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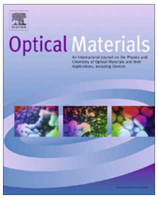

Composition engineering of single crystalline films based on the multicomponent garnet compounds

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ABSTRACT

The paper demonstrates our last achievement in development of the novel scintillating screens based on single crystalline films (SCF) of Ce doped multicomponent garnets using the Liquid Phase Epitaxy (LPE) method. We report in this work the optimized content and excellent scintillation properties of SCF of $Lu_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$, $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$ and $Tb_xGd_xAl_{5-y}Ga_yO_{12}$ garnet compounds grown by the LPE method from PbO—B_2O_3 based melt-solution onto $Gd_3Al_{2.5}Ga_{2.5}O_{12}$ and YAG substrates.

We also show that the $Tb_{1.5}Gd_{1.5}Al_{2.5}Ga_{2.5}O_{12}$:Ce SCF possess the highest light yield (LY) in comparison with all ever grown garnet SCF scintillators. Namely, the LY of these SCF exceeds by 3.8 and 1.85 times the LY values of the best samples of YAG:Ce and LuAG:Ce SCF scintillators, respectively. The SCF samples of the mentioned compounds show low thermoluminescence in the above room temperature range and relatively fast scintillation decay time $t_{1/e}$ in the 180–200 ns range.

1. Introduction

Development of microimaging technique with using X-ray or synchrotron radiation for application in the industry, materials science, biology and paleontology requires fabrication of the scintillating screens for visualization of X-ray images with high spatial resolution [1,2]. For this purpose, the visible emitting scintillating screens based on the thin (up to 20 μm) single crystal and single crystalline films of Ce doped $Y_3Al_5O_{12}$ (YAG) and $Lu_3Al_5O_{12}$ (LuAG) garnets grown by the Liquid Phase Epitaxy (LPE) method have been used for the first time, and the spatial resolution of the detector in the *micron range* has been achieved [2–4]. After that, following the demand of such an actual task, the single crystalline films of Eu^{3+}, Tb^{3+} doped $Gd_3Al_5O_{12}$ (GGG) and Sc^{3+} doped LuAG garnets [2,3,5], single Tb^{3+} and double Tb^{3+}, Ce^{3+} doped LSO orthosilicates [6–15] as well as Ce^{3+}, Tb^{3+} and Eu^{3+} doped $LuAlO_3$ (LuAP) and (Gd,Lu)AlO_3 (GLAP) perovskites [5,16–20] were also successfully developed in the last decade for microimaging using the LPE method.

Meanwhile, the possibility of obtaining the highest spatial resolution of X-ray images in the *submicron range* strongly requires development of new thin (a few μm) scintillating film screens with extremely high absorption ability of X-rays which is proportional to ρZ_{eff}^4, where ρ is the density and Z_{eff} is the effective atomic number of scintillators [1,2].

The multicomponent $(Lu,Gd,Tb)_3(Al,Ga)_5O_{12}$ garnets have higher density ($\rho = 6.7–6.8\ g/cm^3$) and effective atomic number (61–66) [21] as compared to the commonly used YAG, LuAG and GGG garnets for fabrication of SCF scintillators [2–5]. Therefore, the solid solutions of these garnets are also very promising materials for creation of SCF scintillators for visualization of X-ray images with higher (in the submicron range) spatial resolution. This conclusion is confirmed also by the results of our previous works [21–26] and works of other authors [27,28], which considered the growth of different types of multicomponent garnet compounds by the LPE method and their luminescent and scintillation properties.

Recently, the two novel concepts at creation of a detector for microtomography have been also proposed [16,20]. The first concept is based on using the complex multilayer-film scintillator

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with separate pathway for registration of the optical signal from each film layer scintillator and final overlapping of the images coming from the different parts of the complex scintillator [16]. Using such multilayer-film scintillators one can significantly improve the contrast and resolution of images even in the submicron range. The second concept of creation of a detector for microtomography is connected with engineering “K-edge of X-ray absorption” multilayer-film scintillators using the solid solution of oxide compounds containing the Lu, Gd and Tb ions [16,20]. In such a way the absorption ability of the multilayer scintillator can be significantly improved in the 20–65 eV range due to the significant broadening of the edge of X-ray absorption in such multicomponent materials [16,20]. Such two novel concepts also demand the creation of different sets of heavy and efficient SCF scintillators which can be deposited onto the *same non-luminescent or luminescent substrates*.

The bulk crystals of the $Lu_{3-x}Gd_xAl_{5-x}Ga_xO_{12}$ and $Gd_3Al_{5-x}Ga_xO_{12}$ multicomponent garnet compounds are now on the top list of scintillators with very high (up to 50,000 Photon/MeV) light yield (LY) [31]. For this reason, these garnets are also very promising materials for creation of the scintillation screens with high absorption ability for X-rays [25–28]. With the aim of increasing the energy transfer efficiency from the host of multicomponent garnets to the Ce^{3+} ions, the $Lu_{3-x}Tb_x$ Al_5O_{12} and $Gd_{3-x}Tb_xAl_5O_{12}$ SCFs were also crystallized by the LPE method and their luminescent and scintillation properties were briefly reported as well [29,30]. The Ga co-doped analogs of these garnets can be also considered as very interesting matrixes for this purpose. At the same time, the possibility of growth of the efficient SCF scintillators on the basis of the mentioned garnets by the LPE method needs the technological and experimental evidence. For this reason, in our work we present also the results of research directed on creation of the new types of scintillating screens based on the SCF of Ce doped $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$, $Tb_3Al_{5-y}Ga_yO_{12}$ and $Tb_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$ multicomponent garnets by the LPE method.

For composition engineering of garnet compounds, we apply in our work the combination of the “Ce^{3+} 5d-level positioning” [31] and “band-gap engineering” strategies [32–34] in the SCF of Ce^{3+} doped $Lu_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$, $Gd_3Al_{5-y}Ga_yO_{12}$, $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$, $Tb_3Al_{5-y}Ga_yO_{12}$ and $Tb_xGd_xAl_{5-y}$ Ga_yO_{12} multicomponent garnets using: (i) the substitution by Gd^{3+} and Tb^{3+} cations of the dodecahedral sites of $Lu_3Al_5O_{15}$ garnet lattice at the concentration **x** = 1–3.0; (ii) the substitution by Ga^{3+} ions of the Al^{3+} cations both in the tetrahedral and octahedral positions of the garnet host in the concentration range **y** = 1.5–3.0. We have also expected enhancement of the energy transfer possibility from the host to the Ce^{3+} ions in $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$, $Tb_3Al_{5-y}Ga_yO_{12}$ and $Tb_xGd_xAl_{5-y}Ga_yO_{12}$ multicomponent garnet compounds using sublattices of Gd^{3+} and Tb^{3+} cations at x = 1.5–3.0 and y = 1.5–2.5.

2. LPE growth of $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$:Ce and $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$:Ce SCF

Due to the relatively large variety of the lattice constants (Fig. 1), the SCF of **$Lu_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$:Ce**, $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$:Ce, and $Tb_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$:Ce garnets were grown from supercooling melt solutions using PbO—B_2O_3 flux onto $Gd_3Al_{2.5}Ga_{2.5}O_{12}$ (GAGG) substrates with a lattice constant of 12.228 Å and onto YAG substrates with a lattice constant of 12.0 Å. Namely, four sets of optical quality perfect $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$:Ce, $Tb_3Al_{5-y}Ga_yO_{12}$:Ce and $Tb_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$:Ce SCF samples with x and y values changing in the x = 0–3 and 1.5–3.0 ranges, respectively, were successfully crystallized onto YAG and GAGG and YAG and substrates with the (1 1 0) and (1 0 0) orientations, respectively, using traditional PbO—B_2O_3 flux (Fig. 1 and Table 1), which enables to obtain very high structural quality of SCF scintillators for microimaging applications [3,6,19,20].

Typically SCF grown from PbO based flux contain Pb^{2+} ions (usually with the concentration below 30 ppm [35]), which act as luminescent and trapping centers and decrease their LY. Therefore using the BaO based flux can be also considered for producing SCF scintillators because the components of this flux do not contaminate the film and have very small negative effect on scintillation properties as in the case of using the PbO flux [25–28,35,36]. Unfortunately, very high viscosity of this flux leads to formation of different macroscopic defects and strongly increases the roughness of SCF surface [26,35,36]. For this reason, the SCF scintillator screens for application in microimaging are produced now only from PbO based flux [6,8,19,20].

The composition of SCF samples was determined using a JEOL JSM-820 electronic microscope equipped with EDX micro-analyzer with IXRF 500 and LN2 Eumex detectors. From microanalysis of the content of $Lu_{3-x}Tb_xAl_{5-y}Ga_yO_{12}$:Ce and $Tb_{3-x}Gd_xAl_{5-y}Ga_yO_{12}$:Ce SCFs we have also found that the segregation coefficient of Gd, Tb, Ga and Ce ions in LuAG based host at LPE growth onto YAG and GAGG substrates from PbO—B_2O_3 flux is equal to about 0.85–0.9; 0.95–1.1, 0.65–0.75 and 0.003–0.008, respectively.

The XRD measurements (spectrometer DRON 4, CuK_α X-ray source) were used for characterization of the structural quality of

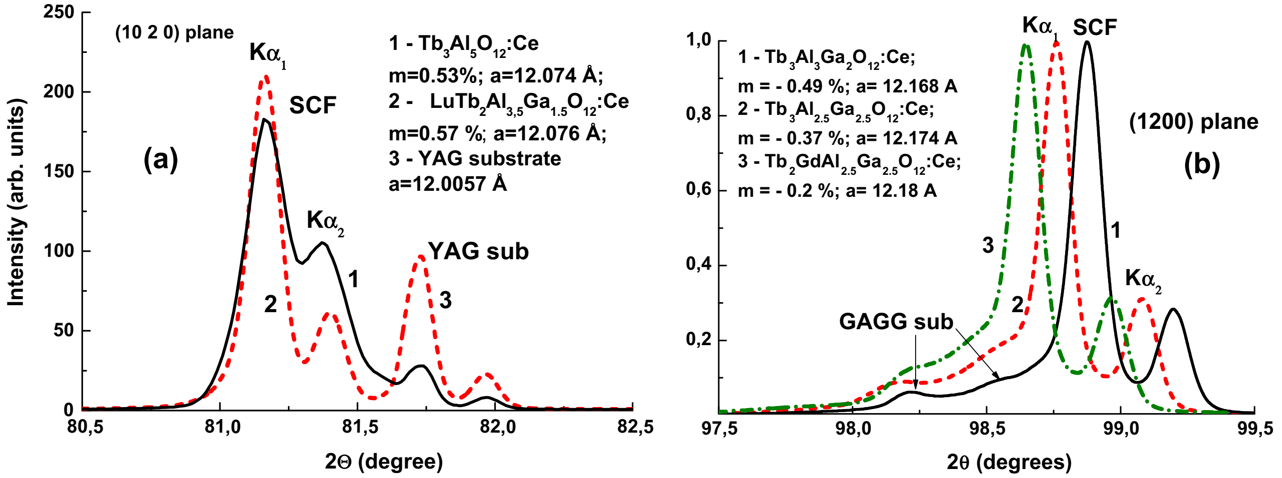

Fig. 1. (a) XRD pattern of (8 8 0) planes of the $Lu_{3-x}Tb_xAl_5O_{12}$ SCFs with different x values: x = 0 (1), 1.0 (2), 2.0 (4), 3.0 (5), grown onto YAG substrate (3) with (1 1 0) orientation; (b) XRD pattern of (1 2 0 0) planes of the $Tb_{3-x}Gd_xAl_{5-x}$ Ga_yO_{12}:Ce SCFs at x = 1.0 (3) and 0 (2, 3) and y = 2 (1) and 2.5 (2, 3) grown onto GAGG substrates with (1 0 0) orientation.

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