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Influence of lead-related centers on luminescence of Ce^{3+} and Pr^{3+} centers in single crystalline films of aluminium perovskites and garnets

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ABSTRACT

Luminescence characteristics of Ce^{3+}- and Pr^{3+}-doped aluminium perovskite ($LuAlO_3$, $YAlO_3$) and garnet ($Lu_3Al_5O_{12}$, $Y_3Al_5O_{12}$) single crystalline films, prepared by the liquid phase epitaxy method with the use of the PbO-based flux, were investigated by the time-resolved spectroscopy methods in the 80–300 K temperature range. The influence of various lead-related centers on the characteristics of the Ce^{3+}- and Pr^{3+}-related luminescence centers was studied. It was found that the presence of lead-related centers in the single crystalline films results in a decrease of the quantum efficiency and appearance of undesirable slow components in the luminescence decay kinetics. The possibilities of improving the scintillation characteristics of the single crystalline films were considered.

1. Introduction

Single crystals (SC) of aluminium perovskites ($LuAlO_3$ – LuAP and $YAlO_3$ – YAP) and garnets ($Lu_3Al_5O_{12}$ – LuAG and $Y_3Al_5O_{12}$ – YAG) doped with Ce^{3+} and Pr^{3+} ions have been considered for fast scintillator applications (see, e.g., Nikl et al., 2008 and references therein). The single crystalline films (SCF) of the Ce^{3+}- and Pr^{3+}-doped aluminium perovskites and garnets prepared by the liquid phase epitaxy (LPE) method were found to have better scintillation properties as compared with the corresponding SC due to the absence of the so-called "antisite" defects (Y^{3+} or Lu^{3+} ions in the Al^{3+} sites) (Zorenko et al., 2005, 2007a,b, 2008). However, the SCF prepared with the use of the PbO-based flux are contaminated by Pb^{2+} ions. Both the single and the dimer Pb^{2+}-based centers can exist in the SCF. The emission and excitation bands of these centers, identified by Babin et al. (2007, 2009), can overlap with the Ce^{3+}- or Pr^{3+}-related bands. This leads to the energy transfer processes between mentioned centers and has a negative influence on the scintillation properties of these SCF. In the present work, the influence of different lead-related centers on the luminescence characteristics of Ce^{3+} and Pr^{3+} centers was studied.

2. Experimental procedure

Undoped and Ce^{3+}- and Pr^{3+}-doped SCF of aluminium perovskites and garnets with a different lead content were grown by the LPE method from the melt-solution based on the $PbO–B_2O_3$ flux in a Pt crucible (Zorenko et al., 2005, 2008).

The steady-state emission and excitation spectra were measured at the set-up, consisting of a deuterium lamp, two monochromators and a photomultiplier with an amplifier and recorder. All the necessary corrections of the spectra were made. The luminescence decay kinetics and time-resolved emission and excitation spectra were measured at a modified Spectrofluorometer 199S (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flash-lamp (IBH Scotland). The detection was performed by an IBH-04 photomultiplier module, using the method of a time-correlated single photon counting. Deconvolution procedure (SpectraSolve software package) was applied to extract the true decay times from the multiexponential approximation.

3. Experimental results and discussion

The characteristics of the Pb^{2+}-related, Ce^{3+} and Pr^{3+} centers in the SCF studied are shown in Table 1. From the comparison of the positions of the absorption and emission bands of single and dimer Pb^{2+}-based centers with those of Ce^{3+} and Pr^{3+} centers, the following features are expected which can influence the luminescence characteristics of the Ce^{3+}- and Pr^{3+}-doped materials: (i) the energy transfer from the excited lead-related centers to the Ce^{3+}- and Pr^{3+} centers; (ii) the energy transfer from the excited Ce^{3+} or Pr^{3+} ions to the lead-related centers; (iii) the reabsorption of the localized exciton emission in the absorption bands of Ce^{3+} and Pr^{3+}

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Table 1
Maxima positions (in eV) of the absorption (E_{abs}) and emission (E_{em}) bands of single and dimer Pb^{2+}-based centers (Babin et al., 2007, 2009; Zorenko et al., 2007b, 2008), Ce^{3+} centers (Blazek et al., 2004; Krasnikov et al., 2005; Zorenko et al., 2007b) and Pr^{3+} centers (Drozdowski et al., 2005; Gorbenko et al., 2009; Peichal et al., 2009). $T = 80$ K.

SCF	Single Pb^{2+}		Dimer Pb^{2+}		Ce^{3+}		Pr^{3+}	
	E_{abs}	E_{em}	E_{abs}	E_{em}	E_{abs}	E_{em}	E_{abs}	E_{em}
LuAG	4.75	3.60	3.97	3.20	3.61; 2.8	3.36; 3.12 2.46; 2.22	4.35; 5.17	4.05; 3.81 3.46; 3.31
YAG	4.75	~3.60	3.95	3.22	3.69; 2.71	3.42; 3.18 2.25; 2.11	4.28; 5.21	3.94; 3.73 3.37; 3.16
LuAP	5.04	~3.65	3.85	3.15	4.52; 4.25; 4.10	3.48; 3.30	~5.4	4.93; 4.35
YAP	4.98	3.65	3.87	3.15	4.52; 4.25; 4.10	3.51; 3.27	~5.4	4.96; 4.43

centers; (iv) the overlap of the emission bands of the lead-related and the luminescence Ce^{3+} and Pr^{3+} centers.

3.1. Energy transfer from excited lead-induced centers to impurity ions

In LuAG:Ce and YAG:Ce SCF, the emission band of single Pb^{2+} centers is strongly overlapped with the 3.6–3.7 eV absorption band of Ce^{3+} centers (see Table 1). Hence, an effective energy transfer from single Pb^{2+}-based centers to Ce^{3+} centers takes place. These effects were studied by Babin et al. (2007, 2009). It was shown that the energy transfer results in the appearance of the Pb^{2+}-related band in the excitation spectrum of the Ce^{3+} emission and of a slow (μs) component in this emission decay, as well as in the thermal quenching of the Ce^{3+} emission.

No slow component was found in the decay kinetics of the Ce^{3+}-related emission of garnets under excitation in the absorption band of dimer lead centers (Babin et al., 2009). It means that no energy transfer from the dimers to Ce^{3+} ions takes place. No energy transfer both from the single and the dimer Pb^{2+} centers to Pr^{3+} ions was found in the SCF of Pr^{3+}-doped aluminium perovskites and garnets.

3.2. Energy transfer from excited Ce^{3+} or Pr^{3+} ions to lead-induced centers

In the luminescence decay kinetics of dimer Pb^{2+} centers in Ce^{3+}-doped perovskite SCF, two components are observed with the decay times ≈20 ns and 460–470 ns at 80 K (see, e.g., Fig. 1). The slower component surely arises from the dimers, as its emission spectrum (shown in the inset) coincides with the emission spectrum of dimer Pb^{2+} centers, obtained at the steady-state conditions (Babin et al., 2009), and the decay time is similar to that, observed for the dimer Pb^{2+} centers in garnets (Babin et al., 2009). As the emission and excitation spectra of the Ce^{3+} and dimer Pb^{2+} centers overlap (Table 1), the weak fast component can arise from Ce^{3+} ions.

As the emission spectrum of Ce^{3+} centers in the perovskite SCF overlaps with the absorption band of dimer Pb^{2+} centers (Table 1), an energy transfer from Ce^{3+} to the dimers takes place. It results in ≈1.3 times faster decay of the Ce^{3+} emission in SCF (Fig. 2, curve 1) as compared with the decay time (16–18 ns) characteristic for this emission in SC (Weber, 1973; Mareš et al., 1992, 1995), and in the appearance of the slow dimer-related emission under excitation in the Ce^{3+}-related absorption region (around 4.3 eV where the emission of the dimers cannot be directly excited) (see curve 2 and the inset).

The energy transfer from Pr^{3+} centers to dimer Pb^{2+} centers, caused by the overlap of the Pr^{3+} emission band with the absorption band of the dimers, was observed in LuAG:Pr and YAG:Pr SCF by Gorbenko et al. (2009). It results in the shortening of the decay time of the Pr^{3+} emission (from 18–19 ns in SC to 13–14 ns in SCF) and in the reduction of quantum efficiency of the Pr^{3+} emission in the SCF of these garnets.

In perovskites, the emission bands of Pr^{3+} overlap with the absorption band of the single Pb^{2+} centers located, according to Zorenko et al. (2007b), at ≈5.0 eV (Table 1). Therefore, the energy transfer from Pr^{3+} to the Pb^{2+} centers is possible. It can result in the reduction of the quantum efficiency of SCF as compared with SC. However, this effect was not investigated as the number of single Pb^{2+} centers in the perovskite SCF studied was negligible.

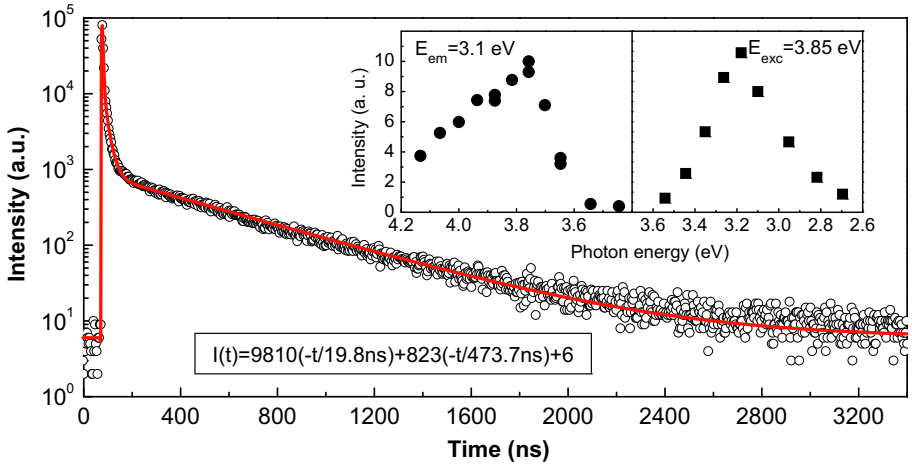

Fig. 1. Decay curves measured at 77 K for the emission of dimer Pb^{2+} centers in LuAP SCF. $E_{em} = 3.1$ eV, $E_{exc} = 3.85$ eV. In the inset, the excitation and emission spectra measured at $t = 900$ ns after the excitation pulse.

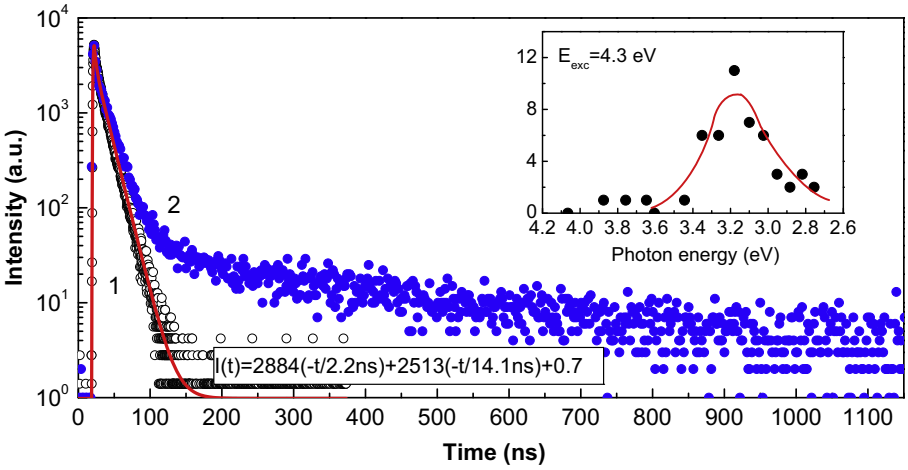

Fig. 2. Decay curves measured at 77 K for the emission of Ce^{3+} (curve 1) and dimer Pb^{2+} (curve 2) centers in LuAP SCF. $E_{exc} = 4.3$ eV. The emission spectra measured at $t = 900$ ns after the excitation pulse (the inset).

3.3. Reabsorption of the localized exciton emission in the absorption bands of Ce^{3+} and Pr^{3+} centers

In the SCF of perovskites and garnets, a slow 4.2–4.3 eV emission was found under excitation in the exciton energy range (Babin et al., 2007; Zorenko et al., 2008) and ascribed to the exciton localized near Pb or/and Pt ions introduced into the SCF at their preparation. The scintillation characteristics of the Ce^{3+}-doped perovskites and Pr^{3+}-doped garnets can be considerably influenced by a strong overlap of the 4f–5d absorption bands of Ce^{3+} and Pr^{3+} ions with the broad (FWHM ≈ 1 eV) 4.2–4.3 eV emission band. As the decay of this emission is slow, it also leads to the appearance of undesirable slow components in the scintillation decay of these materials.

3.4. Overlap of the emission bands of the lead-induced and impurity centers

In Ce^{3+}-doped perovskites and Pr^{3+}-doped garnets, the emission bands of the lead-related and impurity centers are strongly overlapped (see Table 1). As a result, in the spectral range characteristic for the Ce^{3+} and Pr^{3+} centers, besides the fast Ce^{3+} and Pr^{3+}-related decay components, additional weak slow lead-related components appear in the luminescence decay.

4. Conclusions

The features considered in this paper indicate to the negative influence of lead-induced centers on the scintillation characteristics of SCF of Ce^{3+}- and Pr^{3+}-doped aluminium perovskites and garnets which depends on the type of the lead-induced center and on the host material. The substitution of trivalent Y^{3+} or Lu^{3+} ions by relatively large divalent Pb^{2+} ions in the crystal lattice of perovskites and garnets is possible only in case the charge and volume of a Pb^{2+} ion are effectively compensated. In the case of single Pb^{2+} centers, the compensation can be achieved by small tetravalent ions (Scott and Page, 1977), but in the case of dimer lead centers, most probably, by oxygen vacancies (Babin et al., 2009). To decrease the number of undesirable lead-induced centers in the SCF prepared with the use of the PbO-based flux and to improve the scintillation characteristics of these SCF, the number of the corresponding compensating defects in these SCF should be considerably reduced.

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