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Optical spectroscopy of Ce^{3+} ions in $Gd_3(Al_xGa_{1-x})_5O_{12}$ epitaxial films

N.V. Vasil'eva [a,*], D.A. Spassky [b,c], I.V. Randoshkin [a], E.M. Aleksanyan [c,d], S. Vielhauer [c], V.O. Sokolov [e], V.G. Plotnichenko [e,f], V.N. Kolobanov [g], A.V. Khakhalin [g]

[a] Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilov Street, Moscow 119991, Russia
[b] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Leninskie Gory 1(2), Moscow 119991, Russia
[c] Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia
[d] A. Alikhanyan National Science Laboratory, 2 Br. Alikhanyan Str., 0036 Yerevan, Armenia
[e] Fiber Optics Research Center, Russian Academy of Sciences, 38 Vavilov Street, Moscow 119333, Russia
[f] Moscow Institute of Physics and Technology, 9 Institutskii per., Dolgoprudny, Moscow Region, 141700, Russia
[g] Physics Department, Lomonosov Moscow State University, 1(2) Leninskie Gory, Moscow 119991, Russia

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ABSTRACT

Epitaxial films of Ce-doped $Gd_3(Al_xGa_{1-x})_5O_{12}$ with $x = 0.00$, 0.22, 0.31, 0.38 formula units were grown using liquid-phase epitaxy method, and their optical properties were studied. The emission of Ce^{3+} ions can be observed only when Al^{3+} ions are incorporated into the garnet structure, resulting in a shift of the 5d Ce^{3+} states from the conduction band to the bandgap. It is shown that the shift is caused by the cumulative effect of gradual low-energy shift of the lowest 5d level of Ce^{3+} and the raise of the garnet bandgap energy with increasing Al^{3+} concentration.

1. Introduction

Yttrium and lutetium garnets and perovskites doped with Ce^{3+} ions have been widely recognized as fast scintillators with high light yield [1 and references therein]. Further improvements of the scintillation properties of garnets resulted in the successful bandgap engineering with Ga-doping [2–4] and partial or complete substitution of the Lu and Y cations with Gd [5–7]. As a result, $Gd_3Al_2Ga_3O_{12}$:Ce^{3+} single crystals were grown with light yield up to 46,000 ph/MeV, energy resolution 4.6% and without changes in the material density compared to Lu-based compounds [7]. However, a variety of point defects, such as vacancies and antisite defects, exists in the as-grown garnet single crystals that worsen the scintillator's performance [8]. The presence of antisite defects is the inevitable consequence of the high melting temperature of bulk crystals grown from melt by the Czochralski method (e.g. $T_m = 1950$ °C for $Y_3Al_5O_{12}$). The substitution of single crystals with thick single crystalline films of garnets grown using liquid phase epitaxy method avoids the problem of creation of antisite defects. The method allows growing films with a scintillation performance not worse than that for single crystals [9]. Here we report on the growth, optical and luminescence characterization of Ce^{3+}-doped $Gd_3(Al_xGa_{1-x})_5O_{12}$ epitaxial films with $x = 0.00$, 0.22, 0.31, 0.38 formula units (f.u.).

2. Experimental

2.1. Growth of epitaxial films

The films were grown on <1 1 1>-oriented $Gd_3Ga_5O_{12}$ substrates using the isothermal liquid-phase epitaxy method. It was shown in [10] that $Gd_3Ga_5O_{12}$ single crystal films can be grown from supercooled $PbO–B_2O_3$ based melt solutions with gadolinium oxide ($C(Gd_2O_3)$) concentrations between 0.2 and 0.5 mol% in the mixture. In our experiments $C(Gd_2O_3)$ was 0.2 mol%. In Fig. 1, a fragment of the concentration triangle of the pseudoternary system $(Gd_2O_3 + CeO_2)–(Ga_2O_3 + Al_2O_3)–(PbO + B_2O_3)$ is given, marking the compositions of the melt solutions from which the epitaxial films were grown.

The melt solution was homogenized in the platinum crucible for at least four hours. The temperature of the melt solution was reduced stepwise to the growth temperature (T_g). For each step, the substrate, secured to a platinum holder, was immersed in the melt solution in a horizontal position for 5 min. The rotation speed of substrate during the growth was 50, 100 or 124 rpm, while the

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[*] Corresponding author at: 38 Vavilov Street, Moscow 119991, Russia. Tel.: +7 499 5038329, fax: +7 499 1350270.
E-mail addresses: natasha@myprism.ru, anton@aha.ru (N.V. Vasil'eva).

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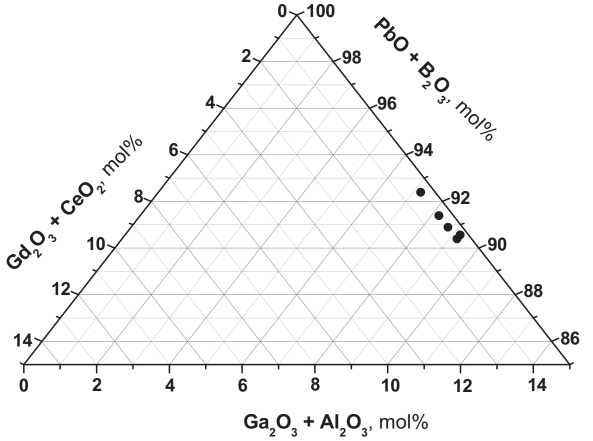

Fig. 1. Fragment of the concentration triangle of the pseudoternary ($Gd_2O_3 + CeO_2$)–($Ga_2O_3 + Al_2O_3$)–($PbO + B_2O_3$) system. The dark circles denote the compositions of melt solutions from which the epitaxial films were grown.

growth times were 5, 15, 30, 60, 70 and 80 min. Twenty nine samples (film–substrate–film) of size 10 mm × 15 mm were grown from five series of $PbO–B_2O_3$ melt solutions (2–9 epitaxial films in each of the series). The temperature range δT, including the saturation temperature (T_{sat}) and the supercooling degree $\Delta T = T_{sat} – T_g$ have been determined for all investigated melt solutions (see Table 1). The maximum thickness of the grown epitaxial films (h_{max}) and its highest growth rate (f_{max}) were determined as well. It should be noted that the growth rate and the value of supercooling degree are low compared to $Gd_3Ga_5O_{12}$ epitaxial films grown in similar conditions with $f_{max} = 0.55$ μm/min and $\Delta T_{max} = 84$ °C [10].

The films grown from the I series melt solution were transparent and yellowish. The films grown from the II–IV melt solutions series were yellowish green. During the growth of films from the V melt solution series we found two growth regions, as in an earlier study [10,11]. In the region with a relatively low supercooling degree $\Delta T < 20$ °C we obtained transparent and yellowish green films. In the region with a high supercooling degree 20 °C < ΔT < 101 °C the grown films were transparent and violet. A detailed list for the epitaxial film growth conditions are given in Table 2.

It was found that spontaneous crystallization takes place in the bulk of the melt solution simultaneously with the films growth. This leads to the appearance of garnet single crystals in the shape of tetragon-trioctahedrons with {2 1 1} faces (Fig. 2). The crystals appear on the melt surface and on the platinum crucible parts. For the V melt solution series spontaneous crystallization of garnet single crystals was observed at $\Delta T > 61$ °C. Therefore we performed the growth of films in the metastable region at $\Delta T < 61$ °C.

The spectral properties of epitaxial films are mainly determined by their chemical composition and distribution of chemical elements in the three sub-lattices of the garnet structure. Therefore, it is very important to determine the absolute values of the segregation coefficient of chemical elements between the liquid and solid phases for the given compound. We have determined the segregation coefficients of Ce^{3+}, Ga^{3+} and Al^{3+}, where

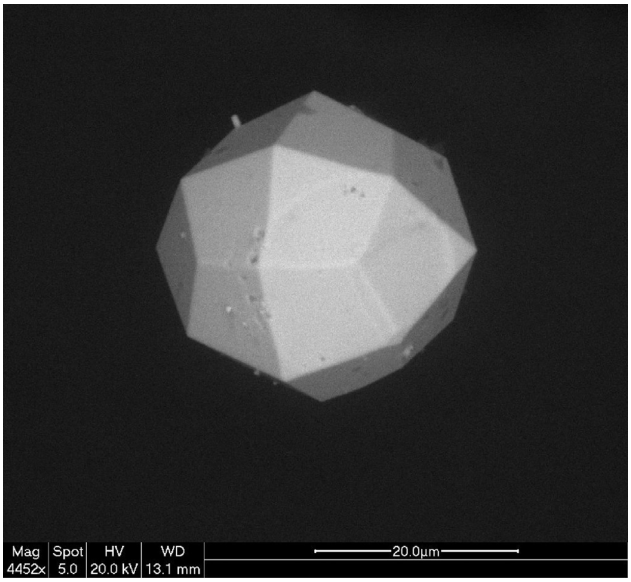

Fig. 2. Microphotography of spontaneously grown garnet single crystal of $Pb_{0.03}Ce_{0.08}Gd_{2.88}(Al_{0.25}Ga_{0.75})_5O_{12}$ composition grown from the II melt solutions series made by a scanning electron microscope.

$K_{Ce} = (X_{Ce}/3)$ film/([$2CeO_2$]/([$2CeO_2$] + [Gd_2O_3])) melt, $K_{Ga} = (X_{Ga}/5)$ film/([Ga_2O_3]/([Ga_2O_3] + [Al_2O_3])) melt, $K_{Al} = (X_{Al}/5)$ film/([Al_2O_3]/([Ga_2O_3] + [Al_2O_3])) melt, Here X_{Ce}, X_{Ga}, X_{Al} are the concentrations of corresponding chemical elements in formula units measured with the scanning electron microscope. The bracketed formulas of compounds describe the concentrations of corresponding oxides in molar percents.

The segregation coefficient of Ce^{3+} is 0.01 for the $Pb_{0.01}Ce_{0.02}Gd_{2.97}Ga_5O_{12}$ film. This coefficient increases from 0.02 to 0.03 with the increase of $C(Al_2O_3)$ from 1.0 to 2.0 mol% in the mixture. The segregation coefficient of Ga^{3+} is 1.0 for the $Pb_{0.01}Ce_{0.02}Gd_{2.97}Ga_5O_{12}$ film. This coefficient decreases from 0.89 to 0.79 with the increase of $C(Al_2O_3)$ from 1.0 to 2.0 mol% in the mixture. The segregation coefficient of Al^{3+} increases from 0.25 to 0.49 with the increase of $C(Al_2O_3)$ from 1.0 to 2.0 mol% in the mixture.

2.2. Experimental methods

The total thickness (2*h*) of the films grown on both sides of the substrate was determined by weighing the substrate prior to and after the epitaxial growth. We neglected the difference in the densities of the grown film and the substrate. To simplify the spectroscopic studies, we did not remove the film from the back side of the substrate.

The quantitative chemical analysis of the grown films was performed with an electron-ion scanning microscope Quanta 3 D FEG and a scanning electron microscope Quanta 600 FEG. Using of

Table 1
Composition of the melt solutions and growth parameters for $Gd_3(Al_xGa_{1-x})_5O_{12}$ epitaxial films.

Series number	$C(CeO_2)$ (mol%)	$C(Al_2O_3)$ (mol%)	Temperature range δT, (°C)	Supercooling degree ΔT, (°C) (min–max)	Thickness, h_{max} (μm)	Growth rate, f_{max} (μm/min)
I	0.2	–	987–966	4–82	10.8	0.30
II	0.2	1.0	939–932	6–34	17.8	0.32
III	0.2	1.5	940–934	4–40	19.2	0.32
IV	0.2	2.0	939–934	4–49	17.0	0.28
V	0.03	2.0	985–962	8–101	15.9	0.37