Novel Scintillating Screens Based on the Single Crystalline Films of Ce Doped Multi-Component $(\mathrm{Gd, Y, Lu, La})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ Garnets

Yuriy Zorenko, Vitaliy Gorbenko, Volodymyr Savchyn, Tanya Zorenko, Alexander Fedorov, and Oleg Sidletskiy

***Abstract*—The paper is dedicated to development of the novel scintillating screens based on single crystalline films of Ce doped multi-component $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ garnets onto $\mathrm{Gd_3Ga_5O_{12}}$ substrates using the liquid phase epitaxy method.**

***Index Terms*—Ce dopant, garnets, liquid phase epitaxy, luminescence, scintillators, single crystalline films.**

I. INTRODUCTION

THE future development of micro-imaging techniques using X-ray radiation strongly demands single crystalline film (SCF) scintillating screens with high ability of X-ray absorption for 2D/3D imaging with micron or even submicron spatial resolution [1].

Our report presents the results of research directed on the creation of new types of scintillating screens based on the SCF of Ce doped $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ multi-component garnets by liquid phase epitaxy (LPE) method. The bulk crystal analogues of such SCF are now on the top list of scintillators with very high light yield (above 60 000 photon/MeV). Therefore, these compounds are also promising materials for creation of the scintillation screens with high absorption ability for X-rays.

In our work we apply the combination of the "band-gap engineering" [3] and "5d-level positioning" strategies [2] to the basic materials—the Ce doped $\mathrm{Y_3Al_5O_{12}}$ (YAG) and $\mathrm{Lu_3Al_5O_{12}}$ (LuAG) garnets, using the alloying with Sc ions in the octahedral positions and Gd ions in the dodecahedral position of the LuAG and YAG hosts.

TABLE I

MISFIT $\mathbf{m}$ BETWEEN THE $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ SCFS AND GGG SUBSTRATE; THE MAXIMA POSITIONS Λ_{AMAX} OF ABSORPTION BANDS, RELATED TO 4f $\rightarrow$ 5d (^{2}E) TRANSITION OF Ce^{3+} IONS AND ENERGY DISTANCE ΔE BETWEEN THEM; THE MAXIMA Λ_{EMAX} OF CL SPECTRA AND LY OF CL UNDER E-BEAM EXCITATION; THE LY OF RL UNDER EXCITATION BY ALPHA-PARTICLES OF Pu^{239} (5.15 MeV) SOURCE FOR DIFFERENT $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ SCFS IN COMPARISON WITH THE STANDARD YAG:Ce SCF SAMPLE

SCF content	**m, %**	**λ^{a}_{max}, nm**	**ΔE, eV**	**λ^{e}_{max}, nm**	**CL LY, a. u.**	**RL LY, %**
YAG:Ce	0	340,459	0.964	550	270	1.0
$\mathrm{Gd_3Sc_2Al_3O_{12}}$:Ce SCF	+ 0.44	337.5; 448	0.899	568	4	0.05
$\mathrm{Gd_{2.5}Y_{0.5}Sc_2Al_3O_{12}}$:Ce	+ 0.30	342, 447	0.862	566	12	0.15
$\mathrm{Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12}}$:Ce	+ 0.08	343, 444	0.823	565	6.5	0.14
$\mathrm{Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}}$:Ce	- 0.06	345, 443	0.813	562	4.3	0.12
$\mathrm{Gd_{1.75}Y_{0.75}Lu_{0.5}Sc_2Al_3O_{12}}$:Ce	- 0.13	344, 442	0.803	560	5	0.09

II. LPE GROWTH OF SCF OF MULTI-COMPONENT GARNETS

The main task in the growth of SCF based on the multi-component garnet compounds by LPE method is the decreasing the misfit $\Delta \mathrm{a}$ between the lattices of SCF and substrate to condition of the SCF growth ($\Delta \mathrm{a} < 0.1\%$ [4]). This can be achieved by the respective choice of substrate and SCF content. Apart from the YAG substrate with lattice constant $\mathrm{a} = 12.01$ Á, typically using for growth of YAG and LuAG based SCFs, we consider in our work the possibility of SCF crystallization by the LPE method onto $\mathrm{Gd_3Ga_5O_{12}}$ (GGG) substrates with $\mathrm{a} = 12.38$ Á. Namely, we have successfully crystallized the sets SCF of Ce-doped $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$, garnets onto GGG substrates with (111) orientation from melt-solution (MS) using the typical $\mathrm{PbO - B_2O_3}$ flux. The values of x in compositions of these garnets were changed from x = 0 to 1.5 (see Table I for details). The concentration of rare-earth oxides $(\mathrm{Gd_2O_3 + Lu_2O_3 + Y_2O_3})$ and $\mathrm{Al_2O_3 + Sc_2O_3}$ oxides in the MS was chosen with typical ratios of 0.25–0.3. The total content of garnet components in the MS was 3.6–5.4 mole %. These values determine the range of temperatures of saturation of corresponding melt-solutions $\mathrm{T_S} = 1010 - 1060^\circ\mathrm{C}$ as well as the ranges of SCF growth temperature $\mathrm{T_g} = 960 - 1022^\circ\mathrm{C}$, respectively.

The content of Ce-doped $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$ SCF under study was determined using a SEM JEOL 6420 electron microscope equipped with JXA-8612 MX setup. The Ce^{3+} content in all the studied SCF was in 0.15–0.5 at.% range. We also estimate the average total content of Pb contamination in these SCF which was equal to 60–150 ppm. Therefore, the Pb contamination in the studied SCF of $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$ garnets was significantly larger than the typical content of Pb

---

Manuscript received May 25, 2013; revised August 03, 2013; accepted August 12, 2013. This work was realized within the Polish National Science Centre (NCN) project No 2012/07/B/ST5/02376 and was supported in part by Ministry Education and Science of Ukraine (project SL-126 F) and NATO (project CBP.NUKR.CLG984305). The investigations at the Superlumi station were performed in the frame of I-20110085 EC and I-20110938 EC projects.

Y. Zorenko was with the Electronics Department, Ivan Franko National University of Lviv, Lviv, Ukraine. He is now with the Institute of Physics, Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland (e-mail: zorenko@ukw.edu.pl).

V. Gorbenko, V. Savchyn, and T. Zorenko are with the Electronics Department, Ivan Franko National University of Lviv, Lviv, Ukraine (e-mail: horbenko@inbox.ru; savchyn@lnu.edu.ua; tanyazorenko@gmail.com).

A. Fedorov and O. Sidletskiy are with the Institute for Scintillation Materials National AS of Ukraine, Kharkiv, Ukraine (e-mail: fedorov@xray.isc.kharkov.com; sidletskiy@isma.kharkov.ua).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TNS.2013.2282260

IEEE Proof Web Version

0018-9499 © 2013 IEEE

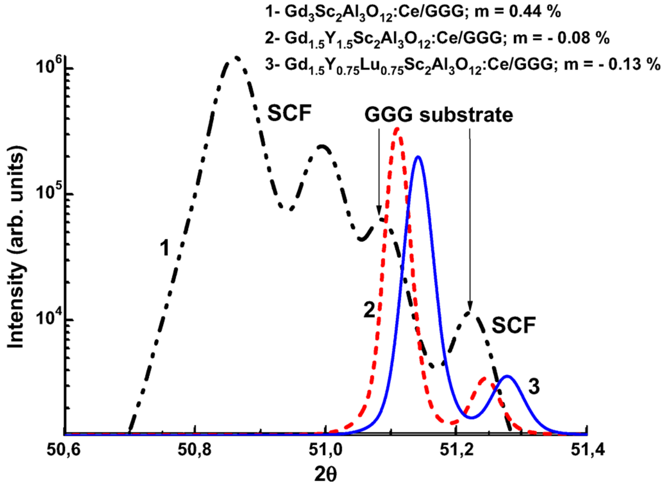


Fig. 1. X-ray pattern of for the $\mathrm{Gd_3Sc_2Al_2O_{12} : Ce}$ (1), $\mathrm{Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12} : Ce}$ (2), $\mathrm{Gd_{1.75}Y_{0.75}Lu_{0.5}Sc_2Al_3O_{12} : Ce}$ (3) SCFs grown onto GGG substrates with (111) orientation. Misfit between the (444) reflexes for SCF and GGG substrates is determined.

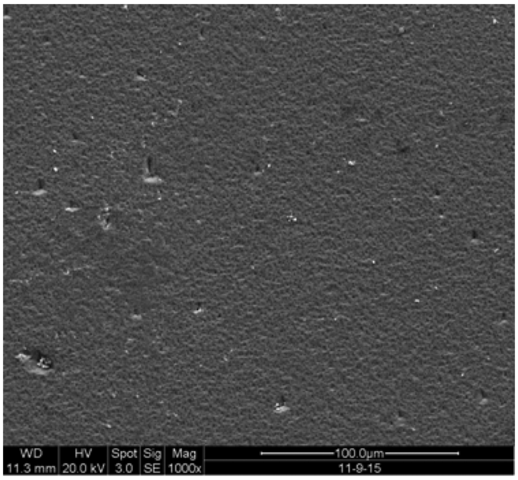
ions in YAG:Ce SCF grown onto YAG substrates (usually below 30 ppm [5]).

The XRD measurements were used for characterization of the structural perfection of SCF and misfit $\boldsymbol{m}$ between SCF and GGG substrate (Table I). We have found that the misfit $\boldsymbol{m}$ of SCF-substrate lattices for all the studied garnet compounds is lies between the -0.13% and $+0.44\%$ (Fig. 1, Table I).

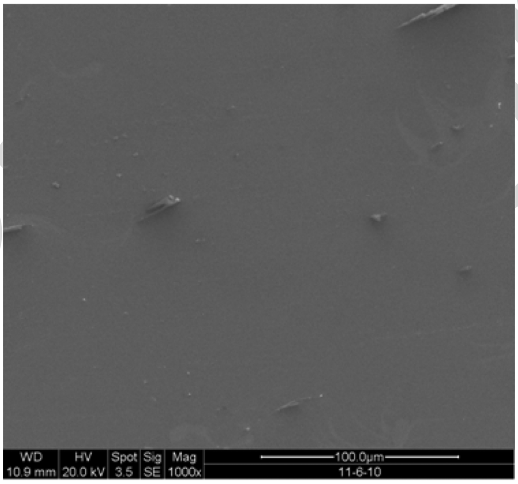
Depending on the SCF composition and SCF/substrate misfit, the SCFs of the garnet compounds under study show difference in the surface morphology: from the uniform surface with small quantity of pits at middle ($\boldsymbol{m} = 0.3\%$) misfit (a) up to high-quality mirror-like surface (b) at small ($\boldsymbol{m} = 0.06\%$) misfit. The best structural quality was observed for the $\mathrm{Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12} : Ce}$ and $\mathrm{Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12} : Ce}$ SCFs which possess the mirror-like surface. For SCF of these compounds, the misfit SCF/substrate does not exceed the values $\mathbf{m} \pm 0.1\%$ (Table I, Fig. 2).

III. Luminescent and Scintillation Properties of $\mathrm{(Gd, Y, Lu)_3(Al, Sc)_5O_{12}}$ SCF

The SCF of garnet compounds under study were characterized by the absorption, cathodoluminescence (CL) spectra and light yield (LY) of CL under pulsed e-beam excitation as well as LY of radioluminescence (RL) under excitation by α-particles $\mathrm{Pu^{239}}$ (5.15 MeV) source (Table I). The absorption spectra SCF of garnet compounds under study were measured at 300 K using a Perkin-Elmer Lambda 950 UV/VIS spectrometer at 300 K. The CL spectra were measured at 300 K with a set-up based on a DMR-4A monochromator and a PMT FEU-106 under pulsed e-beam excitation (a pulse duration of 2 μs and a frequency of $30 - 3$ Hz) with an energy of electrons of 9 keV and a beam current of 100 μA. The LY of SCF was measured using a FEU-110 PMT with maximum sensitivity in the 400–450 nm range under excitation by α-particles of $\mathrm{Pu^{239}}$ source (5.15 MeV) with a shaping time of 0.5 μs.



$\mathbf{m = + 0.3\ \%}$ **(a)**



$\mathbf{m = - 0.06\ \%}$ **(b)**

Fig. 2. Secondary electron images of surface of $\mathrm{Gd_{2.5}Y_{0.5}Sc_2Al_3O_{12} : Ce}$ (a) and $\mathrm{Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12} : Ce}$ (b) SCF grown onto GGG substrates with (111) orientation.

For measurements of the decay kinetics of the $\mathrm{Ce^{3+}}$ luminescence and determination of the fundamental optical characteristics of the studied garnets (positions of $\mathrm{Ce^{3+}}$ f-d levels relatively the bottom of conductive band and energy of formation of excitons bound with the $\mathrm{Ce^{3+}}$ ions), the luminescent spectroscopy of Ce doped $\mathrm{(Gd, Y, Lu)_3(Al, Sc)_5O_{12}}$ SCF was performed at the Superlumi station, HASYLAB, DESY under excitation by pulsed synchrotron radiation (a pulse duration of 0.126 ns) in the 3.7–25 eV range.

In comparison with YAG:Ce SCF, the LY of CL and RL of $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12} : Ce}$ SCF grown onto GGG substrates is low and is not exceed 14–15% (Table I). The maximum of LY of CL and RL of SCFs under study is reached at $\mathrm{x} = 0.5$–0.75 and slightly decreases with increasing the Y and Lu content above $\mathrm{x} = 0.75$ (see Table I). The main reason for the relatively low LY of $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12} : Ce}$ SCF is the significantly larger content of $\mathrm{Pb^{2+}}$ flux related impurity and its higher influence on the LY of SCF of multi-component garnets, grown on the GGG substrates in comparison with the Ce doped YAG SCF grown on the YAG substrates (Table I).

IEEE Proof Web Version

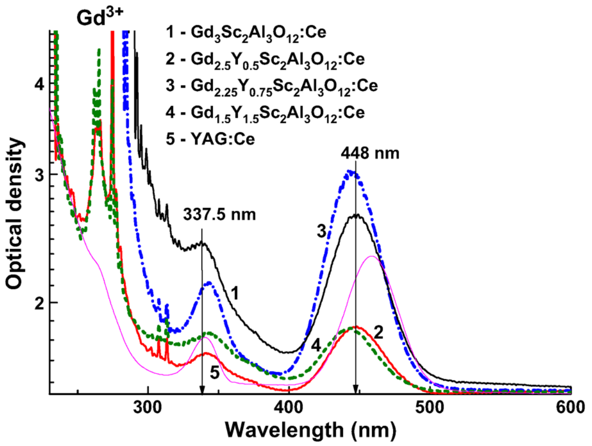


Fig. 3. Absorption spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with $x = 0$, 0.5, 0.75 and 1.5 in comparison with absorption spectra of $Y_3Al_5O_{12}$: Ce SCF standard sample at 300 K. The variation in the optical density of the Ce^{3+} transitions is due to the different SCF thickness and different Ce^{3+} content.

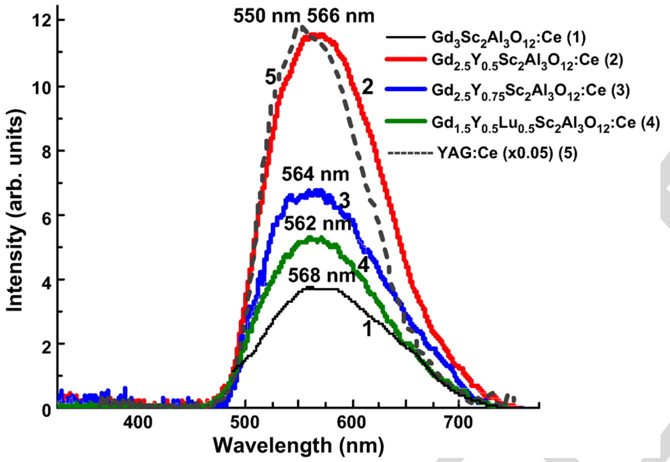


Fig. 4. CL spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with different values $x = 0$, 0.5, 0.75 and 1.5 in comparison with CL spectra of $Y_3Al_5O_{12}$: Ce SCF standard sample at 300 K. The intensity of curve 4 is multiplied by a factor of 0.05.

The absorption spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with $x = 0$, 0.5, 0.75 and 1.5 in comparison with the absorption spectra of the standard $Y_3Al_5O_{12}$: Ce SCF sample were shown in Fig. 3. The variation of the cation content leads to change in the position of the absorption bands related to the 4f → 5d (^2E) transition of Ce^{3+} ions and energy distance ΔE between them. Such changes in the ΔE values reflect the change in the crystal field strength in the dodecahedral positions of garnet lattice where the Ce^{3+} ions are localized. Namely, based on the respective ΔE values, we have assumed that the crystal field strength in $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce garnet is by 16% smaller than that for YAG:Ce.

The CL spectra of $(Gd,Y)_3Sc_2Al_3O_{12}$: Ce SCF with different Gd/Y ratios are shown in Fig. 4. It is necessary to note that the CL spectra of all the investigated garnet compounds do not show any luminescence of the antisite defects in the UV range what is typical for single crystal (SC) counterparts of these garnets [6]. Due to low temperature of crystallization (about 1000°C) this type of defects is completely absent in SCFs.

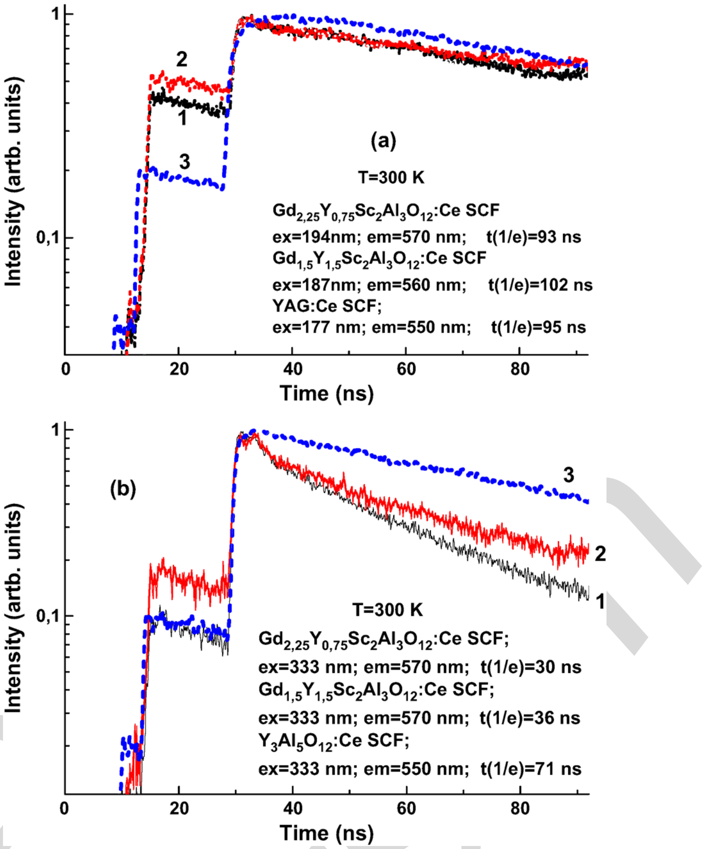


Fig. 5. Decay kinetics of Ce^{3+} emission at 300 K in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF at $x = 0.75$ (curves 1) and 1.7 (curves 2) in comparison with YAG:Ce SCF (curves 3) under excitation in the exciton range of the mentioned garnet hosts (a) and Ce^{3+} related absorption bands at 333 nm (b).

In comparison with the CL spectrum YAG:Ce SCF (Fig. 4, curve 5), the CL spectra of $Gd_{3-x}(Y,Lu)_xSc_2Al_3O_{12}$: Ce SCF with different Gd/Y/Lu ratios are wider and shifted to the orange range (Fig. 4, curves 1–4). At the same time, at increasing the Y content from $x = 0$ to 1.5, the maximum of the Ce^{3+} emission spectrum shows the short-wavelength shift from 568 nm to 562 nm (Fig. 4, curves 1–4, respectively).

The decay kinetics of the Ce^{3+} emission in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with $x = 0.75$ and 1.5 is shown in Fig. 5 (curves 1 and 2, respectively). Under excitation in the exciton range of the respective garnet hosts the decay kinetics of the Ce^{3+} luminescence in SCF of the studied garnets is comparable with the decay kinetics of the Ce^{3+} emission in YAG:Ce SCF [Fig. 5(a)]: the corresponding t(1/e) values are equal to 93 and 102 ns for $Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12}$: Ce and $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce SCFs in comparison t(1/e) value of the 95 ns range for the YAG:Ce SCF. Meanwhile, the decay kinetics of the Ce^{3+} luminescence is significantly faster in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCFs under excitation in the band at 333 nm related to the intrinsic 4f-5d transition of Ce^{3+} ions [Fig. 5(b), curves 1, 2]; the corresponding t(1/e) values lies in the 30–36 ns range in comparison with a value of 71 ns for YAG:Ce SCF.

The excitation spectra of the Ce^{3+} luminescence in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with different x values are shown in Fig. 6. In comparison with the excitation spectrum

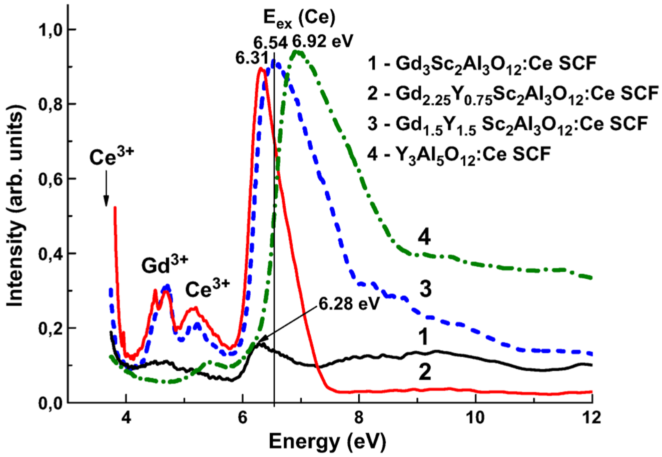


Fig. 6. Excitation spectra of Ce^{3+} emission at 8 K in $(Gd_{3-x}Y_x)Sc_2Al_3O_{12}$: Ce SCF with different Gd/Y ratios. $E_{ex}(Ce)$ values show the shift of 0.173 eV per one formula units of Y in Gd sites.

of the Ce^{3+} luminescence in YAG:Ce SCF (Fig. 6, curve 4), the main peak of excitation spectra of $Gd_3Sc_2Al_3O_{12}$: Ce SCF, corresponding to the energy of creation of an exciton bound with Ce^{3+}, is shifted in the low-energy range to 6.28 eV (Fig. 6, curve 1). We have also found that in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF, the energy of creation of the exciton bound with the Ce^{3+} ions shows the high-energy shift of 0.173 eV per one formula unit of Y^{3+} ions in the positions of Gd^{3+} cations (Fig. 6).

IV. CONCLUSIONS

The single crystalline film (SCF) scintillators based on the Ce-doped multi-component $Gd_{3-x}(Y,Lu)_xSc_2Al_3O_{12}$ garnets with x values from 0 to 0.5, 0.75 and 1.5 were successfully crystallized by the LPE method onto GGG substrates from melt-solutions based on the $PbO - B_2O_3$ flux.

Of all the studied garnet compounds, the best light yield (LY) of luminescence under e-beam excitation and excitation by α-particles of Pu^{239} (5.15 MeV) source is observed in the $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF at $x = 0.5$–0.75.

We have also found the significantly large influence of Pb^{2+} flux related impurity on the LY of Ce^{3+} emission in $Gd_{3-x}(Y,Lu)_xSc_2Al_3O_{12}$ SCF, grown on the GGG substrates, in comparison with the YAG:Ce SCF analogue, grown by the LPE on the YAG substrates at relatively the same conditions [5]. This effect is caused by the larger lead contamination in SCFs of Gd-Y-Lu based garnets, grown onto GGG substrates, in comparison with YAG counterpart due to the relative larger dimension of the dodecahedral positions in these garnet hosts, where the Pb^{2+} ions are localized. Thus, it is desirable to use the lead-free fluxes for producing the SCF scintillators based on the multi-component garnet compounds to achieve their higher LY. Such a type of fluxes, namely BaO based fluxes, were successfully applied for producing the YAG:Ce and LuAG:Ce SCF scintillators with LY comparable with that for their crystal counterparts [7]. Therefore, we expect that using BaO based fluxes for growing SCF of multi-component garnets gives the possibility to estimate the real potential of the compounds under study for producing the scintillating screens.

REFERENCES

[1] T. Martin and A. Koch, "Recent development in X-ray imaging with micrometer spatial resolution," *J. Synchrotron Rad.*, vol. 13, pp. 180–194, 2006.
[2] K. Kamada, T. Endo, K. Tsutumi, J. Pejchal, M. Nikl, K. Tsutumi, Y. Fujimoto, A. Fukabori, and A. Yoshikawa, "Composition engineering in Ce doped $(Lu,Gd)_3(Ga,Al)_5O_{12}$ single crystal scintillators," *Cryst. Growth Des.*, vol. 11, pp. 4484–4490, 2011.
[3] M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B. P. Uberuaga, D. A. Andersson, K. J. McClellan, and C. R. Stanek, "Band gap engineering for shallow trap removal in $RE_3Al_5O_{12}$ garnets," *Phys. Rev. B*, vol. 84, p. 081102(R), 2011.
[4] Y. Zorenko and V. Gorbenko, "Growth peculiarities of the $R_3Al_5O_{12}$ ($R = $ Lu, Yb, Tb, Eu-Y) single crystalline film phosphors by liquid phase epitaxy," *Radiat. Meas.*, vol. 42, pp. 907–910, 2007.
[5] Y. Zorenko, J. A. Mares, P. Prusa, M. Nikl, V. Gorbenko, V. Savchyn, R. Kucerkova, and K. Nejezchleb, "Luminescence and scintillation characteristics of YAG:Ce single crystalline films and single crystals," *Radiat. Meas.*, vol. 45, pp. 389–391, 2010.
[6] Y. Zorenko, A. Voloshinovskii, V. Savchyn, T. Vozniak, M. Nikl, K. Nejezchleb, V. Mikhailin, V. Kolobanov, and D. Spassky, "Exciton and antisite defect-related luminescence in $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ garnets," *Phys. Stat. Sol. (b)*, vol. 244, pp. 2180–2189, 2007.
[7] M. Kucera, K. Nitsch, M. Kubova, N. Solovieva, M. Nikl, and J. A. Mares, "Ce-doped YAG and LuAG epitaxial films for scintillation detectors," *IEEE Trans. Nucl. Sci.*, vol. 55, no. 3, pp. 1201–1205, Jun. 2008.

IEEE Proof Web Version

Novel Scintillating Screens Based on the Single Crystalline Films of Ce Doped Multi-Component $(\mathrm{Gd, Y, Lu, La})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ Garnets

Yuriy Zorenko, Vitaliy Gorbenko, Volodymyr Savchyn, Tanya Zorenko, Alexander Fedorov, and Oleg Sidletskiy

***Abstract*—The paper is dedicated to development of the novel scintillating screens based on single crystalline films of Ce doped multi-component $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ garnets onto $\mathrm{Gd_3Ga_5O_{12}}$ substrates using the liquid phase epitaxy method.**

***Index Terms*—Ce dopant, garnets, liquid phase epitaxy, luminescence, scintillators, single crystalline films.**

I. INTRODUCTION

THE future development of micro-imaging techniques using X-ray radiation strongly demands single crystalline film (SCF) scintillating screens with high ability of X-ray absorption for 2D/3D imaging with micron or even submicron spatial resolution [1].

Our report presents the results of research directed on the creation of new types of scintillating screens based on the SCF of Ce doped $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ multi-component garnets by liquid phase epitaxy (LPE) method. The bulk crystal analogues of such SCF are now on the top list of scintillators with very high light yield (above 60 000 photon/MeV). Therefore, these compounds are also promising materials for creation of the scintillation screens with high absorption ability for X-rays.

In our work we apply the combination of the "band-gap engineering" [3] and "5d-level positioning" strategies [2] to the basic materials—the Ce doped $\mathrm{Y_3Al_5O_{12}}$ (YAG) and $\mathrm{Lu_3Al_5O_{12}}$ (LuAG) garnets, using the alloying with Sc ions in the octahedral positions and Gd ions in the dodecahedral position of the LuAG and YAG hosts.

TABLE I
MISFIT m BETWEEN THE $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ SCFS AND GGG SUBSTRATE; THE MAXIMA POSITIONS Λ_{AMAX} OF ABSORPTION BANDS, RELATED TO $4\mathrm{f} \rightarrow 5\mathrm{d}\ (^2\mathrm{E})$ TRANSITION OF Ce^{3+} IONS AND ENERGY DISTANCE $\Delta\mathrm{E}$ BETWEEN THEM; THE MAXIMA Λ_{EMAX} OF CL SPECTRA AND LY OF CL UNDER E-BEAM EXCITATION; THE LY OF RL UNDER EXCITATION BY ALPHA-PARTICLES OF Pu^{239} (5.15 MeV) SOURCE FOR DIFFERENT $(\mathrm{Gd, Y, Lu})_3(\mathrm{Al, Sc})_5\mathrm{O}_{12}$ SCFS IN COMPARISON WITH THE STANDARD YAG:Ce SCF SAMPLE

SCF content	m, %	λ^{a}_{max}, nm	ΔE, eV	λ^{e}_{max}, nm	CL LY, a. u.	RL LY, %
YAG:Ce	0	340,459	0.964	550	270	1.0
$\mathrm{Gd_3Sc_2Al_3O_{12}}$:Ce SCF	+ 0.44	337.5; 448	0.899	568	4	0.05
$\mathrm{Gd_{2.5}Y_{0.5}Sc_2Al_3O_{12}}$:Ce	+ 0.30	342, 447	0.862	566	12	0.15
$\mathrm{Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12}}$:Ce	+ 0.08	343, 444	0.823	565	6.5	0.14
$\mathrm{Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}}$:Ce	- 0.06	345, 443	0.813	562	4.3	0.12
$\mathrm{Gd_{1.75}Y_{0.75}Lu_{0.5}Sc_2Al_3O_{12}}$:Ce	- 0.13	344, 442	0.803	560	5	0.09

II. LPE GROWTH OF SCF OF MULTI-COMPONENT GARNETS

The main task in the growth of SCF based on the multi-component garnet compounds by LPE method is the decreasing the misfit $\Delta\mathrm{a}$ between the lattices of SCF and substrate to condition of the SCF growth ($\Delta\mathrm{a} < 0.1\%$ [4]). This can be achieved by the respective choice of substrate and SCF content. Apart from the YAG substrate with lattice constant $\mathrm{a} = 12.01$ Å, typically using for growth of YAG and LuAG based SCFs, we consider in our work the possibility of SCF crystallization by the LPE method onto $\mathrm{Gd_3Ga_5O_{12}}$ (GGG) substrates with $\mathrm{a} = 12.38$ Å. Namely, we have successfully crystallized the sets SCF of Ce-doped $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$, garnets onto GGG substrates with (111) orientation from melt-solution (MS) using the typical $\mathrm{PbO - B_2O_3}$ flux. The values of x in compositions of these garnets were changed from $\mathrm{x} = 0$ to 1.5 (see Table I for details). The concentration of rare-earth oxides $(\mathrm{Gd_2O_3 + Lu_2O_3 + Y_2O_3})$ and $\mathrm{Al_2O_3 + Sc_2O_3}$ oxides in the MS was chosen with typical ratios of 0.25–0.3. The total content of garnet components in the MS was 3.6–5.4 mole %. These values determine the range of temperatures of saturation of corresponding melt-solutions $\mathrm{T_S} = 1010 - 1060^\circ\mathrm{C}$ as well as the ranges of SCF growth temperature $\mathrm{T_g} = 960 - 1022^\circ\mathrm{C}$, respectively.

The content of Ce-doped $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$ SCF under study was determined using a SEM JEOL 6420 electron microscope equipped with JXA-8612 MX setup. The Ce^{3+} content in all the studied SCF was in 0.15–0.5 at.% range. We also estimate the average total content of Pb contamination in these SCF which was equal to 60–150 ppm. Therefore, the Pb contamination in the studied SCF of $\mathrm{Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}}$ garnets was significantly larger than the typical content of Pb

---

Manuscript received May 25, 2013; revised August 03, 2013; accepted August 12, 2013. This work was realized within the Polish National Science Centre (NCN) project No 2012/07/B/ST5/02376 and was supported in part by Ministry Education and Science of Ukraine (project SL-126 F) and NATO (project CBP.NUKR.CLG984305). The investigations at the Superlumi station were performed in the frame of I-20110085 EC and I-20110938 EC projects.

Y. Zorenko was with the Electronics Department, Ivan Franko National University of Lviv, Lviv, Ukraine. He is now with the Institute of Physics, Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland (e-mail: zorenko@ukw.edu.pl).

V. Gorbenko, V. Savchyn, and T. Zorenko are with the Electronics Department, Ivan Franko National University of Lviv, Lviv, Ukraine (e-mail: horbenko@inbox.ru; savchyn@lnu.edu.ua; tanyazorenko@gmail.com).

A. Fedorov and O. Sidletskiy are with the Institute for Scintillation Materials National AS of Ukraine, Kharkiv, Ukraine (e-mail: fedorov@xray.isc.kharkov.com; sidletskiy@isma.kharkov.ua).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TNS.2013.2282260

0018-9499 © 2013 IEEE

IEEE Proof Print Version

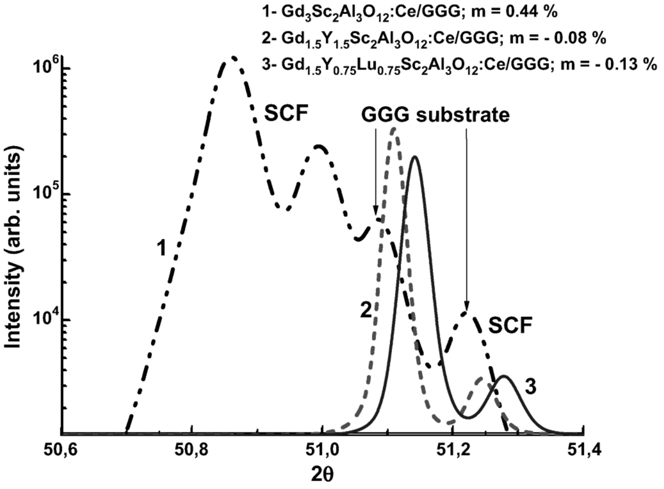


Fig. 1. X-ray pattern of for the $Gd_3Sc_2Al_2O_{12}$: Ce (1), $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce (2), $Gd_{1.75}Y_{0.75}Lu_{0.5}Sc_2Al_3O_{12}$: Ce (3) SCFs grown onto GGG substrates with (111) orientation. Misfit between the (444) reflexes for SCF and GGG substrates is determined.

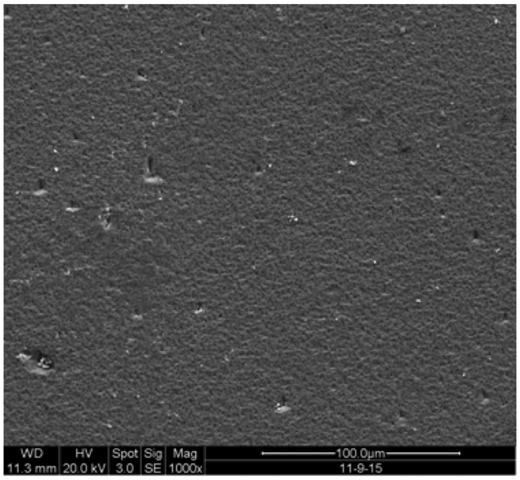
ions in YAG:Ce SCF grown onto YAG substrates (usually below 30 ppm [5]).

The XRD measurements were used for characterization of the structural perfection of SCF and misfit $\boldsymbol{m}$ between SCF and GGG substrate (Table I). We have found that the misfit $\boldsymbol{m}$ of SCF-substrate lattices for all the studied garnet compounds is lies between the -0.13% and $+0.44\%$ (Fig. 1, Table I).

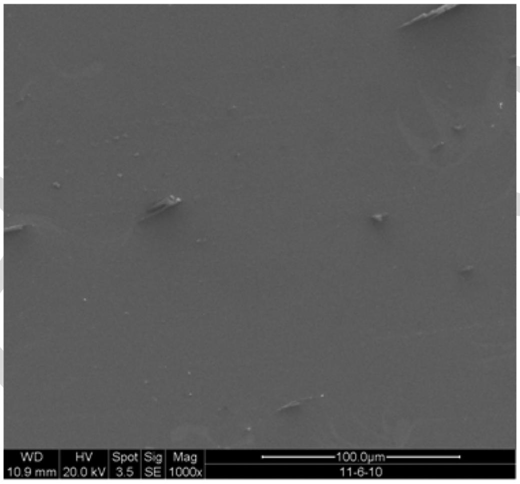
Depending on the SCF composition and SCF/substrate misfit, the SCFs of the garnet compounds under study show difference in the surface morphology: from the uniform surface with small quantity of pits at middle ($\boldsymbol{m} = 0.3\%$) misfit (a) up to high-quality mirror-like surface (b) at small ($\boldsymbol{m} = 0.06\%$) misfit. The best structural quality was observed for the $Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12}$: Ce and $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce SCFs which possess the mirror-like surface. For SCF of these compounds, the misfit SCF/substrate does not exceed the values $\mathbf{m} \pm 0.1\%$ (Table I, Fig. 2).

III. LUMINESCENT AND SCINTILLATION PROPERTIES OF $(Gd, Y, Lu)_3(Al, Sc)_5O_{12}$ SCF

The SCF of garnet compounds under study were characterized by the absorption, cathodoluminescence (CL) spectra and light yield (LY) of CL under pulsed e-beam excitation as well as LY of radioluminescence (RL) under excitation by α-particles Pu^{239} (5.15 MeV) source (Table I). The absorption spectra SCF of garnet compounds under study were measured at 300 K using a Perkin-Elmer Lambda 950 UV/VIS spectrometer at 300 K. The CL spectra were measured at 300 K with a set-up based on a DMR-4A monochromator and a PMT FEU-106 under pulsed e-beam excitation (a pulse duration of 2 μs and a frequency of $30 - 3$ Hz) with an energy of electrons of 9 keV and a beam current of 100 μA. The LY of SCF was measured using a FEU-110 PMT with maximum sensitivity in the 400–450 nm range under excitation by α-particles of Pu^{239} source (5.15 MeV) with a shaping time of 0.5 μs.



m = + 0.3 % (a)



m = - 0.06 % (b)

Fig. 2. Secondary electron images of surface of $Gd_{2.5}Y_{0.5}Sc_2Al_3O_{12}$: Ce (a) and $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce (b) SCF grown onto GGG substrates with (111) orientation.

For measurements of the decay kinetics of the Ce^{3+} luminescence and determination of the fundamental optical characteristics of the studied garnets (positions of Ce^{3+} f-d levels relatively the bottom of conductive band and energy of formation of excitons bound with the Ce^{3+} ions), the luminescent spectroscopy of Ce doped $(Gd, Y, Lu)_3(Al, Sc)_5O_{12}$ SCF was performed at the Superlumi station, HASYLAB, DESY under excitation by pulsed synchrotron radiation (a pulse duration of 0.126 ns) in the 3.7–25 eV range.

In comparison with YAG:Ce SCF, the LY of CL and RL of $Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}$: Ce SCF grown onto GGG substrates is low and is not exceed 14–15% (Table I). The maximum of LY of CL and RL of SCFs under study is reached at $x = 0.5$–0.75 and slightly decreases with increasing the Y and Lu content above $x = 0.75$ (see Table I). The main reason for the relatively low LY of $Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}$: Ce SCF is the significantly larger content of Pb^{2+} flux related impurity and its higher influence on the LY of SCF of multi-component garnets, grown on the GGG substrates in comparison with the Ce doped YAG SCF grown on the YAG substrates (Table I).

IEEE Proof Print Version

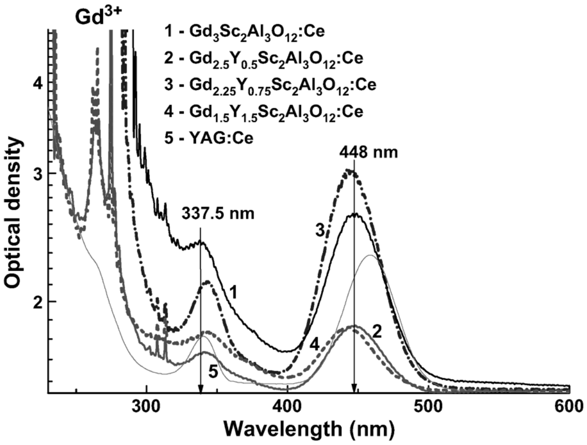


Fig. 3. Absorption spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with x = 0, 0.5, 0.75 and 1.5 in comparison with absorption spectra of $Y_3Al_5O_{12}$: Ce SCF standard sample at 300 K. The variation in the optical density of the Ce^{3+} transitions is due to the different SCF thickness and different Ce^{3+} content.

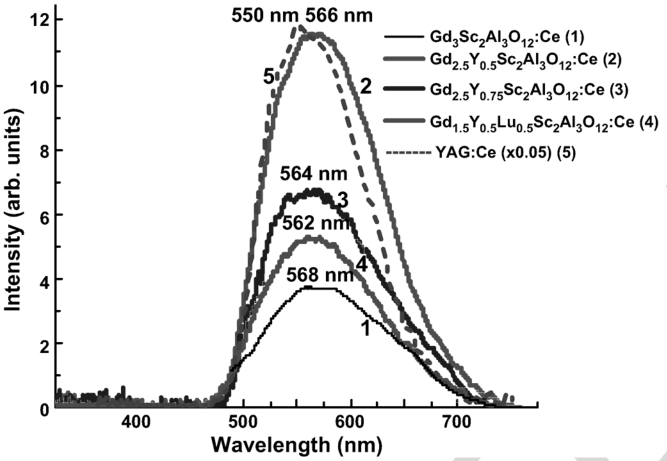


Fig. 4. CL spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with different values x = 0, 0.5, 0.75 and 1.5 in comparison with CL spectra of $Y_3Al_5O_{12}$: Ce SCF standard sample at 300 K. The intensity of curve 4 is multiplied by a factor of 0.05.

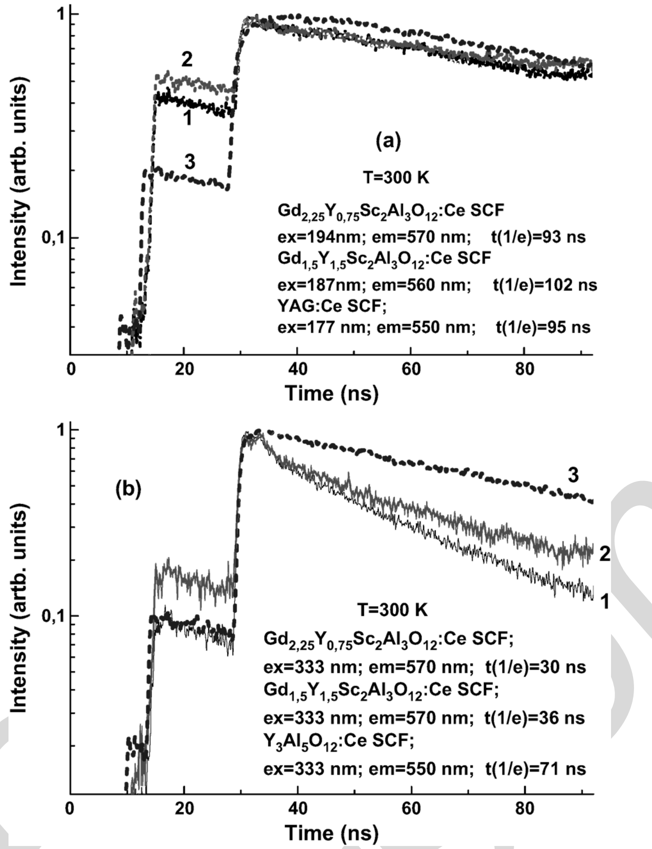


Fig. 5. Decay kinetics of Ce^{3+} emission at 300 K in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF at x = 0.75 (curves 1) and 1.7 (curves 2) in comparison with YAG:Ce SCF (curves 3) under excitation in the exciton range of the mentioned garnet hosts (a) and Ce^{3+} related absorption bands at 333 nm (b).

The absorption spectra of $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with x = 0, 0.5, 0.75 and 1.5 in comparison with the absorption spectra of the standard $Y_3Al_5O_{12}$: Ce SCF sample were shown in Fig. 3. The variation of the cation content leads to change in the position of the absorption bands related to the 4f → 5d (^2E) transition of Ce^{3+} ions and energy distance ΔE between them. Such changes in the ΔE values reflect the change in the crystal field strength in the dodecahedral positions of garnet lattice where the Ce^{3+} ions are localized. Namely, based on the respective ΔE values, we have assumed that the crystal field strength in $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce garnet is by 16% smaller than that for YAG:Ce.

The CL spectra of $(Gd, Y)_3Sc_2Al_3O_{12}$: Ce SCF with different Gd/Y ratios are shown in Fig. 4. It is necessary to note that the CL spectra of all the investigated garnet compounds do not show any luminescence of the antisite defects in the UV range what is typical for single crystal (SC) counterparts of these garnets [6]. Due to low temperature of crystallization (about 1000° C) this type of defects is completely absent in SCFs.

In comparison with the CL spectrum YAG:Ce SCF (Fig. 4, curve 5), the CL spectra of $Gd_{3-x}(Y, Lu)_xSc_2Al_3O_{12}$: Ce SCF with different Gd/Y/Lu ratios are wider and shifted to the orange range (Fig. 4, curves 1–4). At the same time, at increasing the Y content from x = 0 to 1.5, the maximum of the Ce^{3+} emission spectrum shows the short-wavelength shift from 568 nm to 562 nm (Fig. 4, curves 1–4, respectively).

The decay kinetics of the Ce^{3+} emission in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with x = 0.75 and 1.5 is shown in Fig. 5 (curves 1 and 2, respectively). Under excitation in the exciton range of the respective garnet hosts the decay kinetics of the Ce^{3+} luminescence in SCF of the studied garnets is comparable with the decay kinetics of the Ce^{3+} emission in YAG:Ce SCF [Fig. 5(a)]: the corresponding t(1/e) values are equal to 93 and 102 ns for $Gd_{2.25}Y_{0.75}Sc_2Al_3O_{12}$: Ce and $Gd_{1.5}Y_{1.5}Sc_2Al_3O_{12}$: Ce SCFs in comparison t(1/e) value of the 95 ns range for the YAG:Ce SCF. Meanwhile, the decay kinetics of the Ce^{3+} luminescence is significantly faster in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCFs under excitation in the band at 333 nm related to the intrinsic 4f-5d transition of Ce^{3+} ions [Fig. 5(b), curves 1, 2]; the corresponding t(1/e) values lies in the 30–36 ns range in comparison with a value of 71 ns for YAG:Ce SCF.

The excitation spectra of the Ce^{3+} luminescence in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF with different x values are shown in Fig. 6. In comparison with the excitation spectrum

IEEE Proof Print Version

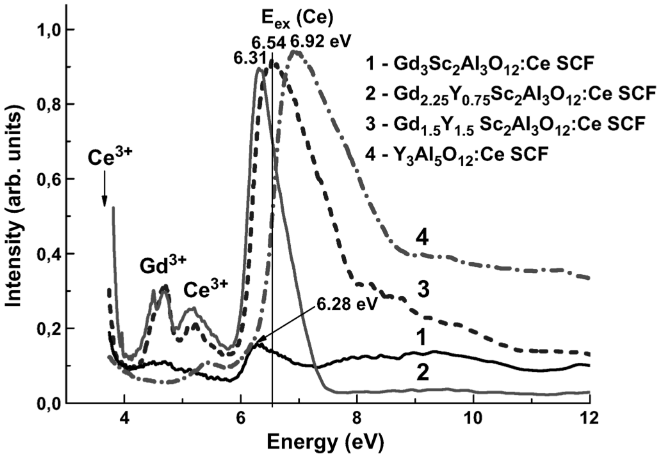


Fig. 6. Excitation spectra of Ce^{3+} emission at 8 K in $(Gd_{3-x}Y_x)Sc_2Al_3O_{12}$: Ce SCF with different Gd/Y ratios. $E_{ex}(Ce)$ values show the shift of 0.173 eV per one formula units of Y in Gd sites.

of the Ce^{3+} luminescence in YAG:Ce SCF (Fig. 6, curve 4), the main peak of excitation spectra of $Gd_3Sc_2Al_3O_{12}$: Ce SCF, corresponding to the energy of creation of an exciton bound with Ce^{3+}, is shifted in the low-energy range to 6.28 eV (Fig. 6, curve 1). We have also found that in $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF, the energy of creation of the exciton bound with the Ce^{3+} ions shows the high-energy shift of 0.173 eV per one formula unit of Y^{3+} ions in the positions of Gd^{3+} cations (Fig. 6).

IV. CONCLUSIONS

The single crystalline film (SCF) scintillators based on the Ce-doped multi-component $Gd_{3-x}(Y,Lu)_xSc_2Al_3O_{12}$ garnets with x values from 0 to 0.5, 0.75 and 1.5 were successfully crystallized by the LPE method onto GGG substrates from melt-solutions based on the $PbO - B_2O_3$ flux.

Of all the studied garnet compounds, the best light yield (LY) of luminescence under e-beam excitation and excitation by α-particles of Pu^{239} (5.15 MeV) source is observed in the $Gd_{3-x}Y_xSc_2Al_3O_{12}$: Ce SCF at $x = 0.5$–0.75.

We have also found the significantly large influence of Pb^{2+} flux related impurity on the LY of Ce^{3+} emission in $Gd_{3-x}(Y,Lu)_xSc_2Al_3O_{12}$ SCF, grown on the GGG substrates, in comparison with the YAG:Ce SCF analogue, grown by the LPE on the YAG substrates at relatively the same conditions [5]. This effect is caused by the larger lead contamination in SCFs of Gd-Y-Lu based garnets, grown onto GGG substrates, in comparison with YAG counterpart due to the relative larger dimension of the dodecahedral positions in these garnet hosts, where the Pb^{2+} ions are localized. Thus, it is desirable to use the lead-free fluxes for producing the SCF scintillators based on the multi-component garnet compounds to achieve their higher LY. Such a type of fluxes, namely BaO based fluxes, were successfully applied for producing the YAG:Ce and LuAG:Ce SCF scintillators with LY comparable with that for their crystal counterparts [7]. Therefore, we expect that using BaO based fluxes for growing SCF of multi-component garnets gives the possibility to estimate the real potential of the compounds under study for producing the scintillating screens.

REFERENCES

[1] T. Martin and A. Koch, "Recent development in X-ray imaging with micrometer spatial resolution," *J. Synchrotron Rad.*, vol. 13, pp. 180–194, 2006.

[2] K. Kamada, T. Endo, K. Tsutumi, J. Pejchal, M. Nikl, K. Tsutumi, Y. Fujimoto, A. Fukabori, and A. Yoshikawa, "Composition engineering in Ce doped $(Lu,Gd)_3(Ga,Al)_5O_{12}$ single crystal scintillators," *Cryst. Growth Des.*, vol. 11, pp. 4484–4490, 2011.

[3] M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B. P. Uberuaga, D. A. Andersson, K. J. McClellan, and C. R. Stanek, "Band gap engineering for shallow trap removal in $RE_3Al_5O_{12}$ garnets," *Phys. Rev. B*, vol. 84, p. 081102(R), 2011.

[4] Y. Zorenko and V. Gorbenko, "Growth peculiarities of the $R_3Al_5O_{12}$ ($R =$ Lu, Yb, Tb, Eu-Y) single crystalline film phosphors by liquid phase epitaxy," *Radiat. Meas.*, vol. 42, pp. 907–910, 2007.

[5] Y. Zorenko, J. A. Mares, P. Prusa, M. Nikl, V. Gorbenko, V. Savchyn, R. Kucerkova, and K. Nejezchleb, "Luminescence and scintillation characteristics of YAG:Ce single crystalline films and single crystals," *Radiat. Meas.*, vol. 45, pp. 389–391, 2010.

[6] Y. Zorenko, A. Voloshinovskii, V. Savchyn, T. Vozniak, M. Nikl, K. Nejezchleb, V. Mikhailin, V. Kolobanov, and D. Spassky, "Exciton and antisite defect-related luminescence in $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ garnets," *Phys. Stat. Sol. (b)*, vol. 244, pp. 2180–2189, 2007.

[7] M. Kucera, K. Nitsch, M. Kubova, N. Solovieva, M. Nikl, and J. A. Mares, "Ce-doped YAG and LuAG epitaxial films for scintillation detectors," *IEEE Trans. Nucl. Sci.*, vol. 55, no. 3, pp. 1201–1205, Jun. 2008.

IEEE Proof
Print Version