Intrinsic and Ce^{3+}-Related Luminescence in Single Crystalline Films and Single Crystals of LuAP and LuAP:Ce Perovskites

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Abstract—**Intrinsic and Ce-related luminescence of LuAP:Ce single crystalline films (SCF) in comparison with their bulk single crystal (SC) analogs were analyzed for the first time using the time-resolved luminescence spectroscopy under synchrotron radiation excitation. Difference in luminescent properties of SCF and SC are due to the absence of the Lu-at-Al-site antisite defects (AD) and extremely low concentration of vacancy-type defects (VD) in SCF. SCF contamination by Pb ions from flux is noted, which gives rise to an additional emission band in UV range. In SCF, the absence of emission and trapping centers formed by the mentioned AD and VD can explain their favorable timing characteristics with respect to SC. The role of Pb^{2+} trace impurities in LuAP-based SCF scintillators is considered as well.**

Index Terms—**Antisite and vacancy type defects; intrinsic and Ce-related luminescence; LuAP:Ce single crystal and single crystalline films, scintillators.**

I. INTRODUCTION

SINGLE crystals (SC) of $LuAlO_3$:Ce perovskites (LuAP:Ce) with high effective atomic number ($Z_{ef} = 65$) grown by Czochralski or Bridgman methods are well known scintillators for medical applications [1], [2]. The technology of Liquid Phase Epitaxy (LPE) offers also the possibility of obtaining the high density single crystalline film (SCF) scintillators with garnet and perovskite structures [3], [4]. SCF of $AAlO_3$ (A = Y, Lu) perovskites grown by LPE from melt-solution based on PbO-B_2O_3 flux at low (up to $1100°C$) growth temperatures are characterized by extremely low concentrations of antisite defects (AD) of Y_{Al} or Lu_{Al} type and oxygen vacancy-type defects (VD) in comparison with the corresponding SC analogs [3], [4]. Therefore such SCF's are very convenient model objects for studying the intrinsic, especially exciton-related luminescence, in complex oxides [5], [6]. For instance, the exciton transition, the energy gap,

and their temperature dependences have been recently exactly determined in LuAP SCF [6]. However, SCF contamination by the Pb^{2+} ions from flux is also noted which significantly influenced the Ce^{3+} luminescence and light yield of LuAP:Ce SCF scintillators [4].

In this paper the intrinsic and Ce^{3+}- related emission in LuAP and LuAP:Ce SC and SCF are further studied and mutually compared. The role of Pb^{2+} trace impurities in LuAP- based SCF scintillators is also considered.

II. SAMPLES AND EXPERIMENTAL TECHNIQUE

LuAP and LuAP:Ce SCF with thickness 21–36 μm were grown by LPE on YAP substrates from melt-solution (MS) based on PbO-B_2O_3 flux from Pt-crucible using the raw materials of 5 N purity. LuAP and LuAP:Ce SC analogs were grown from the melt by the Czochralski methods. The cerium concentration in LuAP SC and SCF of 0.085 at. % and 0.16 at. %, respectively, was determined by using a DS-130 Akashi microanalyzer. Luminescence characteristics of LuAP and LuAP:Ce SC and SCF with thickness of 36 μm and 22 μm, respectively, were investigated under excitation by synchrotron radiation (SR) at BW3 and Superlumi experimental station in HASYLAB at DESY, Hamburg with an energy of 300–1000 eV and 3.7–40 eV, respectively. Excitation spectra were corrected for the intensity and spectral dependence of the excitation energy, while emission spectra, measured with the same ARC monochromator and PEM Hamamatsu R6358P, were not corrected.

It is worth noting that the investigation of time-resolved emission spectra excited by SR *is enormously informative* for studing the peculiarities of the intrinsic and impurity-related luminescence of the SCFs scintillators of complex oxides (garnets and perovskites) in comparison with their bulk SCs analogs (see, for examle [5], [6]). In particular, the 7.0–15 eV- SR excitation both exciton and fundamental absorption range permits one *to deposit excitation energy only within the volume* of LuAP-based SCF phosphors (up to 0.2 μm [5]) that is impossible upon excitation by X- and γ-ray sources. This offers the possibility of studying exciton and impurity-related luminescence in SCFs of these compounds with no "background" emission of centres associated with AD and vacancy-type defects which are always present in SCs analogue of this perovskite [7]. Finally, using the 300–1000 eV SR sources is very useful for investigation of low-intensive exciton-related phenomena under high-energy excitation, especially in cases of SCF.
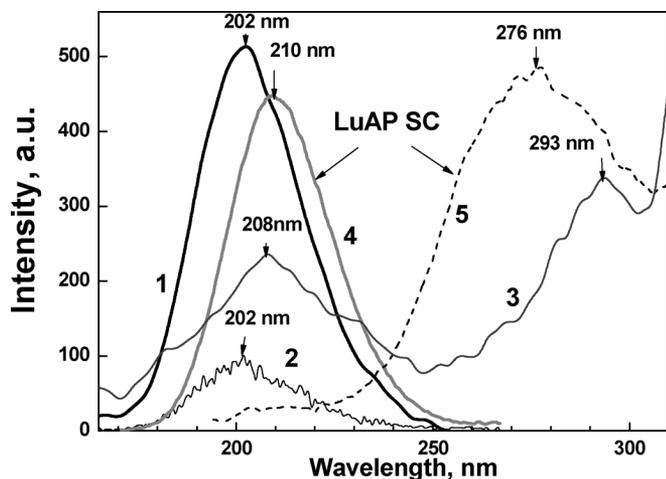
Fig. 1. Emission spectra of LuAP SCF (1–3) at 9 K (1, 2) and 300 K (3) in comparison with spectra of LuAP SC (4, 5) under excitation by SR with an energy of 800 eV (1–3), 8.25 eV (4) and 7.94 eV (5) measured in the integral regime (1, 3–5) and in time interval 0–1.5 ns after ending of SR pulse (2).
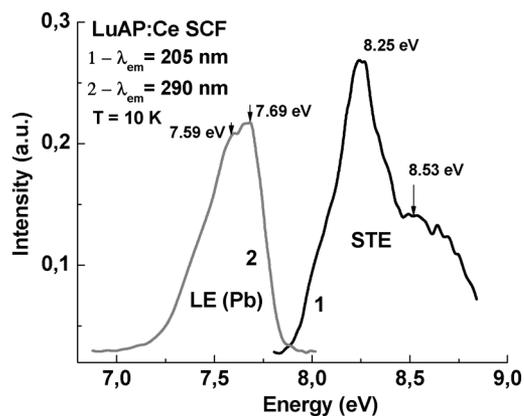

Fig. 2. Excitation spectra of STE (1) and LE (Pb) (2) emission in LuAP:Ce SCF.

III. Results and Discussion

The position of self-trapped exciton (STE) emission band peaked at 202 nm (6.13 eV) at 9 K and 208 nm (5.95 eV) at 300 K (Fig. 1, curve 1–3) was determined for the first time in the emission spectra of LuAP SCF (Fig. 1, curve 1–3). The position of the corresponding exciton emission band in LuAP SC at 210 nm (5.9 eV) at 10 K (Fig. 1, curve 4) is significantly shifted to the low-energy side with respect to that in SCF (curve 1). Due to an enhanced concentration of Lu_{Al} ADs in LuAP SC [7] this emission band is ascribed to the exciton localized around Lu_{Al} AD (LE (AD) luminescence), which can explain its low-energy shift with respect to STE emission [5].

The STE emission is excited in the complex band in exciton range which presents the superposition of two bands peaked at 8.25 and 8.53 eV (Fig. 2, curve1). These sub-bands of emission prevail in the spectra of fast component and slow component, respectively. The fine structure of excitation band shows that the relaxed excited states (RES) of STE emission have at least two (singlet and triplet) radiative levels (Fig. 2) as recently observed also in YAP SCF [5].

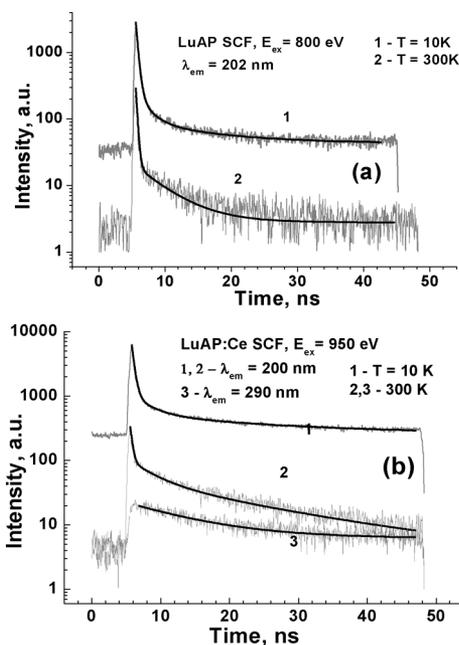| SCF samples and temperature	τ_1, ns	A_1	τ_2, ns	a_2	τ_3, ns	a_3
STE, λ_{em} = 200-205 nm						
LuAP:Ce, 10 K	**0.35**	2124	**3.0**	535	**25.8**	266
LuAP, 10 K	**0.32**	2599	**2.7**	144	**30.5**	36
LuAP:Ce, 300 K	**0.27**	232	**3.4**	51	**18.2**	45
LuAP, 300 K	**0.16**	243	2.1	17	15.2	37
LE (Pb), λ_{em}= 290 nm						
LuAP:Ce 300 K	**0.1**	3.2	7.16	38	35.6	16
Ce^{3+}, λ_{em} = 350-382 nm						
LuAP:Ce, 10 K	**0.66**	2037	**7.32**	9586	**22.7**	1017
LuAP:Ce, 10 K	**0.34**	161	**8.95**	1791	**28.0**	1081
LuAP:Ce, 300 K	**1.36**	174	**5.92**	1233	**18.0**	1720

Fig. 3. The decay kinetics of STE luminescence (a, b, curves 1 2) and LE (Pb) emission (b, 3) in LuAP (a) and LuAP:Ce (b) SCF at 9 K (1) and 300 K (2,3). The 3-exponential fits of the decay curves are given by the solid line. The parameters of fitting procedure are presented in the Table I.

Complex decay kinetics with the lifetimes of super-fast (0.21–0.3 ns), fast (2.7–3.4 ns) and middle (18.3–30.5 ns) emission components (Table I) was observed in the STE emission in LuAP and LuAP:Ce SCF at 9 K and 300 K (Fig. 3(a) and (b), respectively, and Table I). Increase of the temperature from 9 K to 300 K leads to significant intensity and decay time decrease of the STE emission (Table I). Such complex emission decay can indicate the superposition of two components with different nature. Specifically, the existence of the super-fast (0.2–0.3 ns) and two slower (2.7–3.4 and 18.3–30.5 ns) decay components of STE luminescence can reflect the formation of single and
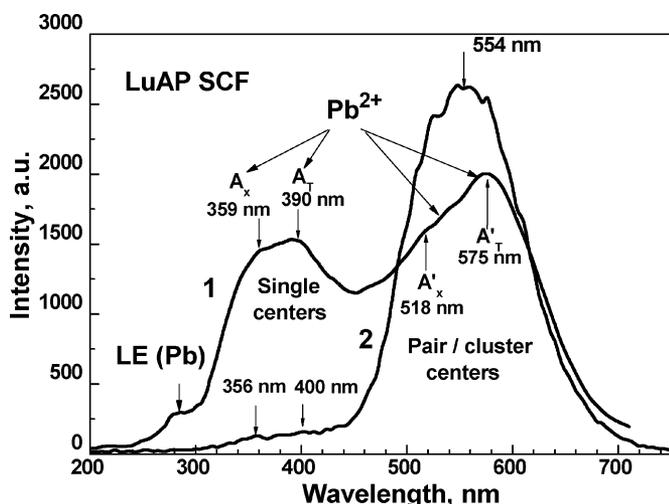
Fig. 4. Luminescence of LuAP SCF at 10 K (1) and 300 K (2) under excitation by SR with an energy of 7.68 eV in the exciton range (1) and 11.25 eV in the range of interband transitions (2).

triplet states of STE emission, respectively, in agreement with data obtained recently for STE emission decay in garnets [8]. It is worth noting that due to a high repetition frequency of SR pulse and necessarily narrow observation time gate (50 ns) the decay times of any slower components of the STE emission can not be well evaluated.

The lower-intensity intrinsic emission of LuAP (Fig. 4) and LuAP:Ce SCF (Fig. 5) peaked at 293 nm (4.22 eV) is probably related to the localized exciton (LE) around impurity/defect centers [4], [5]. For SCF such centers can be formed mainly by the Pb^{2+}-related trace impurity centers coming from the flux during SCF growth [5]. The compensation of the charge and volume of Pb^{2+} centers in SCF is usually achieved by the Pt^{4+} (from the crucible) contamination, see in detail [9], [10]. The intensity of this band notably increases at RT (Fig. 5(b)). The position and intensity of intrinsic emission bands in LuAP SC in UV range (Fig. 1, curve 5) significantly differ from those in SCF (curve 3) due to the presence of high concentration of VD and the existence of the LE (VD) emission bands peaked at 276 nm (4.485 eV).

The excitation spectrum of the LE (Pb) centers emission shown in Fig. 2 (curves 2) shows a complex pattern around 7.6–7.7 eV. The fine structure of this band (two components peaked at 7.59 and 7.69 eV), might be due to the formation of the singlet ant triplet excited states of the LE (Pb) center.

The decay kinetics of LE (Pb) emission is shown in Fig. 3(b), curve 3. Similarly to the STE decay, the decay curve of the LE (Pb) emission presents the superposition of three components with the lifetimes of super-fast (0.1 ns), fast (7.2 ns) and middle (35.6 ns) emission components. Thus, a similar consideration of their nature related to the formation of singlet and triplet states of LE (Pb) emission can be also applied.

In the longer-wavelength region, the emission spectra of LuAP SCF (Fig. 4) under high-energy excitation (curve 2) or excitation in the exciton range (curve 1) show two bands at 359–390 nm and 518–575 nm ranges, which are ascribed to the single and pair/cluster Pb^{2+}-based centers, respectively,
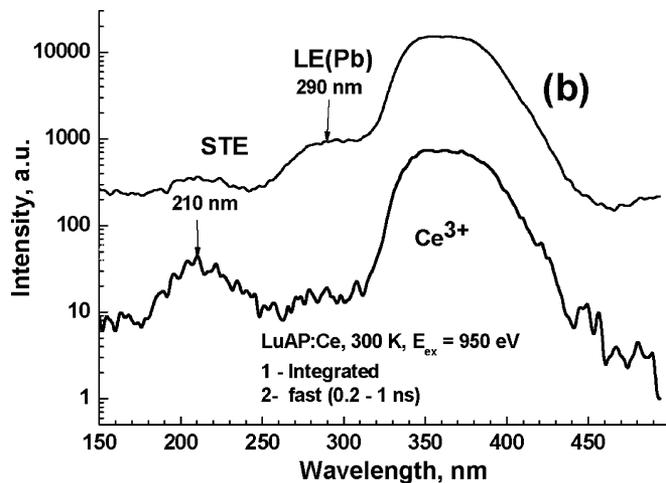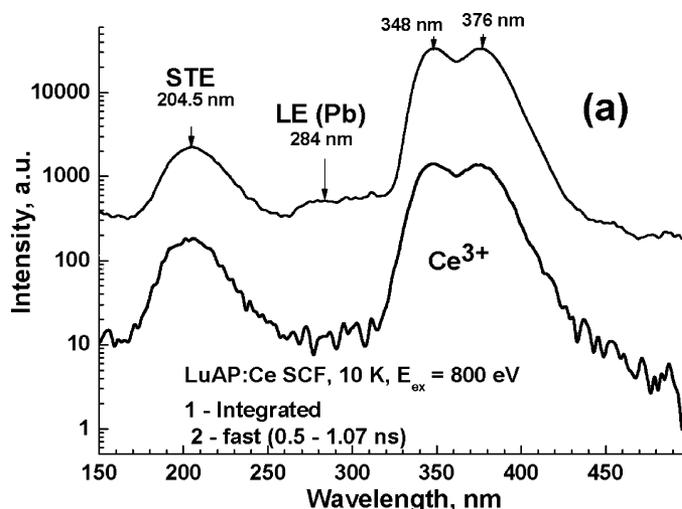

Fig. 5. Emission spectra of LuAP:Ce SCF at 10 K (a) and 300 K (b) measured in the different time windows indicated in the legends.

similarly to the luminescence of ns^2 ions (Pb^{2+}, Bi^{3+}) in SCF of garnets [10], [11]. The intensity of these bands in the UV and visible ranges shows different dependence on the total content of the lead ions in SCF; specifically, the intensity of visible emission increased while the UV emission decreased with the increasing of the Pb^{2+} ions concentration. The doublet structure of these bands (A_X, A_T and A'_X, A'_T components) is due to the Jahn-Teller effect working on the $^3P_{1,0} \rightarrow ^1S_0$ transition of both Pb^{2+}-related centers.

The intensity and position of intrinsic emission bands in LuAP SC in UV range (Fig. 1, curves 4, 5) are significantly modified with respect to those in SCF (Fig. 1, curves 3–5) due to the AD and VD presence and the induced existence of LE emission bands peaked at 5.9 eV and 4.485 eV, respectively. In Ce-doped LuAP compounds, the presence of LE (AD) and LE (VD) centers in SC, as well as the Pb^{2+} trace impurity and LE (Pb) centers in SCF, has strong influence on the energy transfer processes from the host to impurity ions and the delay of the charge carrier delivery to Ce^{3+} ions arises [4], [5].

The emission spectra of LuAP:Ce SCF measured in the different time windows at 10 K and 300 K are shown in Fig. 5. Typical Ce^{3+} emission in LuAP:Ce SCF in the doublet bands
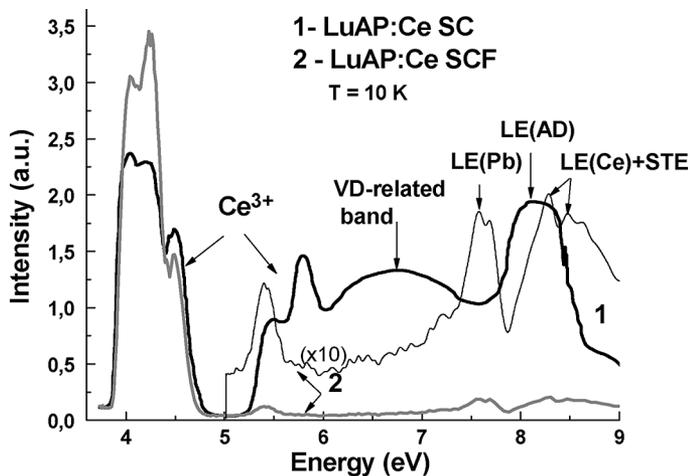
Fig. 6. Excitation spectra of Ce^{3+} emission (at 360 nm) in LuAP:Ce SC (1) and SCF (2) at 10 K.

Fig. 7. Decay kinetics of Ce^{3+} luminescence at 350 nm at 10 K (1) and 300 K (2) in LuAP:Ce SCF.

Fig. 8. Decay kinetics of Ce^{3+} luminescence at 350 nm in LuAP:Ce SC (1) and SCF (2, 3) under excitation by SR with an energy of 15.1 eV (1), 11.25 eV (2) and 800 eV (3) at 300 K.

peaked at 348 nm and 376 nm (Fig. 5) at 10 K and 300 K is caused by the radiative transitions from the 5d^1 state to the ^{2}F$_{5/2,7/2}$ ground state levels of Ce^{3+} ions.

At 10 K the excitation spectra of Ce^{3+} emission in LuAP:Ce SCF in comparison with LuAP:Ce SC are shown in Fig. 6.

These excitation spectra of SC and SCF contain three main bands in the 4.055–4.49 eV range and two weaker bands in the 5.40–5.80 eV range corresponding to the transitions between the 4f(^{2}F$_{5/2}$) level of ground state and 5d(3t$_2$) and the 5d(2e) levels of 5d^1 state of Ce^{3+} ion, respectively. The excitation of Ce^{3+} emission in LuAP:Ce SCF and SC in the exciton range (Fig. 6, curves 2) at 9 K occurs in the narrow bands peaked correspondingly at 8.28 and 8.49 eV. The positions of these bands are very close to the positions of the excitation bands of STE emission in LuAP SCF (Fig. 2). The existence of the two excitation maxima of the Ce emission in LuAP:Ce SCF indicates that the excited state of an exciton bound around a Ce^{3+} ion has probably also two radiative levels.

The doublet excitation band peaked at 7.59 eV and 7.69 eV for LuAP:Ce SCF in the excitation spectrum of Ce^{3+} emission occurs only in SCF. Most probably, these bands are caused by the Pb^{2+} impurity from the PbO-based flux, and correspond to the excitons bound with the Pb^{2+} ions (LE (Pb) emission) [5]. The LE (Pb) emission band peaked at 4.22 eV is well overlapped with the Ce^{3+} absorption/excitation bands located in 4.0–4.5 eV range (Fig. 6). This enables the effective Pb^{2+} → Ce^{3+} energy transfer in LuAP:Ce SCF similarly to observed early in LuAG:Ce SCF [9].

It is worth noting that the Ce^{3+} emission in LuAP:Ce SC is also excited in the band peaked at 6.75 eV (Fig. 6, curve 2) which are apparently related to the intrinsic lattice defects of LuAP SC [4], [11]. Striking difference in the excitation spectra of LuAP:Ce SCF and SC consists in the noticeably lower intensity of the VD-related complex excitation bands (Fig. 6, curve 1). This point to considerably lower concentration of these defects in SCF (curve 1) in comparison with LuAP:Ce SC (curve 2).

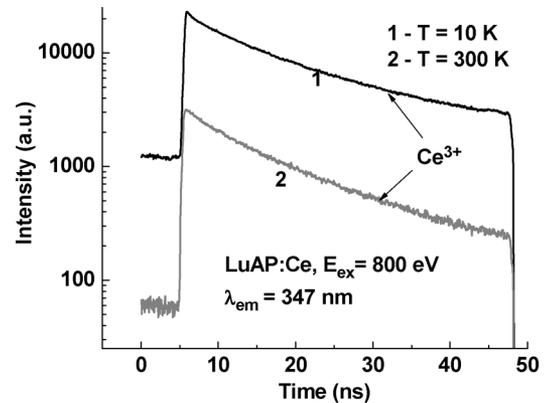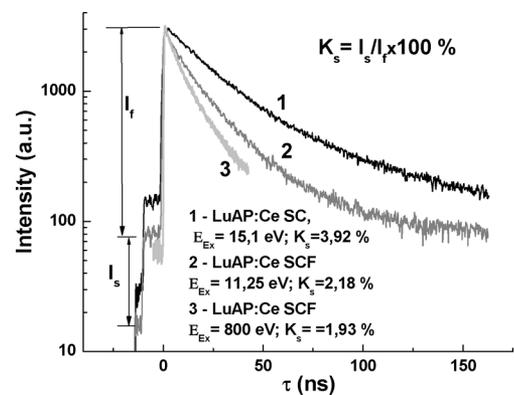The decay kinetics of Ce^{3+} emission in LuAP:Ce SCF at 300 K and 10 K is shown in Fig. 7. A lifetime of 22.9 ± 5.1 ns

of the main components of the Ce^{3+} emission decay under high energy excitation has been determined (Table I). Slightly non-exponential forms of the decay curve, especially at 10 K, and presence of the additional fast (7.4 ± 1.5 ns) components of the luminescence are most probably caused by the overlapping of the Ce^{3+} emission spectra and the UV emission band of the Pb^{2+} trace impurity peaked approximately at 360–390 nm (Fig. 4). Some difference in the form of decay curves at 10 K and 300 K can be explained by the temperature quenching of the single-Pb^{2+}-related centers luminescence in RT range. However, the interaction among closely lying excited sites in the host lattice could be considered as well to explain such an effect [13]. Another reason for such a non-exponential decay is the energy transfer between the Ce^{3+} and Pb^{2+}-related pair/cluster centers due to overlapping of the Ce^{3+} emission band and excitation band of the mentioned Pb-based centers emitting in the 560–580 nm range.

The comparison of the emission decay of Ce^{3+} ions in LuAP:Ce SC and SCF scintillators under high-energy excitation are shown in Fig. 8. As can be seen from this figure, the decay kinetics of Ce^{3+} luminescence in SCF is notably faster than that in the SC analogues. At the same time, the decay curves of both scintillators are slightly non-exponential due to the presence of some amount of slow components. For estimation of the slow component content in the scintillation decay of LuAP:Ce

TABLE II
COMPARISON OF CONTENT OF SLOW COMPONENTS FOR LuAP:CE SC AND SCF

Scintillators	Content of slow components Ks, %
LuAP:Ce SC	3.92
$Lu_{0.3}Y_{0.7}AP$:Ce SC	4.06 [4]
$Lu_{0.6}Y_{0.4}AP$:Ce SCF	2.9 [4]
LuAP:Ce SCF	1.93-2,18

SC and SCF we have used the ratio between the intensity I_s of decay components which are slower than the repetition frequency of SR and the intensity $I_f(t)$ of the rising part of scintillation pulse as $K_s = [I_s/I_f(t)] * 100\%$ (Fig. 8). For LuAP:Ce SC and SCF, $K_s = 3.92\%$ and 2.18% and 1.93% values, respectively, were obtained under high-energy SR excitation with an energy of 15.1 eV and 11.25 and 800 eV (Fig. 8, curves 1 and 2, 3, respectively). It is worth to note that both in the LuAP:Ce and LuYAP:Ce SC the content of the slow components in the scintillation decay is by 1.4–1.9 times higher than that in SCF (Table II) what reflects the large participation of AD and VD in the energy transfer process to the Ce^{3+} ions in these SC scintillators.

IV. CONCLUSION

Intrinsic luminescence of LuAP SCF is dominated by the STE emission in the regular sites of perovskite lattice in the band peaked at 6.13 eV (9 K) and 5.95 eV (at 300 K) and by the lower-intensity emission of excitons localized around Pb^{2+} trace impurity (LE (Pb emission) in the band peaked at 4.42 eV (9 K) and 4.30 eV (at 300 K).

In contrast to SCF, the intrinsic luminescence of LuAP SC is determined mainly by the UV emission of excitons localized around the Lu_{Al} antisite defects and vacancy defects in the bands peaked at 5.9 eV and 4.485 eV, respectively.

The mentioned defects in LuAP:Ce SC slow down the energy transfer towards Ce^{3+} ions. Concentration of these defects is significantly larger in SC than in SCF of LuAP:Ce. As a consequence, the Ce-doped LuAP and LuYAP SCF show faster decay kinetics of the Ce^{3+} emission and lower contribution of slower

components in the scintillation decay in comparison with the SC analogues.

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