Phosphors based on Ce:(Pb,Gd)₃(Al,Ga)₅O₁₂ epitaxial films: synthesis, optical properties, application

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Abstract: Ce-doped (Pb,Gd)₃(Al,Ga)₅O₁₂ single crystalline garnet films were grown using liquid-phase epitaxy method from supercooled PbO-B₂O₃-based melt solutions on substrates from Gd₃Ga₅O₁₂ and Gd₁Al₂Ga₂₇O₃₅ single crystals. Optical absorption and photo- and cathodoluminescent properties of these epitaxial garnet films were studied. Ce-doped (Pb,Gd)₃(Al,Ga)₅O₁₂ garnet films can be used as a fast phosphor in the design of a PIF-01 electron-optical converter.

1. Introduction

Gadolinium - aluminum - gallium garnet doped with cerium ions (Ce:Gd₃Al₂Ga₅O₁₂, Ce:GAGG), is considered as a promising scintillation material among garnet crystals. Currently, 2-in. size Ce 1%-Gd₃Al₂Ga₂₇O₃₅ single crystal grown by Czochralski method shows a scintillation light yield approximately 58,000 photons/MeV [1]. The scintillation decay time (and its relative intensity) was 172 ns (88%) for the fast component in this crystal. The emission wavelength was 516 nm. Along with bulk single crystals, single crystalline films find their application as scintillation screens [2, 3]. Films can be grown by liquid-phase epitaxy (LPE) from supercooled melt solutions such as PbO - B₂O₃, B₂O₃ - B₂O₅ or BaO – B₂O₅ - BaF₂. The difference between epitaxial films and their bulk single crystal analogs is the presence of additional optical absorption, which is caused by impurity ions, which are introduced into the films from the melt solution and crucible material. For instance, the impurity ions in the epitaxial films grown from supercooled PbO-B₂O₃-based melt solutions are Pb⁺⁺, Pb⁺⁺⁺, Pt⁺⁺⁺ ions.

Cerium ions are the most common activator for scintillation detectors. The emission of Ce³⁺ arises due to an allowed 5d-4f electronic transition. As a result Ce doped scintillators are characterized by a high scintillation light yield and a fast decay time (tens of ns). The luminescence of the Ce³⁺ ion in the Gd₃Ga₅O₁₂ crystal at room temperature and atmospheric pressure is completely quenched due to the location of the 5d₁ level of Ce³⁺ in the conduction band [4, 5], but under high pressure [6] or with the partial substitution of Ga with Al in the Gd₃Ga₅O₁₂ host Ce³⁺ emission can be observed [7].
In this work we report the results of the study of the influence of Ga/Al ratio variation on optical absorption, photo- and cathodoluminescent properties of epitaxial films Ce:(Pb,Gd)₃(Al,Ga)₅O₁₂, grown by LPE. Our main goal is to obtain samples with a maximum photoluminescence intensity of Ce³⁺ ions and to investigate the applicability of epitaxial films as a fast phosphor in the design of a PIF-01 electron-optical converter.

2. Experimental methods
The epitaxial films Ce:(Pb,Gd)₃(Al,Ga)₅O₁₂, were grown with standard isothermal LPE method. A schematic drawing of the set-up is given in the Figure 1. Before the growth of the films, the melt solution was homogenized in the platinum crucible for at least four hours.

The films were characterized by X-ray diffraction on a Bruker D8 Discover A25 Da Vinsi Design X-ray diffractometer (CuKα radiation). 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 250–550 nm wavelength range at room temperature. The optical density D was derived from the transmission using the formula 
\[ D = \ln(T_{sf}/T_{fsf}) \]
where Tₛ is the transmission spectrum of the substrate and Tₛₚ 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. Photoluminescence spectra of the films were measured at 300 K in the 400–700 nm region at Eₑₓ = 165, 451 and 440 nm using specialized spectroscopic set-ups. The set-ups allowed to perform the measurements of luminescence and luminescence excitation spectra in UV and VUV spectral regions. A 150 W Xe lamp combined with monochromator MDR-206 was used as the excitation source in UV spectral region. The luminescence was detected using a 150 W deuterium discharge lamp Hamamatsu L1835 as an excitation source in VUV spectral region.

3. Results and discussions
Ce-doped (Pb,Gd)$_3$Al$_5$Ga$_{5-x}$O$_{12}$ single crystalline garnet films with $2 < x < 5$ were grown using LPE method from supercooled PbO–B$_2$O$_3$-based melt solutions at concentrations $C$(Gd$_2$O$_3$) = 0.2, 0.3, 0.4 and 0.5 mol %; $C$(Ce$_2$O$_3$) = 0.03, 0.2 and 0.3 mol % and $C$(Al$_2$O$_3$) from 2 to 5 mol % in the mixture on single crystal garnet substrates: Gd$_3$Ga$_5$O$_{12}$ (GGG) with the (111) orientation and Gd$_3$Al$_{12}$Ga$_{2-2x}$O$_{12}$ (GAGG) with the (320) orientation.

X-ray diffraction analysis showed that all films have a garnet type structure [8]. X-ray diffraction patterns obtained in the 0/2θ scan mode showed only strong 444 and 888 reflections from the films and the same weak reflections from its substrate, attenuated by the film. For example, for Pb$_{0.02}$Ce$_{0.02}$Gd$_{1.22}$Al$_{0.78}$O$_{12}$ film grown from a melt solution at concentrations of gadolinium oxides of 0.2 mol %, cerium – of 0.2 mol % and aluminum – of 2.2 mol %, the unit-cell parameters of the substrate $a_i == 12.3829$ Å and film $a_f = 12.269$ Å were determined from the peak positions (the relative lattice mismatch $(a_i - a_f)/a_f$ is 0.9%). The unit-cell parameter of the substrate agrees with JCPDS Powder Diffraction File data for GGG (card no. 76_2290). It was found that the unit-cell parameter decreases with the increasing of film thickness.

The profiles of the asymmetric 880 and 12.60 reflections indicate that the films were single crystalline and grew epitaxially on its substrates. SEM images of the surface of Ce:(Pb,Gd)$_3$Al$_{1-x}$Ga$_x$$_{5}$O$_{12}$ films at $0 \leq x < 5$ are shown in the Figure 2. The surface of the Ce:(Pb,Gd)$_3$Ga$_5$O$_{12}$ film is smooth. With the introduction of aluminum ions in the composition of the film lattice mismatch parameters of the film and substrate increases and the surface becomes rough, consisting of intergrowths of single crystalline grains oriented both in the direction of the [111] axis and in the plane of the substrate. With increasing of film thickness, surface smoothing occurs.

![Figure 2](image_url)

Figure 2. Electron images of the surface of films: a) - Pb$_{0.02}$Ce$_{0.03}$Gd$_{2.99}$Ga$_{5}$O$_{12}$; h = 3.6 μm (marker – 10 μm, magnification 5010$^4$); b) - Pb$_{0.01}$Ce$_{0.03}$Gd$_{2.94}$Al$_{1.27}$Ga$_{2.1}$O$_{12}$; h = 16.4 μm (marker – 50 μm, magnification 2000$^4$); c) - Pb$_{0.01}$Ce$_{0.05}$Gd$_{2.94}$Al$_{1.08}$Ga$_{1.94}$O$_{12}$; h = 33.8 μm, (marker – 50 μm, magnification 2000$^4$); d) - Pb$_{0.01}$Ce$_{0.02}$Gd$_{2.97}$Al$_{1.13}$Ga$_{1.87}$O$_{12}$; h = 43.3 μm, (marker – 10 μm, magnification 8000$^4$).

Study of the effect of the substitution of gallium ions with aluminum ions on optical absorption of cerium ions in the Ce:(Pb,Gd)$_3$Ga$_5$O$_{12}$ films was performed by measuring the transmission spectra (Figure 3). Two absorption bands in the range from 300 to 360 nm (level 5d$_2$) and from 390 to 550 nm (level 5d$_1$), corresponding to the parity allowed electronic transitions 4F($^5$D$_{5/2}$) - 5d$_1$ Ce$^{3+}$ ions were detected. These bands confirm the incorporation of cerium ions into the composition of the films.
Narrow absorption bands in the range from 240 to 313 nm, corresponding to electron transitions $^4S_{7/2}$ → $^4I_{15/2,7/2}$ Gd$^{3+}$ ions in the transmission spectra of GGG substrates were also observed.

The normalized optical density spectra are presented in Figure 3b. The absorption band in the range from 250 to 300 nm, corresponding, according to [9], to the $^1S_0 \rightarrow ^3P_1$ electronic transition in Pb$^{2+}$ (6s$^2$) ions were observed in the absorption spectra of films with thickness ≤ 32 μm. Two other broad absorption bands correspond to the 4f - 5d$_{1,2}$ Ce$^{3+}$ electronic transition. It was found that with the increase of C(AI$_2$O$_3$) from 2.1 to 5.0 mol % in the mixture at C(CeO$_2$) = 0.2 mol % and C(Gd$_2$O$_3$) = 0.2 mol %, the maxima of these two absorption bands shift in the following way. When the Al/Ga concentration ratio increases from 0.74 to 98.8 in the Ce:(Pb,Gd)$_3$Al$_x$Ga$_{3-x}$O$_{12}$ films (2.13 < x < 4.94), the shift of 4f - 5d$_1$ Ce$^{3+}$ absorption band maximum to longer wavelengths was 30 nm (from 436 to 466 nm).

**Figure 3.** a) - Transmission spectra of GGG substrates (curves 1 and 2) and samples of Ce:(Pb,Gd)$_3$Al$_x$Ga$_{3-x}$O$_{12}$ epitaxial films grown from melt solutions with a concentration in the charge C(CeO$_2$) = 0.2 mol %, C(Gd$_2$O$_3$) = 0.2 mol % and various concentrations of C(AI$_2$O$_3$) from 2.1 to 5.0 mol % indicated in the figure. b) - Spectral dependences of the normalized optical density D/2h on the wavelength of the same epitaxial films.

Analysis of the photoluminescence spectra under excitation at 451 (Figure 4a) and 440 nm (Figure 4b) Ce:(Pb,Gd)$_3$Al$_x$Ga$_{3-x}$O$_{12}$ epitaxial films grown from melt solutions with C(CeO$_2$) = 0.2 and 0.3 mol %, C(Gd$_2$O$_3$) = 0.2 mol % in the mixture and at the concentration variation of C(AI$_2$O$_3$) from 2.1 to 4.5 mol % showed that the films grown from melt solutions with C(AI$_2$O$_3$) = 2.9, 3.1, 4.0 and 4.5 mol % in the mixture had the highest photoluminescence intensity. A blue shift of the emission band maximum from 555 to 550 nm was detected with a decrease in the Al$^{3+}$ ion concentration from 3.14 to 2.13 in the film composition, which is consistent with the results obtained on single crystals of Ce:Gd$_3$(Ga,Al)$_5$O$_{12}$ (1 at. %) [10]. It was found that films grown from a melt solution with C(Gd$_2$O$_3$) = 0.4 mol %, C(CeO$_2$) = 0.2 mol % and C(AI$_2$O$_3$) = 4.5 mol % had the maximum photoluminescence intensity of Ce$^{3+}$ ions peaking at 555 and 532 nm under excitations at 440 (Figure 4b) and 165 nm (Figure 5a), respectively, at T = 300 K.

In the luminescence excitation spectra of Pb$_{0.8}$Ce$_{0.2}$Gd$_{2.96}$Al$_{1.14}$Ga$_{1.86}$O$_{12}$ film grown from melt solutions with C(CeO$_2$) = 0.2 mol %, C(Gd$_2$O$_3$) = 0.4 mol %, C(AI$_2$O$_3$) = 4.5 mol % (1) four pronounced bands were observed. The bands at 448 nm and 343 nm are ascribed to electron transitions from 4f to 5d$_1$ and 5d$_2$ levels of Ce$^{3+}$ ions. The band at 278 nm is a superposition of two bands related to $^1S_0 \rightarrow ^3P_1$ and $^3S_{7/2} \rightarrow ^3P_I$ in Pb$^{2+}$ and Gd$^{3+}$ ions, respectively. The latter indicates the energy transfer from Gd$^{3+}$ and/or Pb$^{2+}$ ions to Ce$^{3+}$ ion. Non-elementary broad peak at 215 nm can be ascribed to the superposition of several bands connected with 4f - 5d$_{3,5}$ transitions in Ce$^{3+}$ and also with charge transfer transitions involving Ce$^{4+}$ ions.
According to our previous study [11] the Pb$_{0.01}$Ce$_{0.03}$Gd$_{2.96}$Al$_{3.14}$Ga$_{1.86}$O$_{12}$ film shows the maximum value of the cathodoluminescence light yield of about 51,500 photons/MeV with fast decay times of the slow component of 61.0 ns (68%).

**Figure 4.** a) - Photoluminescence spectra upon excitation at 451 nm of epitaxial films grown from melt solutions with C(CeO$_2$) = 0.2 and 0.3 mol % and the concentration of C(Al$_2$O$_3$) in the mixture: 2.1 mol % (1), 3.3 mol % (2), 2.7 mol % (3), 2.3 mol % (4), 4.5 mol % (5), 3.1 mol % (6), 4.0 mol % (7), 2.9 mol % (8). b) - Photoluminescence spectra upon excitation at 440 nm of epitaxial films grown from melt solutions with C(Gd$_2$O$_3$) = 0.2 mol %, C(CeO$_2$) = 0.2 mol %, C(Al$_2$O$_3$) = 2.9, 3.1 mol % (1,2); C(Gd$_2$O$_3$) = 0.4 mol %, C(CeO$_2$) = 0.3 mol %. C(Al$_2$O$_3$) = 4.5 mol % (3,4); C(Gd$_2$O$_3$) = 0.3 mol %, C(CeO$_2$) = 0.2 mol %, C(Al$_2$O$_3$) = 4.5 mol % (5); C(Gd$_2$O$_3$) = 0.4 mol %, C(CeO$_2$) = 0.2 mol %, C(Al$_2$O$_3$) = 4.5 mol % (6). Spectra were measured at room temperature.

**Figure 5.** a) - Photoluminescence spectra upon excitation at 165 nm of epitaxial films grown from melt solutions with C(CeO$_2$) = 0.2 mol % and C(Gd$_2$O$_3$) = 0.4 mol %, C(Al$_2$O$_3$) = 4.5 mol % (1), C(Gd$_2$O$_3$) = 0.3 mol %, C(Al$_2$O$_3$) = 4.5 mol % (2), C(Gd$_2$O$_3$) = 0.2 mol %, C(Al$_2$O$_3$) = 4.0 mol % (3), T = 300 K and photoluminescence excitation spectrum of Pb$_{0.01}$Ce$_{0.03}$Gd$_{2.96}$Al$_{3.14}$Ga$_{1.86}$O$_{12}$ film grown from melt solutions with C(CeO$_2$) = 0.2 mol %, C(Gd$_2$O$_3$) = 0.4 mol %, C(Al$_2$O$_3$) = 4.5 mol % (1) upon emission at 540 nm, T = 80 K. b) - Photography of an electron-optical converter of the PIF-01 type with a Pb$_{0.02}$Ce$_{0.05}$Gd$_{2.93}$Al$_{4.25}$Ga$_{0.71}$O$_{12}$ film phosphor.
An analysis of the cathodoluminescence decay kinetics of the films under excitation by a picosecond electron beam in the PIF-01 tube. The cathodoluminescence decay times of the Pb$_{0.02}$Ce$_{0.0}$Gd$_{0.95}$Al$_{1.95}$Ga$_{0.05}$O$_{12}$ film grown from a melt solution $C$(Gd$_2$O$_3$) = 0.4 mol %, $C$(CeO$_2$) = 0.3 mol % and $C$(Al$_2$O$_3$) = 4.5 mol % were 22 ns (20%) for the fast component and 67 ns (80%) for the slow component [12]. Therefore, we conclude that the grown film with such parameters can be used as a fast phosphor in the design of a PIF-01 type electron-optical converter (Figure 5b).

4. Conclusions
The Ce-doped (Pb,Gd)$_3$Al$_4$Ga$_{3}$O$_{12}$ single crystalline garnet films with $2 < x < 5$ were grown using LPE method from supercooled PbO–B$_2$O$_3$-based melt solutions at concentrations $C$(Gd$_2$O$_3$) = 0.2, 0.3, 0.4 and 0.5 mol %; $C$(CeO$_2$) = 0.03, 0.2 and 0.3 mol % and $C$(Al$_2$O$_3$) from 2 to 5 mol % in the mixture. The shift 4f-5d Ce$^{3+}$ of absorption band maxima to longer wavelengths was 30 nm when the Al/Ga concentration ratio increases from 0.74 to 98.8. The film grown from the 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 % demonstrated the highest photoluminescence intensity of Ce$^{3+}$ ions at emission wavelengths 555 and 532 nm under excitations at 440 and 165 nm, respectively, at $T = 300$ K. The energy transfer from Gd$^{3+}$ and/or Pb$^{2+}$ ions to Ce$^{3+}$ ion was shown. The maximum value of the cathodoluminescence light yield of about 51,500 photons/MeV at the decay time of the slow component of 61.0 ns (68%) was obtained for Pb$_{0.02}$Ce$_{0.0}$Gd$_{0.96}$Al$_{1.95}$Ga$_{0.05}$O$_{12}$ film. A film with such parameters can be used as a fast phosphor in the design of a PIF-01 type electron-optical converter.

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