Growth and luminescence properties of Pr^{3+} -doped single crystalline films of garnets and perovskites

V. Gorbenko^{a,*}, Yu. Zorenko^a, V. Savchyn^a, T. Zorenko^a, A. Pedan^b, V. Shkliarskiy^b

^a Laboratory of Optoelectronic materials, Electronic Department, Ivan Franko National University of Lviv, Gen. Tarnavsky 107, 79017 Lviv, Ukraine

^b Lviv Polytechnic National University, S. Bandery, 12, 79013 Lviv, Ukraine

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ABSTRACT

Peculiarities of growth of single crystalline films (SCF) of Pr^{3+} doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ garnets and YAlO_3 and LuAlO_3 perovskites by the liquid phase epitaxy method from melt-solutions based on $\text{PbO-B}_2\text{O}_3$ flux as well as luminescent and scintillation properties of these SCFs were studied in this work. Dependence the intensity of the Pr^{3+} d-f and f-f-luminescence on the activator concentration and influence of Pb^{2+} flux dopant on the light yield of SCFs of the mentioned garnets and perovskites were analyzed.

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1. Introduction

Pr^{3+} ions show intensive and fast emission in the UV range in single crystal (SC) of Y–Lu–Al garnets and perovskites (Zhuravleva et al., 2007; Pejchal et al., 2009). The single crystalline films (SCF) of these compounds can be also applied as cathodoluminescent (CL) screen (Volzenskaja et al., 1988; Hrytskiv et al., 2007), and scintillating screens for high-resolution 2D-imaging (Zorenko et al., 2009). This work is dedicated to growth by the liquid phase epitaxy (LPE) method and detailed studying the luminescence and scintillation properties of Pr^{3+} doped SCF of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) garnets, and YAlO_3 (YAP) and LuAlO_3 (LuAP) perovskites. The following main features of the Pr^{3+} luminescence in these SCF are considered in this work: (i) dependence of intensity of the d-f and f-f- Pr^{3+} luminescence in Y–Lu–Al garnets and perovskites on the activator concentration; (ii) influence of flux contamination on the light yield (LY) of the Pr^{3+} luminescence in these SCF with respect to SCs (Pejchal et al., 2009) and Ce-doped SCF analogues (Zorenko et al., 2007) of the same content.

2. SCF growth and experimental techniques

The Pr^{3+} doped YAG and LuAG and YAP and LuAP SCFs were grown by LPE methods from melt-solution (MS) based on $\text{PbO-B}_2\text{O}_3$ flux on YAG and YAP substrates, respectively. The conditions of growth of these SCF are summarized in Table 1.

The R_1 – R_3 molar ratios are determined by the following quantities of MS: the solubility and kinematics properties of the flux (R_1); the garnet or perovskite phases for crystallization (R_2); the temperature of saturation of MS and range of growth temperatures (R_3). The values of molar ratio R_3 and R_4 (Pr_2O_3 content in MS) directly influences the LY of SCFs of garnets and perovskites (Fig. 1). Namely, we determined the optimum ranges of concentrations in MS of SCF-forming components $R_3 = 0.027$ – 0.031 (Fig. 1a) and $R_4 = 0.055$ – 0.065 (Fig. 1b), at which the highest LY of these SCFs is achieved (Table 1).

The CL spectra and LY of CL of Pr-doped SCF phosphors were measured at 300 K with a set-up based on a DMR-4 monochromator and a FEU-106 PMT under pulsed e-beam excitation (9 KeV, 100 μA) with a pulse duration of 2 μs and a frequency of 3–30 Hz. The LY of the radioluminescence (RL) of SCFs were measured in the UV and visible ranges using a detector based on FEU-100 and FEU-110 PMTs with maxima sensitivity ranges of 250–3 nm and 450 nm, respectively, and a multi-channel single-photon counting system working in the time interval 0.5 μs under excitation by α -particles of Pu^{239} sources (5.15 MeV). The decay kinetics of Pr^{3+} luminescence were measured at 300 K in the time interval 0–200 ns under excitation by synchrotron radiation with a pulse duration of 0.126 ns at Superlumi station (HASYLAB, DESY).

3. Experimental results and discussion

The Pr^{3+} ions in YAG:Pr and LuAG:Pr SCF show the intensive and fast emission in the 290–450 nm range with the main maxima at 323

* Corresponding author. Tel.: +380 97 4629746; fax: +380 322 448585.

E-mail address: vgorbenko@inbox.ru (V. Gorbenko).

Table 1

Conditions of growth of Pr-doped (Y,Lu)AG and (Y,Lu)AP SCF.

Conditions of growth	YAG:Pr	LuAG:Pr	YAP:Pr	LuAP:Pr
$R_1 = [\text{PbO}]/[\text{B}_2\text{O}_3]$	12	12	11.8	11.8
$R_2 = [\text{Y}_2\text{O}_3(\text{Lu}_2\text{O}_3)]/[\text{Al}_2\text{O}_3]$	0.28	0.22	0.98	0.96
$R_3 = \Sigma R_2\text{O}_3/[\text{PbO} + \text{B}_2\text{O}_3]$	0.028	0.031	0.027	0.031
$R_4 = [\text{Pr}_2\text{O}_3]/[\Sigma R_2\text{O}_3]$	0.0015–0.1	0.031–0.084	0.01–0.104	0.01–0.105
Temperature of growth, °C	970–995	980–995	980–1000	990–1010
Substrate rotation, rev/min	100	100	100	100
SCF growth rate, $\mu\text{m}/\text{min}$	0.4–1.5	0.22–1.16	0.5–1.0	0.15–1.0
Thickness of SCF, μm	7–34	4–32	2.5–27	2.9–34

and 305 nm and a decay time of 13 and 17 ns, respectively, caused by the $5d^14f^1 \rightarrow 4f^2(^3\text{H}_4, ^3\text{H}_5, ^3\text{H}_6, ^3\text{F}_{3(4)})$ transition of Pr^{3+} ions (Fig. 2a). These transitions in YAP:Pr and LuAP:Pr SCF yield fast emission in the 235–325 nm range with the most intensive bands peaked at 240 and 250 nm and a decay time of 7.8 and 8 ns, respectively (Fig. 2b). The sharp-line emission bands in the visible range in Pr-doped SCF of garnets and perovskites, peaked at 487, 501 and 563 nm as well as 609–620, 638 and 663 nm with decay time in the μs range, are related to transitions from the $^3\text{P}_0$ and $^1\text{D}_2$ levels of the $4f^2$ shell to the $^3\text{H}_{4,5,6}$ levels of the ground state of Pr^{3+} ions.

The ratio of intensities of the d-f/f-f luminescence depends on oxide host and is substantially large in SCF of Pr-doped garnets (Fig. 2a). Namely, the content of the visible f-f emission in LuAG:Pr SCF is lower than that in YAG:Pr SCF (curves 1 and 2, respectively). In opposite to SCF of Pr-doped garnets, the intensity of the fast d-f emission in the CL spectra of YAP:Pr and LuAP:Pr SCF is notable lower than that of the f-f emission (Fig. 2b, curve 1 and 2, respectively). The ratio of intensities of the d-f/f-f luminescence decreases with raising the Pr content both in SCF of garnets and perovskites (Fig. 3 and Table 3).

The LY of YAG:Pr and LuAG:Pr SCF in the UV range is significantly lower (by 2.2–2.4 times) than that of their SC analogues (Table 2). These data contradict with the results of investigations of the LY of Ce-doped YAG and LuAG SCF, emitting in the visible range, where the comparable LY of SCF and their SC analogues occurs (Zorenko et al., 2007). The main reason for lower LY of Pr^{3+} -doped SCF of garnets in comparison with bulk SC analogues is the strong quenching influence of Pb^{2+} flux dopant. Therefore, we can conclude that the significantly larger influence of Pb^{2+} ions on the Pr^{3+} emission in the UV range occurs in YAG:Pr and LuAG:Pr SCF in comparison with the influence of this dopant on the Ce^{3+} emission in the visible range in Ce-doped SCF of these garnets.

We observed also acceleration of the decay kinetics of the Pr^{3+} luminescence in YAG:Pr and LuAG:Pr SCF in comparison with their SC analogues. The decay curve for both SCF is widely non-exponential and can be characterized by a mean decay time of 13 and 17 ns, respectively (Fig. 1a, insert), which is different from the lifetime of a 17.5 and 20 ns, respectively in SC of these garnets (Pejchal et al., 2009). Such a shortening of the decay time of the Pr^{3+} luminescence in YAG:Pr and LuAG:Pr SCF is caused by the

Fig. 1. (a) – dependence of LY of CL (1) and RL (2) under excitation by Pu^{239} sources of LuAG:Pr SCF on concentration of Pr_2O_3 in MS; (b) – dependence of LY of RL in series of LuAG:Pr SCF obtained from MS with different R_3 values on growth temperature.

Fig. 2. CL spectra and decay kinetics (insets) of Pr^{3+} luminescence in YAG:Pr (1a), LuAG:Pr (2a), YAP:Pr (1b) and LuAP:Pr (2b) SCF at 300 K.

Fig. 3. CL spectra of LuAG:Pr (a) and YAP:Pr (b) SCF at 300 K grown from MS with a Pr_2O_3 oxide content of 3.0–3.1 (1) and 8.6–10 mol % (2).

energy transfer from Pr^{3+} ions to Pb^{2+} -related centers (Gorbenko et al., 2009).

Similar consideration can be applied for comparison of the LY of YAP:Pr and LuAP:Pr SCF and their SC analogues. Due to the influence of Pb^{2+} dopant, the LY of YAP:Pr and LuAP:Pr SCF in the UV range is lower by 1.6–2.0 times than that of YAP:Pr SC (Table 1). At the same time, the LY of Pr-doped SCF and SC of perovskites is significantly lower (by 3.4–6.7 times) in comparison with the SCF of Pr-doped garnets.

The second reason for reducing the LY of Pr^{3+} -doped SCF of garnets and perovskites in comparison with the LY of Ce^{3+} -doped analogues of these compounds (Table 2) is the presence of the f-f luminescence of Pr^{3+} ions in the visible range, which with respect to the intensive d-f-emission in the UV range plays a role of competing channel for dissipation of the excitation energy. We show that in Pr-doped SCF of garnets and perovskites the cooperative processes of excitation of the Pr^{3+} luminescence are realized (Fig. 3). For (Y,Lu)AG:Pr and SCF these processes consist in creating

Table 2

Relative LY of RL of the Pr-doped (Y–Lu)AG and (Y–Lu)AP SCFs in UV and visible ranges in comparison with YAP:Ce SC and YAG:Ce SCF standard samples under excitation by α -particles of Pu^{239} (5.15 MeV) source.

Compounds	LY in UV range, %	LY in visible range, %
YAP:Ce SC	100	171
YAG:Ce SCF	12.5	100 (12 200 Ph/MeV)
YAG:Pr SCF	36.0	39.0
LuAG:Pr SCF	33.5	27.5
YAG:Pr SC	81.0	67.5
LuAG:Pr SC	80.0	78.5
YAP:Pr SCF	12.0	10.0
LuAP:Pr SCF	15.0	10.0
YAP:Pr SC	24.0	26.0

Table 3

Concentration dependence of relative LY (in %) of d-f and f-f luminescence in YAG:Pr and LuAG:Pr SCF.

SCF content	Concentration of Pr_2O_3 in MS, mol. %	LY of CL, %	
		d-f (300–450 nm)	f-f (450–750 nm)
YAG:Pr	5.0	88.3	11.7
	7.6	81.1	18.9
LuAG:Pr	3.1	88.2	11.8
	8.6	82.5	17.5

by one quantum of the d-f luminescence in the UV range (304–310 nm) two quanta of the f-f emission in the visible (609–620 nm) range (Volzenskaja et al., 1987). This process schematically can be presented as

Particularly, contribution of the f-f luminescence to the total LY of CL of LuAG:Pr and YAG:Pr SCF at the optimal value $R_4 = 6$ mol% amounts to 14.8 and 14.5%, respectively (Table 3).

The cooperative processes of excitation of the f-f luminescence of Pr^{3+} ions in YAP:Pr and LuAP:Pr SCF are more efficient than that in SCF of garnets. For the mentioned perovskites these processes are presented in Wojtowicz et al., 2006 as

i.e. one quantum of the d-f luminescence (235–239 nm) in UV range creates two quanta of the f-f luminescence in the visible range (480 nm). The efficiency of this process substantially increases with raising the Pr^{3+} content, therefore the dominant emission YAP:Pr and LuAP:Pr SCF in the range of optimal content of Pr_2O_3 oxide in MS of 5.5–6.5 mol% is the f-f luminescence of Pr^{3+} ions. This is the main cause of low scintillation efficiency of Pr^{3+} -doped SC and SCF of these perovskites in comparison with garnet analogues (Table 2).

In conclusion, we show in this work that the UV-emitting phosphors based on single crystalline films (SCF) of Pr^{3+} -doped YAG and LuAG garnets and YAP and LuAP perovskites can be crystallized by the LPE method from melt-solution (MS) based on the $\text{PbO-B}_2\text{O}_3$ flux on YAG and YAP substrates, respectively. We found the optimal molar ratios of the SCF-forming components $R_3 = 0.027$ – 0.031 and Pr_2O_3 oxide $R_4 = 0.055$ – 0.065 in MS at which the highest LY of these SCF in the UV spectral range is achieved.

We also show that the LY of YAG:Pr and LuAG:Pr and YAP:Pr and LuAP:Pr SCFs under high-energy excitation is less by 2.2–2.4 and 1.6–2.0 times, respectively, than the LY of their single crystal (SCs) analogues. The reason for such a decrease of the LY of these SCFs phosphors is very effective quenching of the Pr^{3+} luminescence in the UV range by the Pb^{2+} flux dopant in SCFs of garnets and perovskites.

We found that in Pr-doped SC and SCF of garnets and perovskites there take place the cooperative processes of excitation of the f-f luminescence of Pr^{3+} ions in the visible range from the $^1\text{D}_2$ states (garnets) and $^3\text{P}_0$ states (perovskites) by quanta of the d-f luminescence in the UV range with energy 4.07–3.99 and 5.27–5.18 eV, respectively. The efficiency of these processes increase with rising the Pr^{3+} content and is significantly larger in perovskites than in garnets.

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