Study of optical and luminescent properties of the epitaxial garnet films doped with Ce$^{3+}$

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Abstract. Ce-doped (Pb,Gd)$_3$(Al,Ga)$_5$O$_{12}$ and Ce-doped (Bi,Gd)$_3$(Al,Ga)$_5$O$_{12}$ single crystalline garnet films were grown using liquid-phase epitaxy method from supercooled PbO–B$_2$O$_3$– and Bi$_2$O$_3$–B$_2$O$_3$– based melt solutions on substrates from Gd$_3$Ga$_5$O$_{12}$, Gd$_3$(Al,Ga)$_5$O$_{12}$ and Y$_3$Ga$_5$O$_{12}$ single crystals. Optical absorption, photo- and cathodoluminescent and scintillation properties of the films were studied. Ce-doped (Pb,Gd)$_3$(Al,Ga)$_5$O$_{12}$ and Ce-doped (Bi,Gd)$_3$(Al,Ga)$_5$O$_{12}$ garnet films can be used as a fast phosphor and scintillation screens.

1. Introduction

Epitaxial garnet films doped with Ce$^{3+}$ ions are characterized by superior scintillation properties, which allows their application as a fast phosphor in the design of an electron-optical converter of the PIF-01 type, as well as a scintillation screen for X-ray images visualizing [1,2]. A study of the cathodoluminescence decay kinetics of the Ce-doped (Pb,Gd)$_3$(Al,Ga)$_5$O$_{12}$ films under excitation by a picosecond electron beam in the PIF-01 tube have shown that the cathodoluminescence decay times of the Pb$_{0.92}$Ce$_{0.07}$Gd$_{0.01}$Al$_{4.29}$Ga$_{0.71}$O$_{12}$ film were 22 ns (20%) for the fast component and 67 ns (80%) for the slow component [1]. The films can be grown by liquid-phase epitaxy (LPE) from supercooled melt solutions on single crystal substrates However, the distinctive feature of the method is incorporation of impurity ions from the melt solution into the films during liquid-phase synthesis. In this work, the synthesis was carried out on Gd$_3$Ga$_5$O$_{12}$, Gd$_3$(Al,Ga)$_5$O$_{12}$ and Y$_3$Ga$_5$O$_{12}$ substrates from melt solutions based on PbO – B$_2$O$_3$ and Bi$_2$O$_3$ – B$_2$O$_3$, Pb$^{2+}$ and Bi$^{3+}$, respectively, were incorporated into the films as the impurity ions in these cases.

The goal of the study was to compare the optical and luminescent properties of Ce-doped Gd$_3$(Al,Ga)$_5$O$_{12}$ epitaxial films grown from Pb- or Bi-containing melt solutions.
2. Experimental methods

Ce-doped (Pb,Gd)₃(Al,Ga)₅O₁₂ and Ce-doped (Bi,Gd)₃(Al,Ga)₅O₁₂ garnet films were grown using conventional isothermal LPE method; a schematic drawing of the set-up is given in [3]. The quantitative chemical analysis of the grown films was performed with an electron-ion scanning microscope Quanta 3 D FEG.

To simplify the spectroscopic studies, we did not remove the film from the back side of the substrate. Transmission spectra of the films were measured using Perkin Elmer Lambda 900 spectrophotometer in 200–550 nm wavelength range at room temperature. The optical density D was derived from the transmission using the formula D = [ln(T/T₀)], where Tₘ is the transmission spectrum of the substrate and T is the transmission spectrum of the substrate with grown films on both sides. For the analysis of the absorption spectra of the films, we used the normalized optical density D/2h. It allows to compare the intensity of the absorption bands of the films with different thickness.

The luminescence and excitation spectra were measured at 300 K using conventional laboratory set-ups for luminescence spectroscopy described elsewhere [4].

3. Results and discussion

Ce-doped (Pb,Gd)₃(Al,Ga)₅O₁₂ and Ce-doped (Bi,Gd)₃(Al,Ga)₅O₁₂ single crystalline garnet films were grown using liquid-phase epitaxy method from supercooled PbO–B₂O₃ and Bi₂O₃–B₂O₃ based melt solutions. Gd₃Ga₅O₁₂, Gd₃(Al,Ga)₅O₁₂ and Y₃Ga₅O₁₂ single crystals were used as substrates. The data on the composition of the melt solutions and thickness of investigated films are shown in Table 1. All of the grown films from supercooled PbO–B₂O₃ based melt solution with gadolinium oxide C(Gd₂O₃) concentration of 0.4 mol%, C(CeO₂) = 0.2 mol%, and C(Al₂O₃) = 4.5 mol% in the mixture were greenish - yellow. The grown films from supercooled Bi₂O₃–B₂O₃ based melt solution with C(Gd₂O₃) = 0.4 mol%, C(CeO₂) = 0.5 mol%, and C(Al₂O₃) = 5 mol% in the mixture were yellow.

| Series number | Melt solute | C(Gd₂O₃) (mol %) | C(CeO₂) (mol %) | C(Al₂O₃) (mol %) | Film number | Film composition / substrate | Thickness h (µm) |
|---------------|-------------|------------------|------------------|------------------|-------------|-----------------------------|-----------------|
| I             | PbO – B₂O₃  | 0.4              | 0.2              | 4.5              | I-1         | Pb₀.₀₁Ce₀.₀₂Gd₂₋₂₉Al₁₋₁₋₃Ga₁₋₂₋₃₀₁₂ / Gd₃Ga₅O₁₂ | 43.3            |
|               |             |                  |                  |                  | I-2         | Pb₀.₀₁Ce₀.₀₂Gd₂₋₂₉Al₁₋₁₋₃Ga₁₋₂₋₃₀₁₂ / Gd₃(Al,Ga)₅O₁₂ | 22.4            |
| II            | Bi₂O₃ – B₂O₃| 0.4              | 0.5              | 5.0              | II-1        | Bi₁₋₀₋₁₄Ce₀.₁₄Gd₂₋₂₉₄₋₉₅₄₋₉₉₉₉₀₀₁₂ / Y₃Ga₅O₁₂ | 14.2            |

SEM images of films I-1 and II-1 are presented in Figure 1. As it follows from the images the surface of the I-1 film was rough with bulges (Figure 1,a). The surface of the II-1 film was also rough and consisted of intergrowths of single crystalline grains oriented both in the direction of the [111] axis and in the plane of the substrate (Figure 1,b). It should be noted that films grown on a Gd₃(Al,Ga)₅O₁₂ substrates from PbO–B₂O₃ based melt solution had better surface quality compared to films grown on Gd₃Ga₅O₁₂ substrates.

Studies of the optical absorption of the grown films demonstrated the presence of absorption bands related to Pb²⁺, Gd³⁺, Bi³⁺ and Ce³⁺ ions (Figure 2). The broad band in the range from 260 to 290 nm observed in the absorption of the I-1 film, corresponds to ¹S₀ → ³P₁ electronic transition of Pb²⁺ (6s²)
ions (Figure 2,a) [5]. The narrow band at 273 nm corresponds to the $^8S_{7/2} \rightarrow ^6I_{17/2}$ transition of Gd$^{3+}$ ions [6]. The presence of this band in absorption spectra indicates its shift in the film in comparison to that in the substrate. Such shift suggest a difference in the lattice parameters of the grown film and the substrate, namely, the film is under tensile stress relative to the substrate [7]. Two broad absorption bands in the range from 328 to 348 nm and from 400 to 500 nm correspond to the 4f-5d Ce$^{3+}$ interconfiguration electronic transitions [8]. In the absorption spectrum of the II-1 film, multiple absorption bands were observed as well. The broad absorption band in the range from 253 to 308 nm corresponds to electronic transition $^1S_0 \rightarrow ^3P_1$ of Bi$^{3+}$ (6s$^2$) ions [9]. The narrow band with a maximum at 313 nm corresponds to the $^8S_{7/2} \rightarrow ^8P_{7/2}$ transition of Gd$^{3+}$ ions and two broad absorption bands in the range from 320 to 350 nm and from 415 to 525 nm corresponds to 4f–5d$_2$ and 5d$_1$ transitions of Ce$^{3+}$ ions, respectively.

A red shift of the Ce (5d$_1$) absorption band maxima by 25 nm was observed in the II-1 film in comparison to that in the I-1 film (Figure 2,b). It should be noted that optical losses of the II-1 film are less than in the I-1.

Figure 1. Electron images of the surface of Pb$_{0.01}$Ce$_{0.02}$Gd$_{2.97}$Al$_{3.13}$Ga$_{1.87}$O$_{12}$ film I-1 (marker – 10 μm, magnification 8000×) (a) and Bi$_{0.14}$Ce$_{0.14}$Gd$_{2.72}$Al$_{4.99}$Ga$_{0.01}$O$_{12}$ film II-1 (marker – 20 μm, magnification 4000×) (b).

Figure 2. Normalized optical density spectra of film II-1 (1) and film I-1(2) in the range from 200 to 550 nm (a) and from 300 to 550 nm (b), $T = 300$ K; the numbers identify the films as referenced in Table 1.
Photoluminescence and photoluminescence excitation spectra of the grown films are presented in Figures 3-5. Photoluminescence spectrum of film I-1 is characterized by a broad non-elementary band peaking at 570 nm (2.17 eV), which corresponds to the radiative 5d-4f transitions within Ce$^{3+}$ ions (Figure 3). The photoluminescence excitation spectrum (Figure 4) is characterized by the presence of two broad bands peaking at 448 nm (2.77 eV) and 343 nm (3.61 eV), which are due to 4f-5d$_{1,2}$ transitions in Ce$^{3+}$ ions, and a band at 278 nm (4.46 eV), which is related to Gd$^{3+}$ and/or Pb$^{2+}$ ions (electronic transitions $S_{7/2} \rightarrow 6I_{15/2,7/2}$ in Gd$^{3+}$ ions and $S_0 \rightarrow 3P_1$ in Pb$^{2+}$ ions). The presence of the latter band indicates energy transfer from the Gd$^{3+}$ and/or Pb$^{2+}$ to the Ce$^{3+}$ ions. All of these bands are also observed in the absorption spectrum of this film (Figure 2). The broad band in the range from 200 to 250 nm was ascribed to the superposition of several bands related to the 4f-5d$_{3-5}$ transitions in the Ce$^{3+}$ with a defect-related band and, probably, charge-transfer transitions involving the Ce$^{4+}$ ions.

The maximum of the Ce$^{3+}$ luminescence band shifts by 13 nm (from 570 to 583 nm) to the long wavelength region in the II-1 film in comparison to that in the I-1 film (Figure 3).

Three bands were observed in the photoluminescence excitation spectrum of the II-1 film (Figure 5). The bands at 465 nm (2.67 eV) and 336 nm (3.69 eV) were ascribed to electron transitions from the 4f to 5d$_1$ and 5d$_2$ states of the Ce$^{3+}$ ions. The broad band with a maximum at 279 nm (4.44 eV) corresponds to electronic transitions in Gd$^{3+}$ and Bi$^{3+}$ ions. All of these bands are also observed in the absorption spectrum of this film (Figure 2). The presence of the latter band (at $\lambda = 279$ nm) is indicative of energy transfer from the Gd$^{3+}$ and Bi$^{3+}$ ions to the Ce$^{3+}$ ions. Therefore, Bi$^{3+}$ impurity ions form additional channel of energy transfer to the emission centers.

According to our previous study [4] the I-1 film shows the highest pulsed cathodoluminescence yield (43,100 photons/MeV) and scintillation yield values under $^{133}$Ba excitation (20,000 photons/MeV) among all grown films. The pulsed cathodoluminescence decay times of the I-1 film were 1.8 (1%), 24 (25%), and 60 ns (74%), and the scintillation decay times were 3.9 (7%) and 43.6 ns (93%). The scintillation light yield of I-2 film was also measured under excitation by 5.5 MeV alpha particles from $^{241}$Am as 18 - 21% of the bulk Gd$_3$(Al,Ga)$_5$O$_{12}$:Ce and for I-1 film was less than 30%.

Under excitation by 662 keV photons from $^{137}$Cs, the I-2 film had scintillation decay times and partial intensities of 28 ns (~74%) and 81 ns (~16%), respectively and the I-1 film had values of 51 ns (~86%) and 12 ns (~14%). Thus, the I-2 film had the best scintillation decay times and partial intensities values with comparatively the same scintillation light yield. As can be seen from the above studies the longest component decay times of films grown from supercooled PbO–B$_2$O$_3$- based melt solution with C(Gd$_2$O$_3$) = 0.4 mol%, C(CeO$_2$) = 0.2 mol%, and C(Al$_2$O$_3$) = 4.5 mol% in the mixture was below 100 ns, characterizing these films as a rapid scintillator, which can be used in X-ray scintillators for different applications. The scintillation properties of the films grown from supercooled Bi$_2$O$_3$–B$_2$O$_3$- based melt solution are being investigated.
4. Conclusions
Ce-doped (Pb,Gd)$_3$(Al,Ga)$_5$O$_{12}$ and Ce-doped (Bi,Gd)$_3$(Al,Ga)$_5$O$_{12}$ garnet films were grown using LPE method from supercooled PbO–B$_2$O$_3$- and Bi$_2$O$_3$–B$_2$O$_3$-based melt solutions.

The absorption bands of Pb$^{2+}$, Gd$^{3+}$, Bi$^{3+}$ and Ce$^{3+}$ ions were observed in the optical absorption spectra of the grown films. A red shift of the Ce (5d$_1$) absorption band maxima by 25 nm was observed in the II-1 film in comparison to that in the I-1 film.

The photoluminescence band related to emission of Ce$^{3+}$ ions is peaking at 570 nm for the films grown from PbO–B$_2$O$_3$-based melt solutions, while the maximum shifts by 13 nm to long wavelength region for the films grown from Bi$_2$O$_3$–B$_2$O$_3$-based melt solutions. The photoluminescence excitation spectra demonstrate energy transfer from the Gd$^{3+}$ and/or Pb$^{2+}$ ions and from the Gd$^{3+}$ and Bi$^{3+}$ ions to the Ce$^{3+}$ ions in these films.

The Pb$_{0.01}$Ce$_{0.02}$Gd$_{2.97}$Al$_{3.14}$Ga$_{1.86}$O$_{12}$ film (I-2) grown on a Gd$_3$(Al,Ga)$_5$O$_{12}$ substrate demonstrated better scintillation performance in comparison to the Pb$_{0.01}$Ce$_{0.02}$Gd$_{2.97}$Al$_{3.13}$Ga$_{1.87}$O$_{12}$ film (I-1) grown on a Gd$_3$Ga$_5$O$_{12}$ substrate.

Based on the results of study of the optical and luminescent properties of Ce-doped (Pb,Gd)$_3$(Al,Ga)$_5$O$_{12}$ and Ce-doped (Bi,Gd)$_3$(Al,Ga)$_5$O$_{12}$ epitaxial films, it was concluded that they are promising for application as phosphors and scintillation screens.

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