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Luminescence of La^{3+} and Sc^{3+} impurity centers in $YAlO_3$ single-crystalline films

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Abstract

The luminescence of La_Y^{3+} and Sc_Y^{3+} and Sc_{Al}^{3+} centers created by lanthanum and scandium ions at Y^{3+} and Al^{3+} cation sites of $YAlO_3$ perovskite lattice was investigated. The features of emission of excitons localized at the mentioned centers in $YAlO_3$:La and $YAlO_3$:Sc single-crystalline films were analyzed by means of time-resolved emission spectroscopy and luminescence decay kinetics measurements under excitation by synchrotron radiation at 9 and 300 K.

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Keywords: Perovskites; Single-crystalline films; Luminescence; Excitons; La^{3+} and Sc^{3+}-dopants

1. Introduction

Sc^{3+} and La^{3+} isoelectronic impurities (II) with respect to core cation (e.g. Sc^{3+} with respect to Al^{3+} in Al_2O_3 or La^{3+} with respect to Y^{3+} in $Y_3Al_5O_{12}$) can effectively localize low-energy excitation (electrons and holes or excitons) at the expense of non-Coulomb potential arising at the substitution of core cation by II [1–3]. For this reason, these II are being widely used for creation of luminescence materials emitting in the UV range (250–350 nm) and based on Al_2O_3–Y_2O_3–Lu_2O_3 oxide system of different structural types [4,5]. Within this class of materials the II-related luminescence is well investigated in Al_2O_3:Ga and Al_2O_3:Sc [1,6,7] and, especially, in garnets [1–5,8–10]. The most known phosphors of this kind are single crystals (SC) of $Y_3Al_5O_{12}$:Sc (YAG:Sc) and $Lu_3Al_5O_{12}$:Sc (LuAG:Sc) garnets with high (up to 0.5 with respect to NaI:Tl) light yield (LY) of luminescence [3,4].

Unlike garnets, the II luminescence in perovskites—the other widespread class of the complex multi-sublattice oxides of the Al_2O_3–Y_2O_3–Lu_2O_3 system—remains by now unexplored. Due to this reason, we start our study of the II luminescence in perovskites from the most investigated the $YAlO_3$ (YAP). We have grown and investigated luminescence of single-crystalline films (SCF) of YAP doped by La^{3+} and Sc^{3+} II. It is worth noting that the YAP SCF due to low-temperature (up to 1000 °C) growth conditions in air atmosphere are practically free from vacancy-type defects (mainly oxygen vacancy) and anti-site defects (AD) of Y_{Al}^{3+} type (Y cations in a-sites of Al cations) [11,12]. Therefore, in YAP:La and YAP:Sc SCF, as distinct from their SC analogues, no luminescence centers based on aggregates of II and AD of the $Y_{Al}^{3+}-La$ or $Y_{Al}^{3+}-Sc$ type [4] or F^+ and F-centers (oxygen vacancy with captured one or two electrons, respectively) can be realized [13,14]. Due to this fact the SCF are more convenient model objects for investigation of the II luminescence than their SC analogues grown from high-temperature melt [4,9,10].

The Al^{3+} cations in YAP structure are distributed over the octahedral a- position formed by six oxygen ligands,

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whereas Y^{3+} cations are located in the voids between the octahedrons created by twelve nearest oxygen ions (c-position). It should be noted that in YAP:La single-crystalline film (SCF) the La^{3+} ion with large ionic radius (1.03 Å) is localized probably only at the c-sites of Y^{3+} cations (0.90 Å) [15]. Therefore, luminescent properties of such SCF are expected to be determined exclusively by the La_Y^{3+}-centers. Meanwhile, in YAP:Sc SCF, due to the intermediate value of the ionic radii of Sc^{3+} II (0.745 Å) with respect to Y^{3+} (0.90 Å) and Al^{3+} (0.53 Å) ions [15] it seems plausible to substitute Sc ions at both the Y and Al-sites of YAP host. In SCF of YAG:Sc and LuAG:Sc garnets, the Sc^{3+} are localized at the dodecahedral c-sites of Lu^{3+} cations and octahedral a-sites of Al^{3+} cations, with their concentration up to 0.3 formula unit (f.u.) and their ratio of 2:3 [4,16,17]. At higher scandium concentrations, the Sc^{3+} ions are localized mainly at the a-sites of garnet lattice [4]. Such variability of replacement of the host cations by Sc^{3+} ions might be observed also in perovskites, particularly in YAP. In the latter case, the luminescent properties of YAP:Sc SCF would thus be determined by the presence of Sc_Y^{3+} and Sc_{Al}^{3+} centers.

In this paper, the luminescence centers formation related to the La^{3+} and Sc^{3+} II in YAP SCF are studied using the time-resolved emission and excitation spectroscopy as well as the luminescence decay measurement under excitation by synchrotron radiation (SR) at 9 and 300 K.

2. Samples and experimental technique

The YAP:La SCF were grown by liquid phase epitaxy (LPE) from melt solutions (MS) based on $PbO:B_2O_3$ flux (12:1 mol/mol) on substrates of undoped YAP, see also Refs. [11,12,18,19]. The thickness of SCF was in the 22–35 μm range. The concentration of crystal-forming Y_2O_3 and Al_2O_3 components was 2.7 mol% of the total content of the MS. The concentration of La_2O_3 and Sc_2O_3 doping oxide in the MS was 11.9 and 5.2 mol% of the total content of crystal-forming components. The larger content of La_2O_3 in comparison with Sc_2O_3 oxide was necessary due to the lower segregation coefficient of La^{3+} ions in the LPE growth procedure [16].

Investigation of the luminescence of YAP:La and YAP:Sc SCF at 9 and 300 K was performed under excitation by SR with an energy of 3.7–25 eV at the Superlumi station in HASYLAB at DESY (Hamburg, Germany). Measurements of the time-resolved emission spectra were carried out in the integral regime and also with the time delay relative to the SR pulse (duration of 0.127 ns and repetition time of 200 ns), in time gates of 1.2–6.2 ns and 150–200 ns (mentioned below as the fast and slow components, respectively). The luminescence decay was measured in the 0–200 ns time range at 9 and 300 K. The decay curves were fitted using the exponential approximation $I(t) = \Sigma A_i \exp(-t/\tau_i) + \text{background}$.

3. Results and discussion

3.1. Luminescence of La^{3+} II in YAP SCF

The luminescence spectrum of YAP:La SCF measured in the different time gates at 9 K under excitation by SR with an energy of 7.55 eV (164 nm) in the YAP exciton range [11,12,20,21,25] is shown in Fig. 1. The doping of YAP SCF with La^{3+} II gives rise to appearance of the new complex luminescence band in the UV range with maximum at 3.87 eV (320 nm) (Fig. 1, curve 1). The time-resolved emission spectra measured within the different time gates show that this luminescence band is a superposition of the “fast” and “slow” sub-bands peaked at 4.08 eV (303 nm) and 3.76 eV (329 nm), respectively. On increasing the temperature from 9 to 300 K the fast 4.08 eV band becomes quenched, and at room temperature (RT) region the slow 3.76 eV band is dominant.

The excitation spectra of luminescence in the 4.08 and 3.76 eV bands are presented in Fig. 2a and b, respectively. Due to their extended overlap the emission wavelengths were set at 300 and 380 nm. The La^{3+} II luminescence at 4.08 eV band is excited mostly in the band with maximum at 7.56 eV (164 nm) (Fig. 2a) which is located in the exciton range. The excitation spectra of the 3.76 eV luminescence band (Fig. 2b) also contain the intensive band with maximum at 7.53 eV (164.5 nm), which dominates in the spectrum of the slow component (curve 3), and the band peaking at 7.1 eV (174 nm), which is more intensive in the spectrum of the fast component (curve 2). The latter band is not related to the La II presence and is caused by the short-wavelength emission band of Pb^{2+} flux-related trace impurity, peaked at 3.26 eV with a decay time of several ns [18,19].

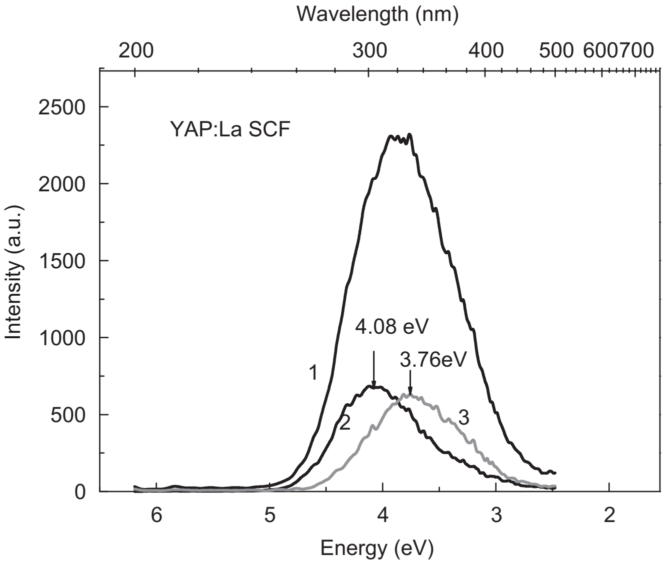

Fig. 1. Emission spectra of YAP:La SCF under excitation by SR with an energy of 7.55 eV at 9 K, measured in time intervals 0–200 ns (1), 1.2–6.2 ns (2) and 150–200 ns (3), after ending of the SR pulse.

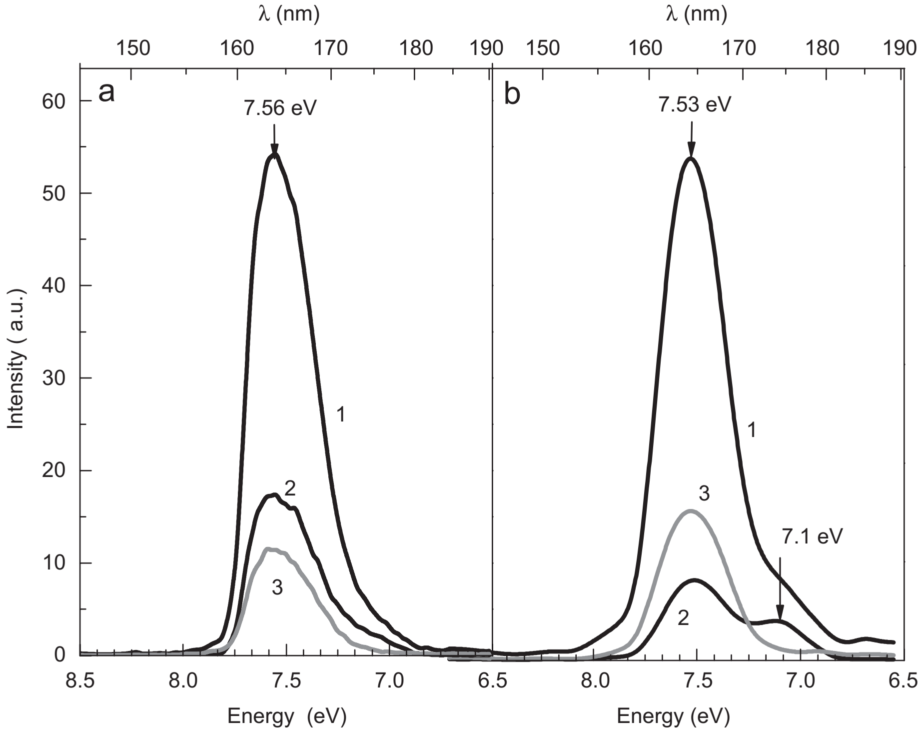

Fig. 2. Excitation spectra of YAP:La SCF at a wavelength of 300 nm (a) and 380 nm (b) at 9 K measured in time intervals 0–200 ns (1), 1.2–6.2 ns (2) and 150–200 ns (3), after ending of the SR pulse.

Due to the practically the same excitation spectra of the 4.08 and 3.76 eV bands in the exciton range (Fig. 2a and b, respectively), we assumed that these bands correspond to the emission of a single center, i.e., they are caused by the transitions from the different branches of the relaxed exited states (RES) of this center with substantially different transition dipole moments similarly to the singlet (σ) and triplet (π) components in the luminescence decay of self-trapped excitons (STE) in alkali halides [22] and some simple oxides [23,24]. At the same time, spectral positions of the corresponding excitation bands of STE luminescence in the undoped (7.88 eV) YAP SCF and exciton emission in La-doped (7.53 eV) YAP SCF differ substantially. Due to the large concentration of the $\mathrm{La}_{\mathrm{Y}}^{3+}$ centers, this fact enables us to ascribe the 4.08 and 3.76 eV luminescence bands in YAP:La SCF to the emission of the bound excitons localized in the vicinity of II. As a result, the energy levels of such excitons perturbed by the presence of La^{3+} II and resulting excitation and emission spectra of this center will shift to the lower energies with respect to the STE luminescence in undoped YAP SCF [25].

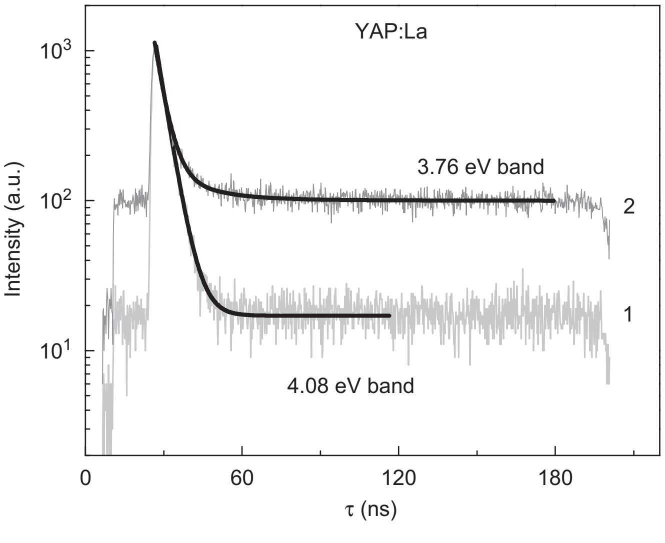

Fig. 3. Luminescence decay of YAP:La SCF at a wavelength of 280 nm (1) and 350 nm (2) under excitation by an SR energy of 7.6 eV at 9 K. Decay curves 1 and 2 for the 4.08 and 3.76 eV emission bands are approximated by the functions $I(t) = 1097\exp(-t/4.04\,\mathrm{ns}) + 13.56\exp(-t/17{,}481\,\mathrm{ns}) + 3.8$ and $I(t) = 953\exp(-t/3.53\,\mathrm{ns}) + 77.6\exp(-t/12.6\,\mathrm{ns}) + 95.5\exp(-t/2407\,\mathrm{ns}) + 18$, respectively. The fits are given by the solid lines.

The luminescence decay kinetics in the 4.08 and 3.76 eV bands measured at wavelengths of 280 and 350 nm is shown in Fig. 3, curves 1 and 2, respectively. Due to the significant overlap of the 4.08 and 3.76 eV bands, their decay kinetics presents a superposition of the components related to both these emissions. Specifically, the decay curve of the 4.08 eV emission can be well fitted by two-component dependence (see caption to Fig. 3, curve 1) and consists of the main fast component with a lifetime of 4.04 ns and a slow tail that is probably caused by the significant overlap of the 4.08 eV band with the slow 3.76 eV-band.

The luminescence decay kinetics of the 3.76 eV band can be well fitted by the three-component dependence (caption to Fig. 3, curve 2). Since the initial part of the decay curve of the 3.76 eV band practically coincides with the decay curve of the 4.08 eV band, the fast component of the luminescence with a lifetime of 3.53 ns probably most is related to the latter emission. At the same time, since the dominating band in the spectrum of the slow emission component under excitation at 7.6 eV is the 3.76 eV band (Fig. 1, curve 3), the middle component with a lifetime of 12.6 ns and the slowest component with the calculated lifetime ~2400 ns can be related exclusively to this band.

Thus, the presence of two components in the luminescence decay of La^{3+} centers at 9 K: the fast (3.76–4.04 ns) and main slow (2407 ns) with more than 97% contribution in the overall emission gives an additional support for the formation of singlet and triplet states of excitons related to this center. In turn, the triplet state of exciton consists of at least two radiation levels with the lifetime of emission components in the ten ns and several μs ranges. However, due to the high repetition frequency of the SR pulse and necessarily narrow observation time gate (200 ns), the decay times of the longer components of La^{3+} emission cannot be well evaluated.

It is worth noting that similar multi-component luminescence decay has been recently observed in other oxide compounds doped with II, in particular, in the Sc^{3+} emission in the Al_2O_3 [6], and has been explained by the radiation decay of an exciton, which is formed in Al_2O_3:Sc from the 2p-type hole localized at the single-charged O^- ions and electron localized at the mixed 3p-states of Al^{3+} and 3d-states of Sc^{3+}. Such a decay kinetics is also typical for the luminescence of excitons bound with the II and AD as a analogue of II in garnets, particular by for the La^{3+} II luminescence in LuAG:La SCF [10] and Y_{Al} and Lu_{Al} AD in YAG and LuAG SC [26].

Hence, the luminescence in the 4.08 and 3.76 eV bands is the luminescence of excitons localized directly at the La_Y centers. It is worth noting that positions of the excitation maxima at 7.56 eV of the 4.08 eV band and 7.53 eV of the 3.76 eV band correspond to the energy positions of the local levels formed by the La_Y centers in the forbidden gap of YAP. Due to early low-temperature quenching of the 4.08 and 3.76 eV emission bands, the La^{3+} II at the c-sites of Y^{3+} cations form a rather shallow trap level for charge carrier localization. Since the bottom of the YAP conduction band is formed by the 4s- and 5d-states of Y^{3+} [27], the substitution of the Y^{3+} cations in the octahedral position by La^{3+} ions with the larger-than-Y^{3+} ionic radius leads to the formation of the La_Y^{3+} centers, which may serve as electron trapping centers [2,3].

3.2. Luminescence of Sc^{3+} II in YAP SCF

The luminescence spectra of YAP:Sc SCF at 300 K (a, b) and 9 K (c, d) under excitation by SR with energies of 7.69–7.64 eV (161–162 nm) and 7.35–7.24 eV (168.5–171 nm) in the exciton range are shown in Fig. 4. As seen from these figures, the doping with Sc^{3+} II results in appearance of the complex luminescence band in the UV range with maximum at 4.27 eV at 300 K and 4.35 eV at 9 K. Using the time-resolved emission spectroscopy (Fig. 4a–d) and Gaussian decomposition of curve 1 in (c) and (d) parts into two components, three sub-bands can be distinguished in the integral luminescence spectrum of the YAP:Sc SCF (Fig. 4, curve 1) caused by the Sc^{3+} II: (i) the band peaking at 4.30 eV (288 nm) at 9 K and 4.26 eV (290.5 nm) at 300 K which dominates in the emission spectra of the fast component at 9 K (Fig. 4c and d, curves 2); (ii) the band at 4.13 eV (300 nm) dominating in the luminescence of the slow component at 300 K (Fig. 4a and b, curves 3); (iii) the band with maximum at 4.72 eV (262 nm) of low intensity that is present only in the luminescence of the fast components at 9 K (Fig. 4c, curve 2). It is necessary to note that close position of the emission bands at 4.26 and 4.13 eV at 300 K (Fig. 4a and b, curves 2 and 3) supports their ascription to a single luminescent center, e.g., similarly to La-related center. This conclusion is also supported by the fact that the ratio between the intensities of these bands is weakly changed under the excitation in different parts of excitation spectra, particularly at 7.64 and 7.23 eV (Fig. 4a and b, curves 2 and 3, respectively). Thus, one can assume that the Sc^{3+}II create in YAP SCF at least two luminescence centers.

The excitation spectra of the luminescence of YAP:Sc SCF at wavelengths of 290 nm at 300 K and 280 nm at 9 K measured in different time gates are presented in Fig. 5a and b, respectively. As follows from the integral emission spectra, the Sc^{3+} II luminescence is excited in the wide complex band peaking at 7.41 eV at 300 K (Fig. 5a, curve 1) and 7.92 eV at 9 K (Fig. 5b, curve 1) in the exciton range, which apparently corresponds to the energy of creation of excitons localized around the Sc^{3+} II in the different sites of YAP lattice. It should be noted that the 7.46 eV maximum in the excitation spectra of the slow component at 300 K (Fig. 5a, curve 3) more probably corresponds to the excitation band of the luminescence in the 4.13 eV band that dominates in the emission spectra of YAP:Sc SCF at RT (Fig. 4a and b, curves 3). This maximum is low-energy shifted with respect to the maximum (7.33 eV) of the fast component (Fig. 5a, curves 3 and 2, respectively). Similarly, the band peaking at 7.92 eV in the excitation spectrum of integral and fast emission components of YAP:Sc SCF at 9 K (Fig. 5b, curve 3) can be attributed mainly to excitation of the luminescence in the 4.72 eV band that dominates in the emission spectra of the fast components at 9 K (Fig. 4c, curve 2). The position of the maximum of the slow components is slightly high-energy shifted by 0.03 eV with respect to the maximum of the fast component (Fig. 5b, curves 3 and 2, respectively). The excitation band peaking at 7.03 eV (176 nm), which is more intensive in the spectrum of the fast component (curve 2), is not related to the Sc II and is most probably caused by the short-wavelength emission band of the Pb^{2+} trace impurities peaking at 380 nm [18,19].

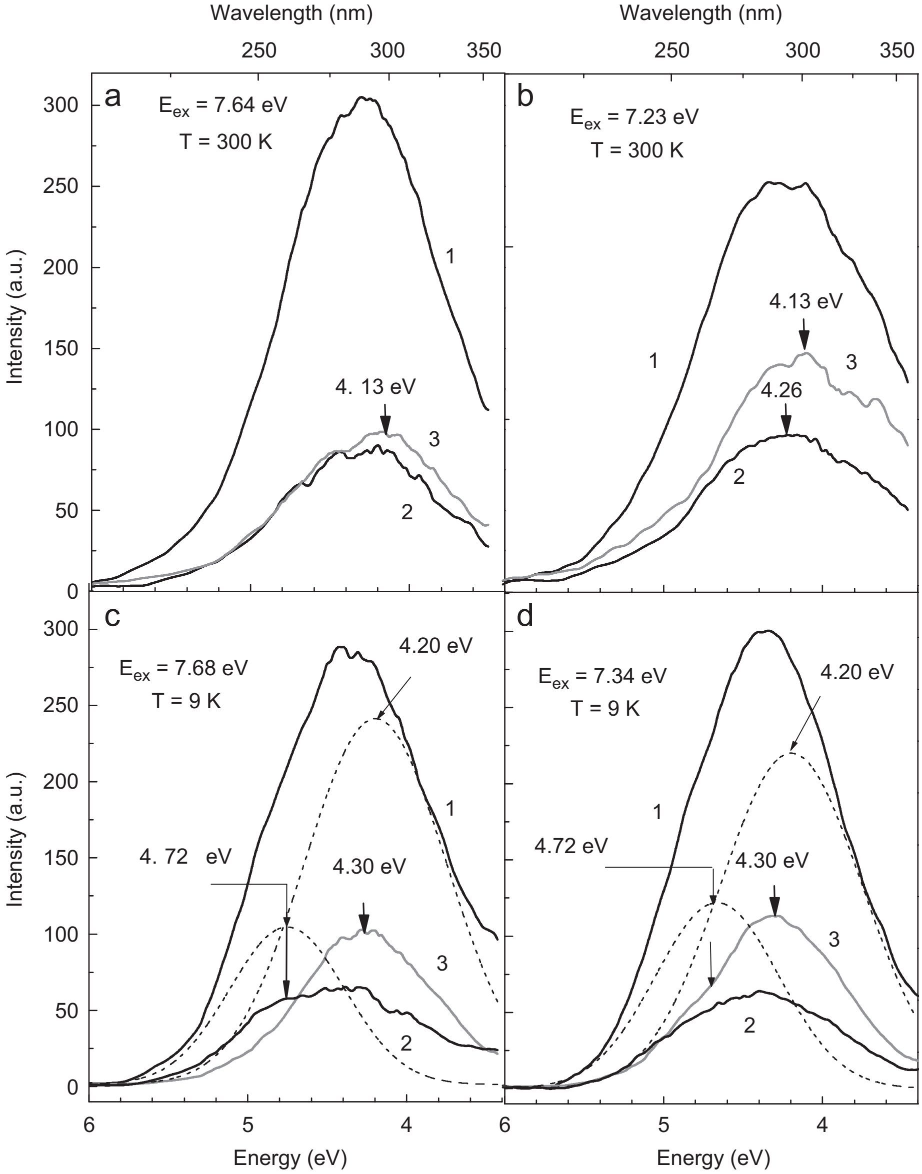

Fig. 4. Emission spectra of YAP:Sc SCF at 300 K (a, b) and 9 K (c, d) under excitation by SR with an energy of 7.64 eV (162 nm) (a), 7.24 eV (171 nm) (b), 7.69 eV (161 nm) (c) and 7.35 eV (168.5 nm) (d) measured in time intervals 0–200 ns (1), 1.2–6.2 ns (2) and 150–200 ns after ending of the SR pulse. The dashed curves are separate Gaussian components obtained in two-gaussian decomposition of curve 1 in (c) and (d).

Due to the spectral location of the above-mentioned excitation bands of the 4.72 and 4.13 eV luminescence in the exciton range (Fig. 5a and b) [10,11], the creation of bound-state excitons localized at the Sc II in the different sites of perovskite lattice are expected in the YAP:Sc SCF, with the corresponding energy of their formation being equal to 7.92 and 7.41 eV, respectively.

This assumption is confirmed by the luminescence decay kinetics of YAP:Sc SCF in the 4.72 and 4.13 eV bands at 9 K and 300 K under excitation within the complex excitation bands (Fig. 6a and b, curves 1 and 2, respectively). Due to the significant overlap of the 4.72 and 4.13 eV luminescence bands, the decay kinetics of these bands was measured under excitation in the 7.69–7.64 and 7.35–7.24 eV ranges, respectively (Fig. 6a and b), which are close to the position of excitation maxima of the mentioned emission bands at 7.92 and 7.41 eV at 9 K and 300 K, respectively (Fig. 5a and b).

Similarly to the decay kinetics of La_Y^{3+} centers, the decay kinetics of the 4.72 eV band at 9 K (Fig. 6, curve 1) can be considered as a superposition of the main fast component with a lifetime of 2.15 ns and the slow tail related to the long-living components of the 4.72 eV luminescence. Since the dominating band in the fast component emission spectrum YAP:Sc SCF at 9 K under excitation at 7.69 eV is the 4.72 eV band (Fig. 4c, curve 2), the fast component with a lifetime of 2.15 ns is related to this band. Increasing the temperature to 300 K leads to a notable decrease of the fast component intensity and increase in the contribution of the slow component of the 4.72 eV emission band (Fig. 6,

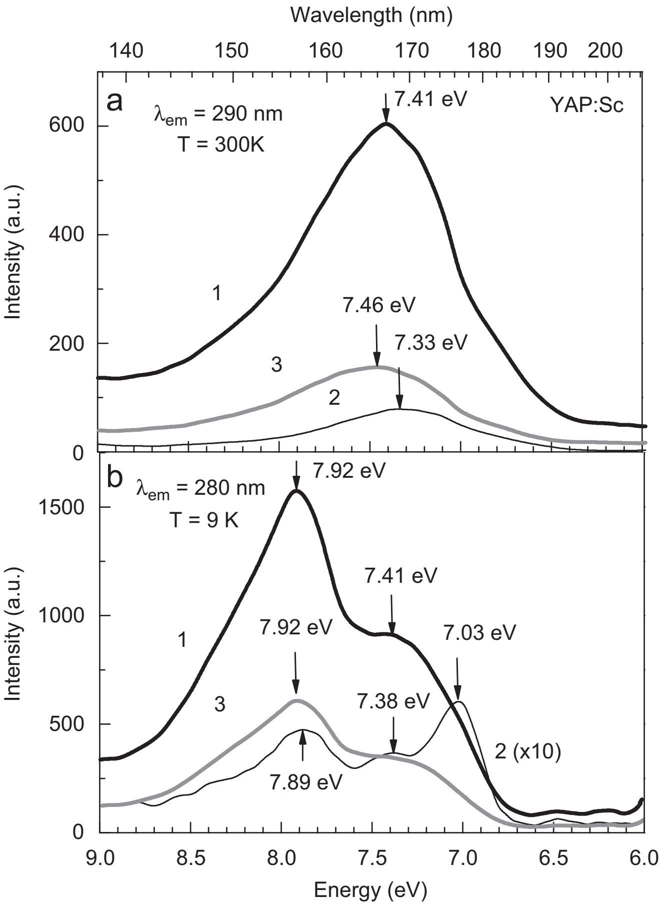

Fig. 5. Excitation spectra of YAP:Sc SCF at a wavelength of 290 nm at 300 K (a) and 280 nm at 9 K (b) measured in the time intervals 0–200 ns (1), 1.2–6.2 ns (2) and 150–200 ns after ending of the SR pulse.

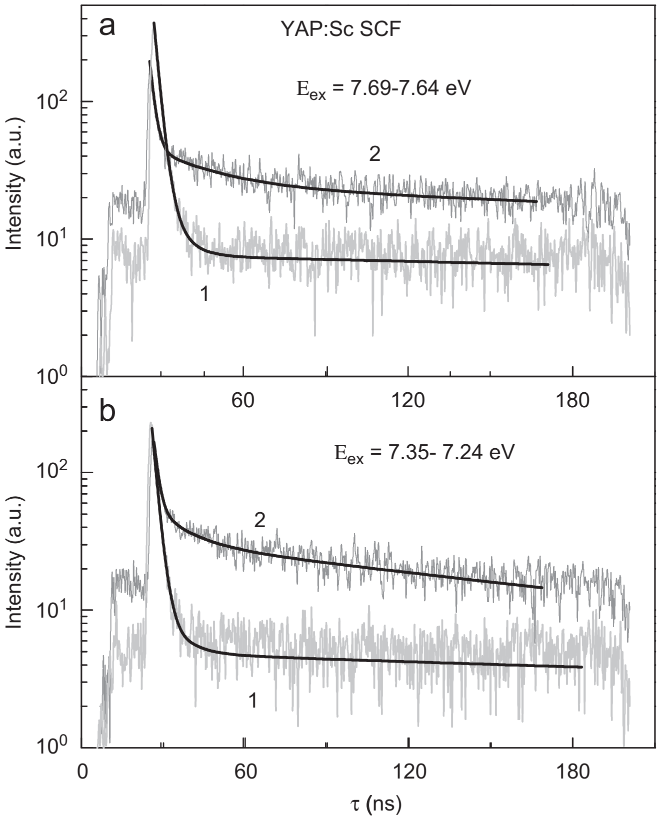

Fig. 6. (a) Luminescence decay kinetics of YAP:Sc SCF at a wavelength of 275 nm (1) and 280 nm (2) under excitation by SR with an energy of 7.69–7.64 eV at 9 K (1) and 300 K (2). Decay curves 1 and 2 are approximated by the functions $I_{9\,K}(t) = 350.8\exp(-t/2.15\,ns) + 6.5\exp(-t/577\,ns) + 1.5$ and $I_{300\,K}(t) = 2.0 + 149.8\exp(-t/1.5\,ns) + 21.7\exp(-t/22.6\,ns) + 22.2\exp(-t/494\,ns)$, respectively; (b)-luminescence decay kinetics of YAP:Sc SCF at a wavelength of 300 nm (1) and 310 nm (2) under excitation by SR with an energy of 7.35–7.24 eV at 9 K (1) and 300 K (2). Decay curves 1 and 2 are approximated by the functions $I_{9\,K}(t) = 198.2\exp(-t/2.00\,ns) + 6.5\exp(-t/305\,ns) + 1.5$ and $I_{300\,K}(t) = 2.3 + 149.8\exp(-t/1.45\,ns) + 24.2\exp(-t/11.5\,ns) + 28.9\exp(-t/166\,ns)$, respectively. All fits are given by the solid lines.

curve 2). Approximating the decay curve of the 4.72 eV band measured at 280 nm at 300 K under excitation by SR with energies of 7.64 eV (Fig. 6a, curve 2) as a superposition of three components enables to estimate the lifetimes and contributions of the fast (1.5 ns) and the slow (22.6 ns and 494 ns) emission components. Specifically, at RT in the emission decay of the 4.72 eV band, the slow components dominate (Fig. 6, curve 2) with corresponding calculated lifetimes of 22.6 and 494 ns. Increasing the temperature to 300 K also leads to a notable shortening of the lifetimes of the fast components of 4.72 eV band emissions from 2.15 to 1.5 ns.

The decay kinetics of YAP:Sc SCF in the 4.30–4.26 eV and 4.13 eV bands is slightly changed with respect to the luminescence decay of the 4.72 eV band (Fig. 6). The decay curves of the above-mentioned bands measured at 300 and 310 nm at 9 K and 300 K (Fig. 6b, curves 1 and 2), respectively, under excitation by SR with energies of 7.35–7.24 eV, can also be considered as a superposition of the fast and slow components at 9 K and the fast and two slow components at RT, respectively, and approximated by the corresponding expressions (see caption to Fig. 6). The component with $\tau = 2.0$ ns, which is dominant in the spectra of fast component at 9 K under excitation at 7.35 eV (Fig. 4d, curve 2), can be attributed to the fast luminescence in the 4.30 eV band. Increasing the temperature to 300 K also leads to the shift of this band to 4.26 eV, decrease of its intensity and contribution in the overall emission, and shortening of the corresponding lifetimes of the fast component from 2.0 to 1.45 ns. Since at RT the dominating band in the slow component emission of the YAP:Sc SCF under excitation at 7.24 eV is the 4.13 eV band (Fig. 4b, curve 3), the intermediate component with a decay time of 11.5 ns and the main slow component with a decay time of 166 ns can be related to this band.

Thus, similarly to YAP:La SCF, existence of two main components in the luminescence decay of 4.72 and 4.30–4.13 eV bands in YAP:Sc SCF gives an evidence of the creation of two types of excitons bound around the Sc II with the RES in the form of the singlet and triplet emitting levels. However, due to narrow observation time gate (200 ns), we can only estimate the fast (in the 10 ns range) and intermediate (in the 100 ns range) components of triplet exciton emission, while the third longer components of Sc^{3+} emission cannot be evaluated.

The difference in the spectral positions of Sc-related bands excited in different parts of the exciton region (7.41 and 7.92 eV, respectively), as well as the decay with different emission lifetimes of 494 and 166 ns for the main slow components at 300 K, respectively, also confirm the above-mentioned assumption that Sc II form two different luminescence centers in YAP:Sc SCF: the "shallower" ones, emitting at 4.72 eV in the low-temperature region, and "deeper" ones, emitting in the 4.26 and 4.13 eV bands at RT. Similarly to the La^{3+}-related bands, the two-component emission spectra and the multi-component luminescence decay of Sc-related bands with the dominating fast components in the ns range at 9 K and the prevailing slow components in the 100 ns range at RT are typical for the radiative recombination of the bound excitons localized directly at the II or AD [6,25,26]. Taking into account the possible variability of replacement of host cations by Sc^{3+} ions also in perovskites, one can suppose that the Sc^{3+} II forms the mentioned luminescence centers due to two different substitution sites in the YAP lattice, provided by the Y^{3+} and Al^{3+} cations. In our previous works [9,10], we have shown that Sc^{3+} II of LuAG:Sc SCF in the dodecahedral sites of Lu^{3+} cations of garnet lattice create a "deeper" Sc^{3+}_{Lu} radiative recombination center with respect to the more "shallow" Sc^{3+}_{Al} center. One can assume by analogy with investigation of the luminescence of YAG:Sc and LuAG:Sc SCF [3,9,10] that the luminescence band of YAP:Sc SCF peaking at 4.26 eV (fast component) and 4.13 eV (slow component), which dominates at RT, is caused by "deeper" Sc^{3+}_{Y} centers, whereas the 4.72 eV emission band at 9 K is due to more "shallow" Sc^{3+}_{Al} centers.

The mechanism of excitation of the La^{3+}_{Y}, Sc^{3+}_{Y} and Sc^{3+}_{Al} centers emission in YAP SCF is presented in Fig. 7. Excitation of the luminescence of La^{3+}_{Y} and Sc^{3+}_{Y} or Sc^{3+}_{Al} centers occurs by creation of bound-state excitons localized around an impurity, with the corresponding energy of formation being equal to 7.56–7.53, 7.41 and 7.92 eV, respectively. Due to the difference in ionic radii, in the structure of electronic shell and ionic cores, as well as in the third ionization potentials between the Sc^{3+} and Y^{3+} or Al^{3+} cations, Sc^{3+}_{Y} and Sc^{3+}_{Al} form the electronic and hole trapping centers, respectively [2,3]. In the framework of this assumption, the excitons localized at Sc^{3+}_{Y} centers are formed due to the transition between the 2p-oxygen states of the upper part of the valence band (VB) and the separated level formed by the Sc^{3+} II in the c-sites of Y^{3+} cations, whereas the excitons localized at Sc^{3+}_{Al} centers are formed due to the transition between the separated level created by the Sc^{3+} II in the a-sites of Al^{3+} cations and the bottom of the conductive band (CB) formed by the 4s + 5d states of Y^{3+} cations [27].

The excitons localized at the La^{3+}_{Y}, Sc_{Y} and Sc_{Al} centers have RES composed from one and three radiative levels (singlet and triplet excitons, respectively). De-excitation of such excitons is a cause of the luminescence of YAP:La SCF in the bands peaking at 4.08 and 3.76 eV (singlet and triplet emissions, respectively). Similarly, the de-excitation of excitons bound around Sc^{3+}_{Y} and Sc^{3+}_{Al} centers in YAP:Sc SCF is a cause of the luminescence, respectively, in the band peaking at 4.72 eV (singlet emission) and in the bands peaking at 4.26–4.30 and 4.13 eV (singlet and triplet emission, respectively). Existence of two types of excitons bound around II with different transition dipole moments results in appearance of the single-exponential fast (2–4 ns) and at least two-exponential slow components (11.5–22.6 and 166–494 or even 2407 ns) in the luminescence decay of YAP:Sc and YAP:La SCF.

4. Conclusion

The luminescence of YAP SCF doped with La^{3+} II in the complex band at 3.87 eV (320 nm) at 9 K results from formation and radiative de-excitation of an exciton bound with La^{3+}_{Y} centers. The complex band of the YAP:La SCF luminescence is a superposition of two emission bands decaying with different times, attributed to the emission from different RES of excitons localized at La^{3+}_{Y} centers. The short-wavelength component of the UV luminescence

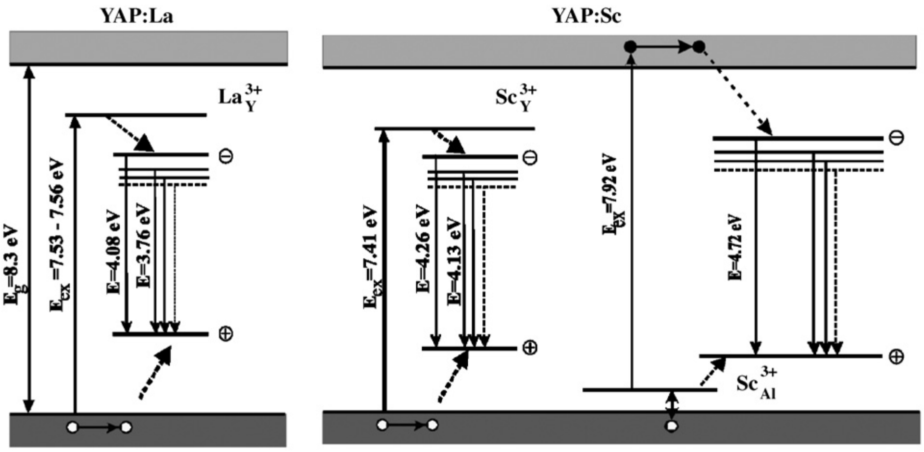

Fig. 7. Scheme of excitation of luminescence of La- and Sc-related centers in YAP SCF.

band located at 4.08 eV (303 nm) and decaying with a lifetime of 4.05 ns is attributed to the emission of singlet exciton, whereas the long-wavelength band located at 3.76 eV (329 nm) and decaying with the dominant lifetime in the hundred ns–μs range is caused by the triplet exciton emission. Single and triplet excitons related to the La_Y^{3+} centers are effectively created at energies of 7.53 and 7.56 eV, respectively.

The luminescence of YAP SCF doped with Sc^{3+} II in the complex band in the UV range at 9 K is a superposition of several emission bands resulting from the formation and radiative de-excitation of an exciton bound with Sc_Y^{3+} and Sc_{Al}^{3+} centers, respectively. The emission band peaking at 4.72 eV (262 nm) with a fast component lifetime of 2.15 ns at 9 K and a main slow component lifetime of ~500 ns at 300 K is attributed to the luminescence of Sc_{Al}^{3+} centers. The band peaking at 4.26 eV (291 nm) with a fast component lifetime of 2.0 ns at 9 K and main slow component peaking at 4.13 eV (300 nm) with a lifetime of 166 ns at 300 K are caused by the luminescence of Sc_Y^{3+} centers. The kinetics of the luminescence decay of Sc_Y^{3+} and Sc_{Al}^{3+} centers, which is characterized by the presence of the fast (1.45–1.5 ns) and the main slow (166–464 ns) components at 300 K, indicates the creation of singlet and triplet excitons, localized at the mentioned centers. The corresponding energies of creation of excitons localized at Sc_Y^{3+} and Sc_{Al}^{3+} centers are 7.42 eV at 300 K and 7.92 eV at 9 K, respectively.

It should be noted that light yield of the luminescence of centers formed by La^{3+} and Sc^{3+} II in Y–Al perovskite is considerably less (by one order of magnitude) than that of the analogous $La_Y^{3+}$and Sc_Y^{3+} centers in Y–Al garnet at RT [3,4]. This is likely due to localization of these II in the large 12-oxygen coordinated cation sites in the perovskite structure, which results in formation of the substantially "shallower" trapping levels in the forbidden band of YAP, as compared to YAG and LuAG, where localization of II at the smaller 8-coordinated dodecahedral cation sites in the garnet lattice takes place [1–5]. In YAP SCF, it results in considerable temperature quenching of the La^{3+} and Sc^{3+} II luminescence and decrease of its light yield at RT range.

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