PbO) SCFs (3a and 4a) in comparison with the spectra of YAP (PbO) (2a) and YAP:Ce (PbO) (3b and 4b) SCFs. The concentration of CeO_2 in the MS was 2 mol% (1b) and 10 mol% (2b–4b).

Figure 5 The CL spectra of YAP (BaO) SCF in comparison with the spectra of YAP (PbO) SCF at 300 K (1) and 80 K (2). The CL intensity in (a) and (b) fragments can be mutually compared.

centers [13]. The LE (Pb) emission band is well overlapped with the mentioned Ce^{3+} absorption bands in YAP:Ce SCF (Fig. 4). Other two emission bands related to single and dimer Pb^{2+} centers are overlapped with Ce^{3+} emission band (Fig. 6). The Pb^{2+} -based centers can also serve as trapping centers. Therefore, the Pb^{2+} centers of different origin strongly compete with Ce^{3+} ions in the process of energy transfer from the host to the emission centers. Most probably these are the main reasons of the low LY of YAP:Ce (PbO) SCF in comparison with YAP:Ce SC analogs (Table 1).

The CL of YAP:Ce (BaO) SCF in comparison with the CL spectra of YAP:Ce (PbO) SCF at 300 K are shown in Fig. 6. The doublet emission band peaked at 370 nm of YAP:Ce (BaO) SCFs is caused by the $5d_1 \rightarrow 4f^1(^2F_{5/2,7/2})$ radiative transition of Ce^{3+} ions. In YAP:Ce (PbO) SCF the luminescence band of Ce^{3+} ions is strongly overlapped with emission band of single Pb^{2+} -based centers. This caused a marked short-wavelength shift of emission spectrum of YAP:Ce (PbO) SCFs with respect to luminescence spectrum of YAP:Ce (BaO) SCF. It is clearly seen from the difference in CL spectra of YAP:Ce (PbO) and YAP:Ce (BaO) SCFs (inset of Fig. 6). The emission band peaked at 341 nm

(3.63 eV) present just the luminescence of single Pb^{2+} centers in YAP:Ce SCF [13].

3.3 PL decay measurements The PL decay kinetics of YAP:Ce (BaO) and YAP:Ce (PbO) SCFs under excitation in Ce^{3+} absorption band at 300 nm are shown in Fig. 7a and b, respectively. The single-exponential course of decay curves up to four orders of magnitude is obtained for the YAP:Ce (BaO) SCF with decay time of 15.7 ns (Fig. 7, curve 2). The average decay time for several presented in Table 1 YAP:Ce (BaO) SCF samples is equal of 16.2 ± 1.1 ns. Such decay time values are very close to typical decay time (17–18 ns) of Ce^{3+} luminescence in YAP:Ce SC [23].

Visible acceleration of the PL decay kinetics takes place in YAP:Ce (PbO) SCF. The decay curve is strongly non-exponential and can be quantitatively approximated by the superposition of two components with decay times of 6.5 and 16.1 ns (Fig. 7, curve 2). For this reason we also calculated average decay time of 13.1 ± 2.2 ns for several YAP:Ce (PbO) SCF samples presented in Table 1 which is widely smaller than for YAP:Ce (BaO) SCF. Most probably, such acceleration of the decay of Ce^{3+} luminescence in YAP:Ce (PbO) SCF can be caused by the energy transfer from Ce^{3+} ions to Pb^{2+} -based centers; namely to the dimer and more complex Pb^{2+} -based centers emitting in the near-UV (385 nm) and visible (550–560 nm) ranges, respectively. The excitation of these Pb-based centers is possible due to the overlap of their excitation bands with the 350–370 nm Ce^{3+} emission band in YAP:Ce [16]. The calculation of integral of normalized decay curves and normalization of their values give the values of 100 and 46%, respectively (see Fig. 7b, curves 1 and 2). From these calculations we can conclude that in YAP:Ce (PbO) SCFs the losses of more than 50% of excitation energy can happen due to energy transfer away from the Ce^{3+} $5d_1$ relaxed excited state to some other center (mentioned Pb^{2+} dimer or more complex Pb^{2+} -based centers) [16]. Such huge losses can partly explain low scintillation efficiency of PbO-grown YAP:Ce SCF (Table 1, Ref. [22]).

Figure 6 (online color at: www.pss-a.com) Normalized CL spectra of YAP:Ce (BaO) SCF (curve 2) in comparison with the CL spectra of YAP (PbO) SCF (curve 1) at 300 K. Inset: the difference between the CL spectra 1 and 2.

3.4 LY measurements Photoelectron LY N_{phels} of Ce-doped YAP:Ce (BaO) and YAP:Ce (PbO) SCFs measured with shaping time of 0.5 μs under excitation by α -particles ^{241}Am (5.4857 MeV) are shown in Table 1. The N_{phels}

Figure 7 (online color at: www.pss-a.com) (a) Normalized luminescence decay kinetics of YAP:Ce (BaO) SCF (1) and YAP:Ce (PbO) (2) SCF at 300 K under excitation in Ce^{3+} absorption band at 300 nm. The exponential fits of decay curves $I = 0.576 \exp(-t/6.5 \text{ ns}) + 0.159 \exp(-t/16.1 \text{ ns}) + \text{const}$ and $I = 1.064 \exp(-t/15.7 \text{ ns}) + \text{const}$, respectively, are given by solid lines. (b) The normalized integral of decay curves presented in figure (a).

measurements from both sides of substrate show rather close values with difference up to $\pm 30\%$. This dispersion of N_{phels} values is caused by the different condition of SCF crystallization on the both sides of substrate resulting in different Ce^{3+} concentration and Pb^{2+} contamination (in the case of growth from PbO-based flux).

As one can see from Table 1, the YAP:Ce (BaO) SCFs show significantly higher LY as compared with YAP:Ce (PbO) SCF samples. LY of the best performing YAP:Ce (PbO) SCF reaches 24% of that of YAP:Ce SC. That is at least 2.5 times higher than LY of the best YAP:Ce (PbO) SCFs (Table 1). It shows the large potential of the BaO-based flux for improving scintillation figure of merit of SCFs based on aluminum perovskites under the assumption that the Ce^{3+} concentration as well as growth conditions can be optimized similarly to those achieved in the case of Pb-based flux.

4 Conclusions The YAP and YAP:Ce SCFs were crystallized for the first time by LPE from the $\text{BaO-B}_2\text{O}_3\text{-BaF}_2$ flux onto YAP SC-oriented substrates. The undoped films show much lower parasitic absorption in UV region and Ce-doped films show significantly higher photoelectron yield and much less distorted luminescence decay with respect to films grown from PbO-based flux. The best performing YAP:Ce (BaO) SCFs reach photoelectron yield of about 24% of that of SC and decay time value 16–17 ns close to that obtained in YAP:Ce bulk SCs.

YAP and YAP:Ce SCFs grown from the PbO-based flux show very good structural and optical perfection. However, Pb^{2+} and Pt^{4+} contamination of the film appears with the detrimental influence on their luminescence and scintillation performance. The accelerated non-exponential photoluminescence decay of Ce^{3+} ions with average decay time of $13.1 \pm 2.2 \text{ ns}$ proves the non-radiative energy transfer from Ce^{3+} ions to Pb^{2+} -based centers of different origin which can be responsible for more than 50% loss of scintillation efficiency. On the contrary the single-exponential decay of Ce^{3+} emission with average decay time

of $16.1 \pm 1.1 \text{ ns}$ in SCFs grown from BaO-based flux points to the absence of any energy transfer loss from the $5d^1$ relaxed excited state of Ce^{3+} center.

Due to calculated Ce^{3+} segregation coefficient (0.01–0.04) the optimization of Ce^{3+} content in SCF (supposed for 4–5 at.% of CeO_2 with respect to YAP crystal-forming components) is required to reach the higher scintillation efficiency yet. Fundamental problem of using the BaO-based flux consists in its very high viscosity and surface tension of the BaO-based melt as well as low SCFs growth rate. As a consequence, worse surface morphology, uniformity, and reproducibility of characteristics of these films are noted, what needs further research. However, in spite of the worse structural and surface properties, the YAP:Ce SCF grown from the BaO-based flux exhibit much better emission and scintillation properties compared to those grown from the PbO-based flux and there is still large potential for the development of this technology.

Acknowledgements This research was partially supported by Czech Science Foundation project No. 202/08/0893 and Ministry of Education and Science of Ukraine (projects SL-28F and DZ-296-2008).

References

- [1] J. M. Robertson and M. W. van Tol, *Thin Solid Films* **114**, 221 (1984).
- [2] Yu. V. Zorenko, P. S. Malutenkov, N. I. Patsagan, I. V. Nazar, V. I. Gorbenko, M. M. Batenchuk, and M. V. Pashkovsky, *Cryst. Prop. Prep.* **36–38**, 226 (1991).
- [3] B. Ferrand, B. Chambaz, and M. Couchaud, *Opt. Mater.* **11**, 101 (1999).
- [4] Yu. Zorenko, I. Konstankevych, M. Globus, B. Grinyov, and V. Lyubinskiy, *Nucl. Instrum. Methods Phys. Res. A* **505**, 93 (2003).
- [5] Y. Zorenko, V. Gorbenko, E. Mihokova, M. Nikl, K. Nejezchleb, A. Vedda, V. Kolobanov, and D. Spassky, *Radiat. Meas.* **42**, 521 (2007).

- [6] Y. Zorenko, V. Gorbenko, I. Konstankevych, T. Voznjak, V. Savchyn, M. Nikl, J. A. Mares, K. Nejezhleb, V. Mikhailin, V. Kolobanov, and D. Spassky, *Radiat. Meas.* **42**, 528 (2007).
- [7] A. Koch, F. Peyrin, P. Heurtier, B. Chambaz, B. Ferrand, W. Ludwig, and M. Couchaud, *Proc. SPIE* **3659**, 170 (1999).
- [8] T. Martin and A. Koch, *J. Synch. Radiat.* **13**, 180 (2006).
- [9] J. Tous, M. Horvath, L. Pina, K. Blazek, and B. Sopko, *Nucl. Instrum. Methods Phys. Res. A* **591**, 264 (2008).
- [10] M. M. Kuklja, *J. Phys.: Condens. Matter* **12**, 2953 (2000).
- [11] C. R. Stanek, K. J. McClellan, M. R. Levy, and R. W. Grimes, *J. Appl. Phys.* **99**, 113518 (2006).
- [12] D. J. Singh, *Phys. Rev. B* **76**, 214115 (2007).
- [13] Yu. Zorenko, V. Gorbenko, A. Voloshinovskii, V. Vistovskii, M. Nikl, E. Mihokova, and K. Nejezhleb, *IEEE Trans. Nucl. Sci.* **55**, 1186 (2008).
- [14] V. Babin, V. Gorbenko, A. Makhov, J. A. Mares, M. Nikl, S. Zazubovich, and Yu. Zorenko, *J. Lumin.* **127**, 384 (2007).
- [15] C. R. Stanek, M. R. Levy, K. J. McClellan, B. P. Uberuaga, and R. W. Grimes, *Nucl. Instrum. Methods Phys. Res. B* **266**, 2657 (2008).
- [16] V. Babin, V. Bichevin, V. Gorbenko, A. Krasnikov, A. Makhov, E. Mihokova, M. Nikl, A. Vedda, S. Zazubovich, and Yu. Zorenko, *Phys. Status Solidi B* **246**, 1318 (2009).
- [17] J. A. Mares, A. Beitlerova, M. Nikl, N. Solovieva, K. Nitsch, M. Kucera, M. Kubova, V. Gorbenko, and Y. Zorenko, *Radiat. Meas.* **42**, 533 (2007).
- [18] M. Kučera, K. Nitsch, M. Kubová, N. Solovieva, M. Nikl, and J. A. Mareš, *IEEE Trans. Nucl. Sci.* **55**, 1201 (2008).
- [19] R. Hiskes and R. A. Burmeister, *Proc. AIP Conf. Magn. Magn. Mater.* **10**, 304 (1972).
- [20] P. Prusa, T. Cechak, J. A. Mares, M. Nikl, Yu. V. Zorenko, V. I. Gorbenko, J. Tous, and K. Blazek, *Appl. Phys. Lett.* **92**, 041903 (2008).
- [21] G. B. Scott and J. L. Page, *J. Appl. Phys.* **48**, 1342 (1977).
- [22] Yu. Zorenko, V. Gorbenko, I. Konstankevych, T. Voznjak, V. Savchyn, M. Nikl, J. A. Mares, K. Blazek, K. Nejezhleb, B. Grinyov, V. Mikhailin, V. Kolobanov, D. Spassky, and B. Grinyov, *SCINT 2005 – Proceedings of the 8th International Conference on Inorganic Scintillators and Their Use in Science and Industrial Applications, Alusta, Crimea, Ukraine, 19–23 September 2005*, edited by A. Gektin and B. Grinyov (Kharkiv, Ukraine, 2006), p. 211.
- [23] M. J. Weber, *J. Appl. Phys.* **44**, 3205 (1973).
- [24] M. Nikl, E. Mihokova, V. Laguta, J. Pejchal, S. Baccaro, and A. Vedda, *Proc. SPIE* **6586**, 65860E (1–13) (2007).
- [25] O. F. Schirmer, K. W. Blazey, and W. Berlinger, *Phys. Rev. B* **11**, 11 (1975).
- [26] V. G. Baryshevsky, M. Korzhik, B. I. Minkov, S. A. Smirnova, A. A. Fyodorov, P. Dorenbos, and C. W. E. van Eijk, *J. Phys.: Condens. Matter* **5**, 7893 (1993).
- [27] Yu. Zorenko, A. Voloshinovskii, V. Gorbenko, T. Zorenko, M. Nikl, and K. Nejezhleb, *Phys. Status Solidi C* **4**, 963 (2007).