Peculiarities of luminescence and scintillation properties of YAP:Ce and LuAP:Ce single crystals and single crystalline films

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Abstract

Luminescent properties and the energy transfer from host to Ce^{3+} ions are analyzed in single crystalline films (SCF) of $\text{YAlO}_3\text{:Ce}$ (YAP:Ce), $\text{Y}_{1-x}\text{Lu}_x\text{AP:Ce}$ (YLuAP:Ce) and $\text{LuAlO}_3\text{:Ce}$ (LuAP:Ce) perovskites in comparison with their single crystal (SC) analogues using the time-resolved luminescence spectroscopy under synchrotron radiation excitation. It is shown that the main peculiarity of luminescent properties of YAP:Ce, YLuAP:Ce and LuAG:Ce SCF is determined by the extremely low concentration of Y_{Al} and Lu_{Al} antisite defects and vacancy-type defects in SCF as compared to SC. The advantages of phosphors based on (Y-Lu)AP:Ce SCF are due to the absence of emission and trapping centers in these SCF which are connected with the above mentioned bulk crystal defects.

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1. Introduction

Ce-doped YAlO_3 (YAP) and LuAlO_3 (LuAP) perovskites are efficient high-response scintillators for medical application (Lempicki et al., 1995; Nikl, 2000). Due to high melting temperatures, low oxygen pressure in growth atmosphere, existence of two cation sublattice and cations of the equal charge state, a variety of point defects exists in single crystal (SC) of perovskites (Stanek et al., 2006). Among them, the Y_{Al} and Lu_{Al} antisite defects (AD) and vacancy-type defects (VD) are of particular importance for their scintillation performance (Nikl, 2005; Zorenko et al., 2004a). AD and VD can often create parent sites for electron or hole capture which usually degrade light yield (LY) and timing characteristics of the scintillators (Nikl et al., 2005; Vedda et al., 2000, 2006).

For some other applications the high-density single crystalline film (SCF) scintillators are developed (Koch et al., 1998,

1999; Zorenko et al., 2002, 2005b). The SCF grown from melt-solution (MS) at low ($< 1000^\circ\text{C}$) temperatures in air are characterized by the absence of AD and by extremely low concentrations of VD as compared with the SC analogues (Zorenko et al., 2004a; 2007a,b). Therefore, we expect that the scintillators based on SCF of perovskites will have better spectral-kinetic characteristics with respect to their SC analogues due to the absence of the emission and trapping centers connected with AD and VD.

The aim of this work was investigation of the time-resolved luminescence of YAP:Ce, YLuAP:Ce and LuAP:Ce SCF in comparison with their bulk SC analogues, as well as the peculiarities of energy transfer to Ce^{3+} ions in the SC and SCF under the synchrotron radiation (SR) excitation.

2. Samples and experimental technique

YAP:Ce and $\text{Lu}_{0.3}\text{Y}_{0.7}\text{AP:Ce}$ (LuYAP:Ce) SC were grown by Crytur (Czech Republic) from melt by the Czochralski

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method from a Mo crucible in reducing atmosphere using the charge containing Y_2O_3 , Lu_2O_3 , CeO_2 (5 N purity) and Al_2O_3 (4 N purity) oxides. The content of Ce ions in the mentioned SC was 0.09 and 0.19 at%, respectively. The sample of YAP:Ce SC with low Ce^{3+} content (a few tens ppm) was also studied for comparison. The Ce-doped YAP, $\text{Lu}_{0.6}\text{Y}_{0.4}\text{AP:Ce}$ and LuAP SCF were grown by the liquid phase epitaxy in the LOM Lviv University (Ukraine) from the MS based on $\text{PbO-B}_2\text{O}_3$ flux and crystal-forming oxides of the same purity on the substrates of undoped YAP SC. The optimal content of CeO_2 oxide in the MS (10–13 mol%) was chosen experimentally and corresponds to the maximum LY of SCF scintillators under excitation by α -particles of Pu^{239} sources (5.5 MeV).

The time-resolved luminescence of YAP:Ce, LuAP:Ce and LuYAP:Ce SC and SCF at 9–300 K were investigated at the Superlumi station in HASYLAB at DESY, Hamburg under excitation by SR with an energy of 3.7–25 eV. The emission and excitation spectra were measured both in the integral regime and in time gates of 1.2–11 ns (fast component) and 150–200 ns (slow component) in the limits of SR pulse with a repetition time of 200 ns and a duration of 0.127 ns. The decay kinetics of luminescence was measured in a time range of 1.2–200 ns at 300 K.

3. Luminescence of SCF and SC of perovskites

The luminescence spectra of YAP:Ce SC with low Ce^{3+} content (a few tens ppm) at 9–220 K under excitation by SR with an energy of 7.835 eV in the exciton range at 9 K (curve 1) and 180 K (curve 2) are shown in Fig. 1. The typical $5d > 4f$ luminescence of Ce^{3+} ion in the doublet bands at 350 and 375 nm as well as the two bands of host emission peaked at 218 and 302 nm are observed in the spectra of this YAP:Ce SC. The 218 and 302 nm bands are related to the luminescence of excitons localized around AD and VD (LE (AD) and LE (VD) bands,

Fig. 1. Emission spectra of the YAP:Ce (~few tens ppm) SC at 9 K (1) and 180 K (2) under excitation by SR with an energy of 7.835 eV in the exciton range. Absorption spectrum of YAP:Ce SC (3) is shown for comparison.

respectively) (Zorenko et al., 2004a; 2007a). It is worth noting that the host emission bands at 218 and 302 nm in YAP:Ce SC are strongly overlapped with the Ce^{3+} absorption bands peaked at 219 and 239 nm and around 300 nm, respectively (Fig. 1, curve 3). As a result of the such overlap, the Ce^{3+} emission in YAP:Ce and LuYAG:Ce SC is partly excited via the host emission.

The time-resolved emission spectra of YAP:Ce and LuYAP:Ce SC and SCF at 300 K measured in the integral (1), fast (2) and slow (2) time gates under excitation by SR in the region of interband transition are presented in Fig. 2. The wide complex bands peaked at 360–365 nm range related to the $5d > 4f$ transition of Ce^{3+} ions are observed in the spectra of all SC and SCF. From the data presented in the Fig. 2 it can be noted that the characteristics features of the Ce^{3+} emission in the YAP:Ce and LuYAP:Ce SC and SCF are as follows: (i) significantly large (~ 20 times) intensity of slow components in $\text{Lu}_{0.3}\text{Y}_{0.7}\text{AP:Ce}$ SC in comparison with the YAP:Ce SC (Fig. 2(a)–(c), respectively, curves 3); (ii) notable lower intensity of the slow components and large intensity of fast components in spectra of YAP:Ce and $\text{Lu}_{0.4}\text{Y}_{0.6}\text{AP:Ce}$ SCF with respect to bulk SC analogues (Fig. 2(a),(b) and (c),(d), respectively, curves 3).

Excitation spectra of the Ce^{3+} luminescence in YAP:Ce SC (a) and SCF (b) and $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SC (c) and SCF (d) at 300 K are shown in Fig. 3. The spectra of all SC and SCF contain three main bands in the 305–275 nm region and two weaker bands in 232–215 nm range corresponding to the transitions

Fig. 2. Spectra of the integral (1), fast (2) and slow (3) emission components in YAP:Ce SC (a) and SCF (b), $\text{Lu}_{0.3}\text{Y}_{0.7}\text{AP:Ce}$ SC (c) and $\text{Lu}_{0.4}\text{Y}_{0.6}\text{AP:Ce}$ SCF (d) at 300 K under excitation by SR with an energy of 14.6 eV (a), (b) and 11.3 eV (c), (d), normalized to the maxima intensity of Ce^{3+} emission band in the integral spectra.

Fig. 3. Excitation spectra of the integral (1), fast (2) and slow (3) components of Ce^{3+} luminescence in YAP:Ce SC (a) and SCF (b) and $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SC (c) and SCF (d) at 9 K.

between the $4f(^2F_{5/2})$ level of ground state to the $5d(^3T_2)$ and $5d(^2E)$ $5d(2e)$ levels of Ce^{3+} ions, respectively. In addition to these bands, the excitation spectra of the fast components of Ce emission in YAP:Ce and $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SC and SCF

also show a wide band at 200 nm most probably caused by the $4f \rightarrow 6s$ transitions of Ce^{3+} ions (Wojtowicz et al., 2002). The excitation of the fast and slow components of Ce emission in $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SCF and SC in the exciton range (Fig. 3, curves 2) at 9 K occurs in the narrow bands peaked correspondingly in 159–155 nm and 156.5–152 nm ranges. The existence of the two excitation maxima of the Ce emission in $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SCF and SC indicates that the excited state of an exciton bound with the Ce^{3+} ions probably has two radiative levels.

The low-intensive excitation bands at 166 and 249 nm for YAP:Ce SCF or 163 and 246 nm for $\text{Lu}_{0.6}\text{Y}_{0.4}\text{AP:Ce}$ SCF occur only in the SCF. Most probably, these bands are caused by the Pb^{2+} impurity, coming in the SCF from the PbO -based flux, and corresponds to the excitation of excitons bound with the Pb^{2+} ions and with the $^1S_0 \rightarrow ^3P_1$ transition of Pb^{2+} ions, respectively (Babin et al., 2007).

It is worth noting that the Ce emission in SC is also excited in the bands peaked at 172 and 186 nm for YAP:Ce SC or at 171 and 191 nm for $\text{Lu}_{0.3}\text{Y}_{0.7}\text{AP:Ce}$ SC (Fig. 3(a) and (c), respectively) which are apparently related to the intrinsic lattice defects of YAP and LuYAP SC (Wojtowicz et al., 2002). The most prominent feature of the excitation spectra of YAP:Ce and LuAP:Ce SCF with respect to SC analogues is noticeably lower intensity of the defect-related excitation bands peaked at 171–172 nm and 185–191 nm (Fig. 3(b) and (c), respectively), what points to the considerably lower concentrations of these defects in SCF in comparison with YAP:Ce SC.

This statement is confirmed by an essential difference in the decay kinetics of Ce^{3+} emission in $\text{Lu}_{1-x}\text{Y}_x\text{AP:Ce}$ SC and SCF (Fig. 4(a) and (b), respectively). Under excitation in the Ce^{3+} absorption bands in the 275–300 nm range, the decay curves for YAP:Ce and LuAP:Ce SC and SCF coincides with lifetimes of emission of 16.2 and 15.4 ns, respectively (Fig. 4(a) and (b), curves 1 and 2). At the same time, under excitation in the region of interband transitions (75–85 nm, $E > 2E_g$), the decay kinetic of Ce emission for SCF and SC are noticeably different; specifically, the YAP:Ce and $\text{Lu}_{0.6}\text{Y}_{0.4}\text{AP:Ce}$ SCF demonstrate the notably faster decay kinetics than their SC analogues (Fig. 4(a) and (b), curves 3 and 4, respectively). Corresponding average decay times of Ce emission at 300 K are equal to 27.8 and 38.6 ns for YAP:Ce SCF and SC, 19.6 ns for $\text{Lu}_{0.6}\text{Y}_{0.4}\text{AP:Ce}$ SCF and 24.3 ns for $\text{Lu}_{0.3}\text{Y}_{0.7}\text{AP:Ce}$ SC, respectively, at the same excitation wavelengths.

For estimation of the slow components content in the scintillation decay we used the ratio between the intensity I_s of decay components which are slower than the repetition frequency of SR and intensity $I(t)$ of rising part of the scintillation pulse as $K_s = [I_s/I(t)] \cdot 100\%$ (Fig. 4). For YAP:Ce SC and SCF the $K_s = 0.74\%$ and 0.07% values, respectively, was obtained (Fig. 4, curves 3 and 4) under high-energy excitation (16.5 eV). Thus, in the YAP:Ce SC the content of the slow components in the scintillation decay is higher by one order of value with respect to SCF (Table 1) that reflects significant participation of AD and VD in the delivery of excitation energy to the Ce^{3+} ions. For LuYAP:Ce SC and SCF the noticeably large values of $K_s = 4.1\%$ and 2.9% as compared to YAP:Ce SC and SCF were obtained (Fig. 4(b), curves 3 and 4, respectively).

Fig. 4. Decay kinetics of Ce emission at 300 K in YAP:Ce (a) SCF (1,3) and SC (2,4), Lu_{0.6}Y_{0.4}AP:Ce (b) SCF (1,3) and Lu_{0.3}Y_{0.6}AP:Ce (b) SC (2,4) excited by SR in the region of interband transitions (75–85 nm) (1,2) and Ce³⁺ absorption band at 280 nm (3,4).

Table 1
Comparison of the content of slow components for SC and SCF of garnets and perovskites

Scintillators	Content of slow components, K _s , %
LuAP:Ce SC	4.06
LuAP:Ce SCF	2.9
YAP:Ce SC	0.42
YAP:Ce SCF	0.07
YAG:Ce SC	6.3 (Zorenko et al., 2007a,b)
LuAG:Ce SC	74.5 (Zorenko et al., 2007a,b)

The largest value of K_s for LuYAP:Ce SC with respect to YAP:Ce SC (Table 1) probably is caused by the highest concentration of AD in Lu-based perovskites. It is worth noting that this result is coherent with the previous theoretical calculation of the AD concentration in perovskites (Stanek et al., 2006). In this work it was shown that the Lu_{Al} AD have lower energy of formation in comparison with Y_{Al} AD what can result in larger concentration of AD in LuAP SC.

Notable difference in K_s values between the LuYAP:Ce SCF and YAP:Ce SCF can be explained by the large contribution of the Pb²⁺ ions emission with the lifetimes of fast and slow

components in ns and μ s ranges, respectively, in the Ce³⁺ luminescence in LuYAP:Ce SCF as a result of overlapping of the corresponding bands peaked around 360–380 nm (Babin et al., 2007). It also explains the atypically faster initial part and slower main part of the decay curve 3 for Lu_{0.6}Y_{0.3}AP:Ce SCF as compared with the decay curve 4 for Lu_{0.3}Y_{0.7}AP:Ce SC (Fig. 4b).

4. Discussion

Observed features of the YAP:Ce and LuAP:Ce SC and SCF luminescence can be explained by the different concentration of AD- and VD-related emission and trapping centers in these phosphors. Since the LE (AD) and LE (VD) emission bands at 220 and 300 nm in SC with typical lifetime in hundred ns range (Zorenko et al., 2004a) considerably overlap the Ce³⁺ absorption bands at 236 and 219 nm and around 290 nm, respectively (Fig. 1), the decay kinetics of Ce³⁺ emission in YAP:Ce and LuYAP:Ce SC possesses the large contribution of slow components resulting from the non-radiative energy transfer between the defect-related centers and Ce³⁺ ions (Zorenko et al., 2007a,b). Another reason for the slow components presence can be an intermediate temporary localization of charge carriers at AD or VD acting as trapping centers (Nikl et al., 2005; Vedda et al., 2000; 2006). For SC of perovskites as compared to garnet SC (Zorenko et al., 2007a,b) substantially smaller contribution of slow components in scintillation decay is found basing on the value of K_s (Table 1). This might be due to the significant difference in the type and concentration of the host defects for these type oxides, first of all, for the Y_{Al} and Lu_{Al}AD, which are thus expected in SC of perovskites with, at least, one order lower concentration.

At the same time, for YAP:Ce and LuYAP:Ce SCF the content of the slow components in the scintillation decay is 1.4–6 times lower compared to SC (Table 1). This reflects the substantially smaller contribution of intrinsic defects in the scintillation decay of SCF phosphors as compared to SC analogs. This finding is consistent with the difference in the excitation spectra of YAP:Ce and LuYAP:Ce SCF with respect to SC (Fig. 2(b) and (a), respectively), which show noticeably lower intensity of the 171–172 and 185–191 nm bands related to the intrinsic lattice defects of YAP and LuYAP SC (Zorenko et al., 2004a). This points to the considerably lower concentrations of these centers in SCF in comparison with YAP:Ce and LuYAP:Ce SC. Due to correlation between the spectral positions of these bands and excitation bands of F⁺ and F centers emission in the exciton region in YAP SC (Zorenko et al., 2004b; 2005a), the nature of this bands more likely corresponds to the transitions from the oxygen-based levels of the upper part of valence band (VB) perturbed by the Ce³⁺ ions and levels of the VD-related centers with one or two trapped electrons (e). After localization of the hole (h) coming from the VB at the Ce³⁺ ion the formation of closely located Ce³⁺(h)–VD (e or 2e) pair centers takes place (Krasnikov et al., 2005; Blazek et al., 2005). Radiative recombination of e–h pair located around such defect/impurity centers can induce slow components in emission of YAP:Ce and LuAP:Ce SC.

5. Conclusion

Unlike the SC analogues, the phosphors based on YAP:Ce, LuYAP:Ce and LuAP:Ce SCF demonstrate the faster decay kinetics of Ce^{3+} emission and low content of slow components in scintillation decay under high-energy excitation. This is caused by the absence in SCF of YAP:Ce and LuYAP:Ce perovskites the additional channels for dissipation of excitation energy via AD and VD-related centers.

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