The study of energy transfer between Ce and Eu ions in $(Pb,Gd)_3(Al,Ga)_5O_{12}$:Ce,Eu epitaxial films

Natalia Vasil'eva[1], Dmitry Spassky[2,3], Sergey Omelkov[3], Dmitrii Vasil'ev[4], Victor Plotnichenko[4]

[1] Moscow Polytechnic University, Moscow, Russia
[2] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Moscow, Russia
[3] Institute of Physics, University of Tartu, Tartu, Estonia
[4] Dianov Fiber Optics Research Center, Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia

E-mail: natasha@myprism.ru

Introduction

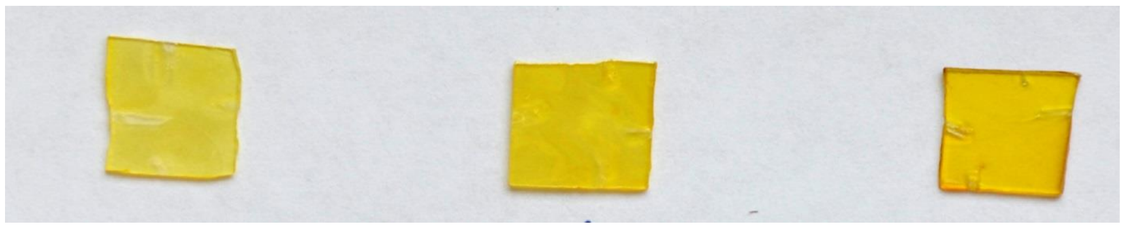
Rare-earth-doped garnets attract attention due to the possibility of their application as scintillators and phosphors. The incorporation of Eu^{3+} ions into garnets (e.g., YAG:Ce^{3+} nanoparticles) allows to increase the photoluminescence intensity in the red spectral region because of the presence of a narrow emission peak of Eu^{3+} ions at a wavelength of 610 nm [1]. A Ce^{3+} luminescence band in the green-yellow spectral region, and a weaker, narrow emission lines of Eu^{3+}, peaking in 580-720 nm region with the most intensive line at 708 nm, were also observed in the $Gd_3(Al,Ga)_5O_{12}$:Ce,Eu single crystal, however, no energy transfer from Ce to Eu was detected [2].

The objectives of this work were to grow epitaxial $(Pb,Gd)_3(Al,Ga)_5O_{12}:Ce^{3+},Eu^{3+}$ films and study optical and luminescence properties of these films.

Growth of epitaxy films

The films were grown with the isothermal liquid-phase epitaxy method on the (111)-oriented $Gd_3Ga_5O_{12}$ substrates [3]. The $Gd_3Ga_5O_{12}$ single crystal films can be grown from supercooled $PbO\text{-}B_2O_3$-based melt solutions with the concentration of gadolinium oxide ($C(Gd_2O_3)$) in the mixture from 0.2 to 0.5 mol%. In our experiments $C(Gd_2O_3)$ was 0.4 mol%, $C(CeO_2)$ = 0.2 mol% and $C(Eu_2O_3)$ = 0.05 mol%. Three samples (film-substrate-film) with sizes 10 mm x 15 mm were grown from $PbO\text{-}B_2O_3$ melt solutions. The maximum thickness of the grown epitaxial films h_{max} was 68 μm and its highest growth rate f_{max} was 0.75 μm/min.

Photography of the epitaxial films



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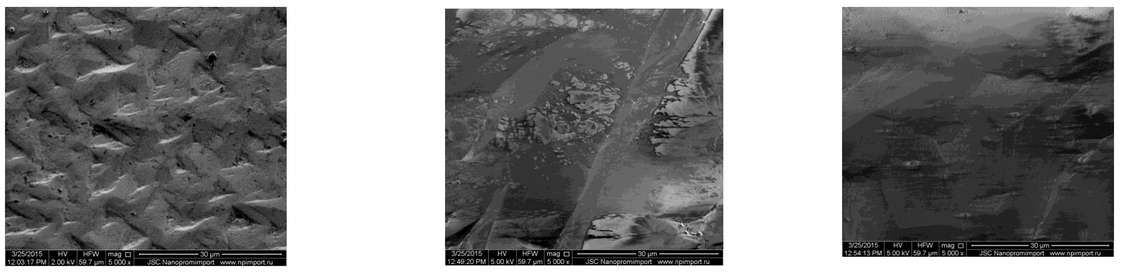

$Pb_{0.06}Ce_{0.05}Eu_{0.26}Gd_{2.63}Al_{3.14}Ga_{1.86}O_{12}$
h=11 μm, T_{sat}-T_g=36°C

$Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$
h=43 μm, T_{sat}-T_g=2°C

$Pb_{0.01}Ce_{0.05}Eu_{0.17}Gd_{2.77}Al_{3.14}Ga_{1.86}O_{12}$
h=68 μm, T_{sat}-T_g=14°C

Results and discussion

Absorption: The spectral dependence of normalized optical density is presented in Fig. 1,2. Two absorption bands were found in films, which are attributed to the electronic transitions from $4f$ ($^2F_{5/2,7/2}$) to $5d_1$ level at 443 nm and $5d_2$ level at range from 320 to 370 nm within Ce^{3+} ions. Another The absorption band is observed at a wavelength of 271 nm and corresponds to the Pb^{2+} ($6s^2, {}^1S_0$) → Pb^{2+} ($6s^1\,6p^1, {}^3P_1$) electronic transition. The observed narrow absorption bands at 392 - 394 nm and in the range 1700-3000 nm corresponds to the $^7F_0 \rightarrow {}^5L_6$ (former range) and $^7F_0 \rightarrow {}^7F_6$, $^7F_1 \rightarrow {}^7F_6$, $^7F_0 \rightarrow {}^7F_5$, $^7F_0 \rightarrow {}^7F_5$ (latter range) electronic transitions within Eu^{3+} ions.

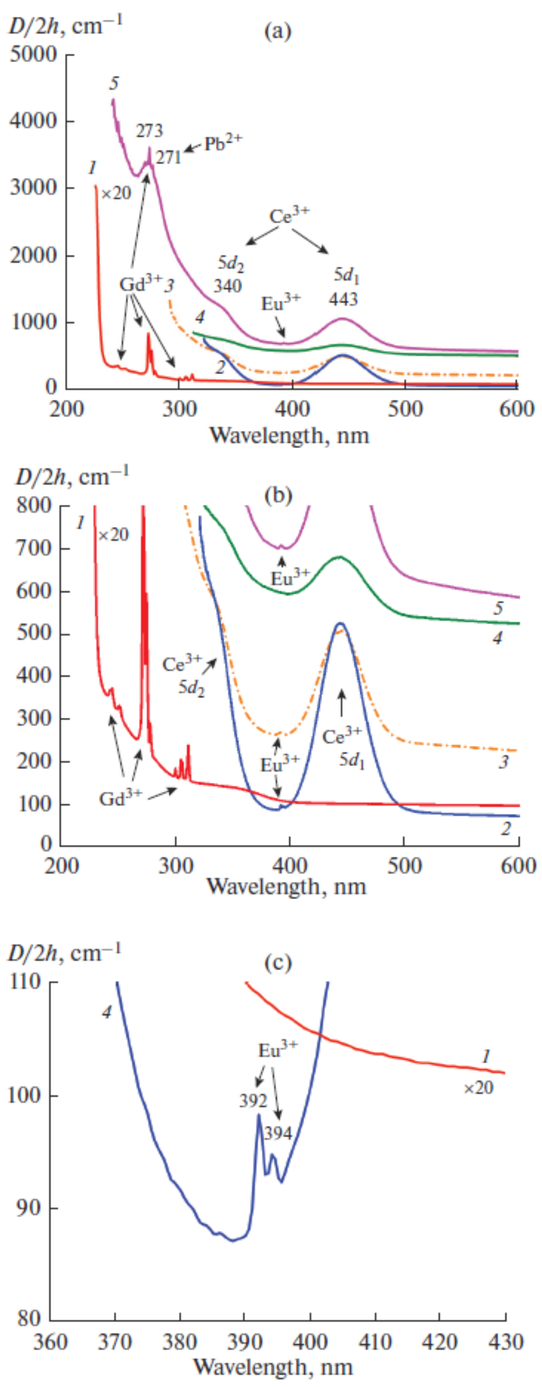

Fig. 1. 300-K normalized optical density spectra of the GGG substrate (1) and epitaxial films (2) $Pb_{0.01}Ce_{0.05}Eu_{0.17}Gd_{2.77}Al_{3.14}Ga_{1.86}O_{12}$, (3) $Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$, (4) $Pb_{0.01}Ce_{0.02}Gd_{2.97}Al_{3.13}Ga_{1.87}O_{12}$, (5) $Pb_{0.06}Ce_{0.05}Eu_{0.26}Gd_{2.63}Al_{3.14}Ga_{1.86}O_{12}$.

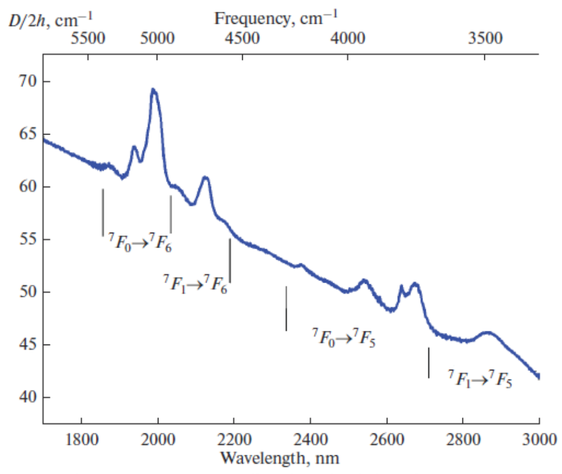

Fig. 2. 300-K normalized optical density spectrum of the epitaxial film $Pb_{0.01}Ce_{0.05}Eu_{0.17}Gd_{2.77}Al_{3.14}Ga_{1.86}O_{12}$.

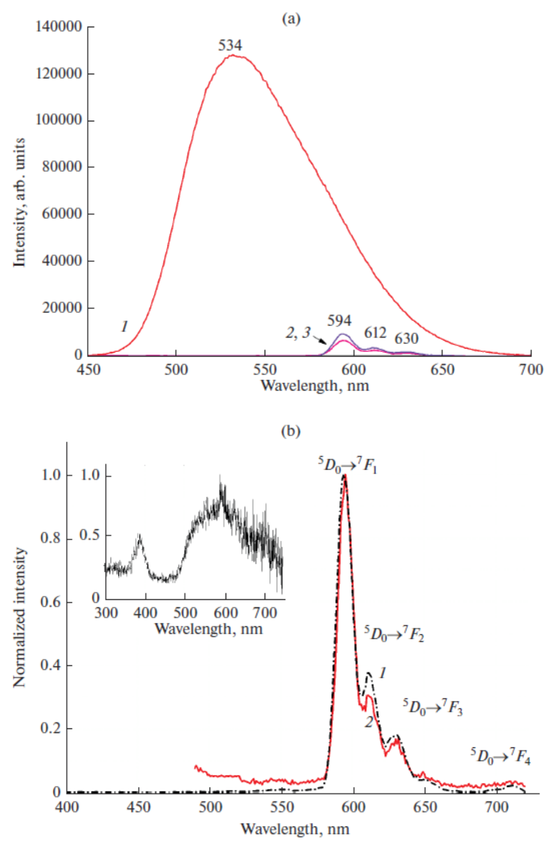

Fig. 3. 300-K photoluminescence spectra of the epitaxial films (a) (1) $Pb_{0.01}Ce_{0.02}Gd_{2.97}Al_{3.13}Ga_{1.87}O_{12}$, (2) $Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$, and (3) $Pb_{0.01}Ce_{0.05}Eu_{0.17}Gd_{2.77}Al_{3.14}Ga_{1.86}O_{12}$ under excitation at 165 nm and (b) $Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$ under excitation at (1) 165 nm and (2) 440 nm.
Inset: cathodoluminescence spectrum of $Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$ film measured in the time range 0-32 ns.

Luminescence: The co-doping of $(Pb,Gd)_3(Al,Ga)_5O_{12}:Ce^{3+}$ films with europium is accompanied by the appearance of narrow emission bands in the red spectral region, which arise due to Eu^{3+} $^5D_0 - {}^7F_J$ transitions. The co-doping also results in the quenching of cerium luminescence (Fig. 3). The effect can be ascribed to the non radiative energy losses as well as to the energy transfer from Ce^{3+} to Eu^{3+}. The conclusion if confirmed by the presence of Ce^{3+} excitation band at 463 nm in the excitation spectrum of Eu^{3+} emission (Fig. 4).

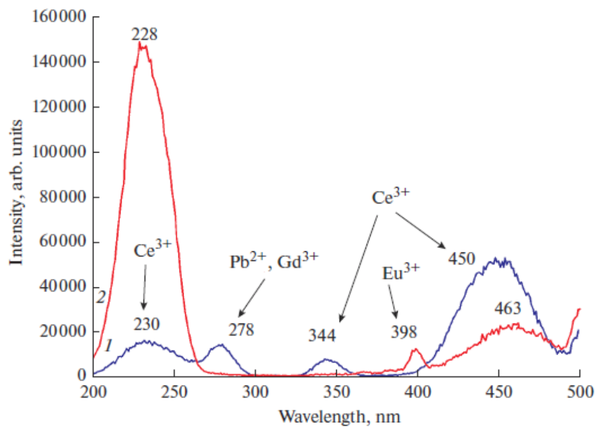

Fig. 4. 80-K photoluminescence excitation spectra of the epitaxial films (1) $Pb_{0.01}Ce_{0.02}Gd_{2.97}Al_{3.13}Ga_{1.87}O_{12}$ and (2) $Pb_{0.01}Ce_{0.04}Eu_{0.23}Gd_{2.72}Al_{3.14}Ga_{1.86}O_{12}$ at emission wavelengths of 540 and 600 nm, respectively.

Conclusions:

- Optical and luminescence properties of $(Pb,Gd)_3(Al,Ga)_5O_{12}$ epitaxial films co-doped with Eu and Ce were studied.
- Co-doping results in the appearance of narrow bands in the red spectral region attributed to emission from Eu^{3+} ions and quenching of Ce^{3+}-related emission.
- An energy transfer from Ce^{3+} to Eu^{3+} ions in $(Pb,Gd)_3(Al,Ga)_5O_{12}$ epitaxial films is shown.

References

1. Lee, J.-W., Lee, J.-H., Woo, E.-J., Ahn, H., Kim, J.-S., and Lee, Ch.-H., *Ind. Eng. Chem. Res.,* 2008, vol. 47, pp. 5994–6000.
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3. Vasil'eva N. V., Spassky D. A., Omelkov S. I., Plotnichenko V. G., and Vasil'ev D. A., *Inorganic Materials,* 2022, vol. 58, No. 2, pp. 165–171.