Luminescence of Pb^{2+} ions in YAG:Pb single-crystalline films

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Luminescence of Pb^{2+} ions in YAG:Pb single-crystalline films (SCF) with different lead content in the range of 0.01–0.3 at% was investigated by means of cathodoluminescence, time-resolved emission/excitation spectra and luminescence decay kinetic under excitation by synchrotron radiation. The nature of Pb^{2+} ion-related emission bands in the UV

and visible ranges and their prevailing excitation mechanism are considered. Strong mixing of the $^1\text{P}_1$ excited states of Pb^{2+} ions and the conduction-band states of the YAG host was found. A scheme of energy levels of Pb^{2+} center in YAG and LuAG is presented.

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1 Introduction Heavy ns^2 -ion (e.g. Bi^{3+} , Pb^{2+}) luminescence in complex oxides usually consists of emission bands in the UV and visible (VIS) ranges [1–6]. Recently, the structure of the photoluminescence and excitation spectra, as well as the decay kinetics of Bi^{3+} and Pb^{2+} ion emission in the UV and VIS ranges in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG), $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) garnet hosts have been reported and analyzed in [7, 8]. At the same time, significant ambiguities in interpretation of the nature of the Bi- and Pb-related UV and VIS emission bands in the mentioned works stimulate us to study in detail the Bi^{3+} and Pb^{2+} luminescence in the aluminum garnet hosts.

From 2003 we started the study of the Pb^{2+} and Bi^{3+} ns^2 -ions luminescence in single-crystalline films (SCF) of oxides of different structural types that were grown by liquid-phase epitaxy (LPE) from Pb- or Bi-containing fluxes. The LPE method enables to change the concentration of Pb^{2+} and Bi^{3+} ions in a wide (10^{-4} – 10^{-1} at%) range that is quite sufficient for both scientific investigations and practical applications regarding the creation of tunable cathodoluminescent screens with emission in the UV and blue spectral ranges [4, 5]. In our previous works, we have considered the luminescence of Bi^{3+} ions in YAG:Bi SCF [9, 10] and luminescence of Pb^{2+} ions in Al_2O_3 [11] and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) SCF [12–15]. In this paper we report the results of an in-

vestigation concerning the luminescence of YAG:Pb SCF with different lead content using the time-resolved luminescence methods under excitation by synchrotron radiation (SR). In comparison with the isostructural LuAG, the YAG compound is characterized by a somewhat larger crystal field strength at the dodecahedral sites of the garnet lattice [16] and a smaller forbidden band gap [15].

2 Samples preparation and experimental technique The YAG:Pb SCF with a thickness of 18–47 μm were grown in LOM, Lviv University by LPE from melt-solution based on PbO – B_2O_3 oxide flux on YAG substrates. The concentration of Pb^{2+} ions in the 0.01–0.3 at% range in YAG:Pb SCF varied as $1/T_g$, where T_g is the growth temperature (see Table 1). The content of lead ions in SCF was determined by using a DS-130 Akashi micro-analyzer.

It should be mentioned that due to their very large ionic radius (1.29 Å for the 8-fold coordination) [17], the Pb^{2+} are localized exclusively in the dodecahedral {c}-sites of Y^{3+} or rare-earth (RE) cations in the garnet lattice. However, in contrast to Bi^{3+} , the Pb^{2+} ion is an aliovalent ion in the crystal structures of oxides of the group III metals. Compensation for their lower charge state at lead concentrations below 0.2 at% takes place at the expense of formation of Pt^{4+} – Pb^{2+} ions (the Pt ion appears in SCF due to chemical

reaction between the flux and the platinum crucible), whereas at the larger content of lead ions the compensation for their excess charge occurs already at the expense of formation of Pb²⁺–Pb⁴⁺ ion pairs [18]. Pt⁴⁺ and Pb⁴⁺ ions, due to their sizes (0.57 Å and 0.94 Å, respectively) [17] and the necessity of local compensation for the volume, are localized in the (a)- and {c}-sites of the Al³⁺ and Y³⁺ or RE cations, respectively [14].

The CL spectra of YAG:Pb SCF at 300 K were measured with a setup based on a SF-4A monochromator and a PMT FEU-100 under steady-state e-beam excitation (10 kV, 5 µA). The LY of CL was detected by the FDUK-2 photodiode in the spatial angle of 1 sr in comparison with standard YAG:Ce SCF sample with a LY of 250 µWt/sr. Time-resolved luminescence of YAG:Pb SCF was investigated at 10 K and 300 K at the Superlumi station (HASYLAB at DESY, Hamburg) under excitation by SR with an energy of 3.7–25 eV and pulse duration of 0.127 ns. The emission and excitation spectra were measured both in the integral regime and in the 1.2–6 ns and 150–200 ns time intervals (fast and slow components, respectively) in the limits of SR pulse regime with the repetition time of 200 ns. The decay kinetics of luminescence was measured in the time range of 0–200 ns at 10 K and 300 K. Emission spectra are not corrected for the spectral dependence of the detection part.

3 Experimental results and discussion CL spectra of YAG:Pb SCF at 300 K show typical luminescence of Pb²⁺ ions consisting of two bands in the UV and visible ranges [3–5, 11, 12, 15] with $\lambda_{\text{max}} = 375$ nm (3.3 eV) and 630 nm (1.97 eV), respectively (Fig. 1). Increasing the concentration of Pb²⁺ ions from 0.035 at% to 0.3 at% by decreasing the growth temperature (Fig. 1) results in a substantial decrease in the intensity of the UV band and an increase of the intensity of the visible band (curves 1–3 in

Figure 1 Dependence of CL spectra of YAG:Pb SCF on concentration of Pb²⁺ ions as a function of SCF growth temperature ($\sim 1/T_g$) (see Table 1).

Table 1 Dependence of maximum (λ_{max}) of the UV luminescence, as well as absolute and relative light yield (LY) of CL on concentration of Pb²⁺ ions in series of YAG:Pb SCFs.

T_g (°C)	lead content in SCF (at%)	λ_{max} (nm)	LY (µWt/sr)	LY (%)
859	0.035	375	20	100
850	0.085	378	12	60
816	0.3	386	8.3	41.6

Fig. 1, respectively). It should be noted that the shape of the short-wavelength tail of the band of the UV luminescence of Pb²⁺ ions in Fig. 2, curves 2 and 3, is distorted to some extent due to an overlap with absorption bands that are probably formed by the charge transfer transitions (CTT) O²⁻ → Pb⁴⁺ with $E_{\text{max}} = 4.2$ eV (295 nm) [12, 18], since the Pb²⁺–Pb⁴⁺ ion pairs can already arise to achieve local charge compensation at higher (0.085–0.3 at%) content of lead ions. Aggregation of Pb ions to still larger aggregates (Suzuku-like phases) has been considered to explain emissions in the red part of spectra in the lead-doped alkali halides [19]. As a result of all the above-mentioned processes the intensity of the UV band decreases and its

Figure 2 Luminescence spectra of YAG:Pb SCF with a lead ion content of 0.085 (a), 0.035 (b) and >0.01 at% (b3), respectively, at 10 K (1, b3) and 300 K (2) under excitation by SR with $E = 20$ eV (1, 2) and 6.76 eV (b3).

maximum is shifted towards the long-wavelengths range to 386 nm (Fig. 1, curve 3, Table 1). The light yield of the CL of YAG:Pb SCF (0.3 at%) being decreased by 2.5 times in comparison with YAG:Pb SCF (0.035 at%) (Table 1).

Since the intensities of the bands in the UV and visible spectral ranges have substantially different dependences on the concentration of lead ions, it is possible to draw the conclusion that they belong to the different types of Pb^{2+} -containing centers. In particular, the UV luminescence of YAG:Pb SCF, which predominates at small concentrations of lead ions, is caused by single Pb^{2+} ions or pairs of Pb^{2+} – Pt^{4+} ions (see also [7, 10, 14]), while the dominant luminescence in the visible range is most probably caused by more complex Pb^{2+} -containing centers. This conclusion has been confirmed by the time-resolved luminescence spectroscopy of Pb^{2+} ions YAG:Pb SCF under excitation by SR.

Emission spectra of YAG:Pb SCF with substantially different content of lead ions 0.085 (a), 0.035 (1b, 2b) and less than 0.01 at% (3b) are shown in Fig. 2. Under excitation by SR with $E = 20$ eV in the region of YAG interband transitions ($E_g = 8.0$ eV) the luminescence spectra of YAG:Pb SCF (below 0.01 at%) at 10 K (Fig. 2b, curve 3) present the superposition of the following emission bands: 1) band of self-trapped excitons (STE) with $\lambda_{\text{max}} = 260$ nm; 2) band of excitons localized around Pb ions (LE(Pb) centers) with $\lambda_{\text{max}} = 292$ nm; 3) two complex bands in the UV and visible ranges that are typical for the luminescence of Pb^{2+} ions in all SCF oxides of different structural types [15]. It can be tentatively suggested that the observed two UV bands are the superposition of two components A_x and A_T with $\lambda_{\text{max}} = 332$ – 338 and 395 – 406 nm, respectively, belonging to radiative transitions from trigonal (X) and tetragonal (T) minima of $^3\text{P}_{1,0}$ triplet relaxed excited states (RES) of Pb^{2+} single ions arising due to the Jahn–Teller effect. The emission bands peaked at 495–496, 604–627 and 777 nm that become most visible for the lead content of 0.035 at% and 0.085 at%, may belong to different types of Pb^{2+} -based complex centers. An increase of lead ion concentration in YAG:Pb SCF results in quenching of STE and LE(Pb) emission and an increase of luminescence yield of Pb^{2+} -based centers in the UV and VIS ranges (curves 1 in Fig. 2a and b, respectively). At increasing the temperature from 10 K to 300 K the intensity of both emission bands of Pb^{2+} ions substantially decreases (curves 2 in Fig. 2b and a, respectively).

The excitation spectra of YAG:Pb SCF luminescence in the UV and visible ranges are shown in Fig. 3. The sharp peak at 6.74 eV in the excitation spectrum of luminescence at 330 nm (curve 1) corresponds to the energy of formation of LE(Pb) centers [14, 15]. The emission of these centers is also excited in the band with $E_g = 7.985$ eV at the onset of YAG interband transitions. The structure of the excitation spectrum of UV emission of YAG:Pb SCF (curve 1) in the YAG transparency region also contains the doublet band with $E_{\text{max}} = 4.55$ eV and 4.61 eV (A-band) and the band with $E_{\text{max}} = 5.195$ eV (B-band) that corre-

Figure 3 Excitation spectra of luminescence of Pb^{2+} -based centers in YAG:Pb (0.035 at%) SCF in the UV (330 nm (1) and 390 nm (2)) and visible (620 nm (3)) ranges.

spond to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ and $^3\text{P}_2$ transitions of Pb^{2+} ions, respectively, as well as a low-intensity band with $E_{\text{max}} = 5.6$ eV. Meanwhile, a characteristic feature of the excitation spectrum of the UV emission in YAG:Pb SCF in comparison with the iso-structural analogue LuAG:Pb SCF [12, 14] is location of C-bands ($^1\text{S}_0 \rightarrow ^1\text{P}_1$ transitions) and D-bands (CCT of ligand-metal type) directly in the range of fundamental absorption of this garnet. For instance, the C-band in LuAG:Pb SCF and in some alkali halides lies ~ 1.5 eV higher than the A-band [14]; i.e., in YAG:Pb SCF this band should have maximum approximately at 6.05 eV (Fig. 3). At the same time, due to the larger YAG crystal field strength and smaller forbidden band gap with respect to LuAG (8.0 eV and 8.15 eV, respectively [15, 16]), the excitation spectrum of the UV emission of YAG:Pb SCF at 390 nm at 10 K does not show a spectrally separated C-band, but contains a shoulder at 6.84 eV and two intensive bands with $E_{\text{max}} = 7.15$ eV and 7.735 eV in the exciton absorption range (Fig. 3, curve 2) that are close to the energy of relaxed excited states (RES) of STE in YAG [15]. This is evidence of significant mixing of $^1\text{P}_1$ excited states of Pb^{2+} ions and states of conduction band (CB) bottom, formed by 4d + 5s-levels of Y^{3+} ions [20].

Excitation of the YAG:Pb SCF emission in the visible (620 nm) range (Fig. 3, curve 3) takes place mainly in the dominating band with $E_{\text{max}} = 5.62$ eV that corresponds to $\text{Pb}^{2+} \rightarrow \text{Pb}^{3+} + e$ photoionization transition and the bands with $E_{\text{max}} = 7.25$ eV and 7.765 eV in the exciton range that coincide with the position of the analogous bands in the excitation spectra of the UV emission of Pb^{2+} ions (Fig. 3, curve 2). Thus, excitation of the Pb-based centers emission in the visible range in YAG:Pb SCF takes place predominantly via the ionization of Pb^{2+} ions and creation of localized excitons (LE). Such LE, probably, are formed by

Figure 4 Luminescence decay kinetics of YAG:Pb SCF in the emission band of LE(Pb) centers (290 nm) (1) and Pb²⁺-based centers in the UV (330 nm) (2) and visible (620 nm) (3) ranges, respectively, under excitation by SR with $E = 6.765$ (1), 4.55 (2) and 5.43 eV (3).

the electrons from CB and the holes localized near lead ions as a result of relocation of the electronic density between Pb³⁺ ions and neighboring oxygen ligands.

The luminescence decay kinetics of YAG:Pb SCF in the bands of LE(Pb) centers (curve 1) as well as the Pb²⁺-based centers in the UV (curve 2) and visible (curve 3) ranges is shown in Fig. 4. Approximation of the emission decay curve of LE(Pb) centers (Fig. 4, curve 1) under excitation by SR with $E = 6.765$ eV by a sum of three components $I(t) = 86 + 236 \exp[-t/(1.4 \text{ ns})] + 28 \exp[-t/(17 \text{ ns})] + 370 \exp[-t/(5600 \text{ ns})]$ most probably indicates the radiative relaxation from two RES (singlet and triplet) levels with corresponding decay times of the faster component of

1.4 ns and the slower component that can be characterized by the lifetime values of 17 ns and 5.6 μ s. Calculated decay time values in the microsecond range are *only indicative* due to the restricted time window, which is given by the high repetition frequency of SR.

Luminescence decay kinetics of Pb²⁺-based centers in the UV and visible ranges (Fig. 4, curves 2 and 3, respectively) differ substantially. Under excitation in the A-band with $E_{\text{max}} = 4.55$ eV (Fig. 3, curve 1) and in the band of Pb²⁺ $\rightarrow$ Pb³⁺ + e photoionization transition with $E_{\text{max}} = 5.62$ eV (Fig. 3, curve 2) the luminescence decay curves for YAG:Pb SCF in the UV (at 330 nm) and visible (at 620 nm) ranges at 10 K (Fig. 4, curves 1 and 2, respectively) are approximated by a sum of two exponents $I_{\text{UV}}(t) = 2.5 + 625 \exp[-t/(0.8 \text{ ns})] + 17 \exp[-t/(6300 \text{ ns})]$ and $I_{\text{VIS}}(t) = 10.5 + 58 \exp[-t/(1.5 \text{ ns})] + 47 \exp[-t/(7900 \text{ ns})]$ and contain intensive fast components with decay times of 0.8 ns and 1.5 ns and slow components with an *indicative* decay time of about 6–8 μ s that, most probably, are caused by the transitions from X- and T-minima of RES of single Pb²⁺ and from the excited state of complex Pb²⁺-based centers (Fig. 2).

Substantial differences between the excitation spectra of emission in the UV and visible ranges indicate different prevailing excitation mechanism of luminescence of single Pb²⁺ ions and more complex Pb²⁺-based centers in YAG and LuAG SCF. The above-described luminescent properties of YAG:Pb and LuAG:Pb SCF [12–14] allow us to draw the conclusion that the dominant excitation mechanism of luminescence of complex Pb²⁺-based centers in YAG:Pb SCF is a photoionization transition from the ¹S₀ state of Pb²⁺ ions to the bottom of the CB. Formation of localized exciton could occur via relocation of electronic density between the Pb²⁺–Pb³⁺ ion pairs and oxygen ligands and formation of a hole trapped by this ion pair followed by recombination with an electron from the CB.

Figure 5 Diagram of energy levels and optical transitions of single Pb²⁺-based centers in YAG and LuAG.

The presence of excitation bands of the ns^2 -ion luminescence of a different nature in SCF of garnets can be caused by strong mixing of the excited states of Pb^{2+} ions and Y^{3+} or Lu^{3+} cations states and those of Pb^{3+} ions and oxygen ligands. Based on the results of investigation of the YAG:Pb SCF luminescence obtained in this paper and LuAG:Pb SCF in [12–14] the proper scheme of energy levels of isolated Pb^{2+} centers in YAG and LuAG host is constructed (Fig. 5). As compared with the scheme presented in [14] the position of the 1P_1 states of Pb^{2+} ions is determined at the bottom of conductive band. As seen in this scheme, in YAG and LuAG host the mixing of the 1P_1 states of Pb^{2+} ions with the states of the CB takes place. This mixing is substantially larger in the case of YAG in comparison with LuAG SCF that is reflected in the different degree of interaction of Pb^{2+} ions with the crystal field of these garnet hosts.

4 Conclusion The cathodoluminescence spectra of YAG:Pb single-crystalline films (SCF) show typical emission of Pb^{2+} ions in the UV and visible spectral ranges consisting of complex bands with $E_{max} = 3.3$ eV and 1.97 eV. The intensities of the bands in the UV and visible ranges show different dependences on the concentration of lead ions in the range of less than 0.01–0.3 at% and belong to the single and complex Pb^{2+} -based centers, respectively. The structure of the emission spectra in the UV and visible spectral ranges, as well as the two-component decay kinetics of this luminescence in the ns and μ s ranges are most probably caused by the $^3P_{1,0} \rightarrow ^1S_0$ transitions from the relaxed states of single and complex Pb-containing centers. Besides this luminescence the low-intensity luminescence of excitons localized in the vicinity of Pb ions (LE(Pb) centers) is also observed in YAG:Pb (0.01–0.035 at%) SCF in the band with $E_{max} = 4.24$ eV.

Substantial differences between the excitation spectra of UV and visible emission bands in YAG:Pb SCF indicate a different prevailing excitation mechanism of luminescence of isolated Pb^{2+} ions and more complex Pb^{2+} -based centers. In YAG:Pb SCF, the dominant excitation mechanism of luminescence of complex Pb^{2+} -based centers is a photoionization transition from the 1S_0 state of Pb^{2+} ions to the bottom of conduction band. The presence of excitation bands of the Pb^{2+} luminescence of a different nature in YAG:Pb SCF and other garnets is caused by strong mixing of the excited and ground states of Pb^{2+} ions with states of Y^{3+} or RE cations and oxygen ligands, respectively. Specifically, in YAG:Pb, the strong mixing of the 1P_1 states of Pb^{2+} ions with the states of the conduction band takes place, which is significantly larger than in isostructural LuAG:Pb [12–14].

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