Time-Resolved Luminescence Spectroscopy of Pure and Doped with Ce^{3+} Ions SrAlF_5 Crystals¹

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Abstract—The results of a study of time-resolved photoluminescence (PL) and energy transfer in both pure and doped with Ce^{3+} ions SrAlF_5 (SAF) single crystals are presented. The time-resolved and steady-state PL spectra in the energy range of 1.5–6.0 eV, the PL excitation spectra and the reflectivity in the energy range of 3.7–21 eV, as well as the PL decay kinetics were measured at 8.8 and 295 K. The lattice defects were revealed in the low temperature PL spectra (emission bands at 2.9 and 4.5 eV) in the undoped SAF crystals. The luminescence spectra of the doped Ce^{3+} :SAF crystals demonstrate a new selective emission bands in the range of 3.7–4.5 eV with the exponential decay kinetics ($\tau \approx 60$ ns at X-ray excitation). These bands correspond to the d – f transitions in Ce^{3+} ions, which occupy nonequivalent sites in the crystal lattice.

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1. INTRODUCTION

SrAlF_5 crystal (SAF) has recently become one of the most promising candidates for the realization of all-solid-state lasers and nonlinear optical devices operating in the ultraviolet (UV) and vacuum ultraviolet (VUV) energy ranges. It has been shown that SAF is highly transparent down to the cutoff wavelength at about 150 nm. The SAF band gap was estimated at about 12 eV [1, 2]. However, there are only few works devoted to the spectroscopic study of the rare earth ions in the SAF host lattice [3–5]. The main goal of the present work is a study of the lattice defects and impurity centers in both the pure and Ce^{3+} -doped SAF crystals by the use of the low-temperature optical and luminescent VUV spectroscopy with time resolution. The preliminary results of our research were presented in [6].

2. EXPERIMENTAL TECHNIQUE AND METHODS

The time-resolved, time-integrated spectra and decay kinetics of photoluminescence (PL) in the energy range 1.3–6.0 eV, time-resolved PL excitation spectra (3.7–21 eV) were measured using synchrotron radiation at SUPERLUMI station (HASLAB, DESY). The registration system comprised of 0.3 m ARC Spectra Pro-300i monochromator and R6358P (Hamamatsu) photomultiplier with multi-alkali photocathode. Simultaneously with the time-integrated luminescence spectra, the spectra in the two time win-

dows were registered: for the fast component delay time was $\delta t_1 = 2.8$ ns, width of time window $\Delta t_1 = 14.4$ ns, for the slow component delay $\delta t_2 = 120$ ns, width $\Delta t_2 = 60$ ns. PL excitation spectra were normalized to equal number of photons irradiating the sample using sodium salicylate. The time resolution of the registration system is approximately 1 ns. Crystals were grown from the corresponding metal fluorides by the use of Czochralsky technique in the Institute of Geology and Mineralogy, Siberian Branch of RAS. The SrAlF_5 crystal belong to the tetragonal symmetry group (the point symmetry group is C_{4h} , the space symmetry is $I4_1/a$ or C_{4h}^6 on Fedorov) [5].

3. EXPERIMENTAL RESULTS

SrAlF_5 . The PL emission spectra of the nominally pure SAF crystals at $T = 300$ K contain the broad band with the maximum at 3.1 eV (FWHM = 0.84 eV). The peak maximum is shifted in energy to 2.9 eV and a new band at 4.5 eV appears at low temperatures. The time-resolved PL spectra show that the maximum of the fast component in 2.9 eV emission band is blue shifted in energy by 50 meV, whereas all the spectra components of the 4.5 eV band match in profiles almost exactly. The PL decay kinetics at 2.95 eV band involves both the exponential component with $\tau = 42$ ns and slow component of the microsecond time-range, in the 4.5 eV emission band the fast component with $\tau = 3.5$ ns dominates (inset at Fig. 1). Both emission bands have absolutely distinct excitation spectrum. They can be excited efficiently over the optical transparency band of a crystal, and with decreased efficiency in the vicin-

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Fig. 1. Time-resolved PL spectra of pure SAF crystals, $E_{\text{exc}} = 7.7$ eV, $T = 8.8$ K: (1) time-integrated spectrum, (2) fast component, (3) slow component. The PL spectra of SAF crystal after X-ray irradiation, $E_{\text{exc}} = 3.35$ eV (4) and 4.45 eV (5), $T = 90$ K. Insert: PL decay kinetics of SAF crystals at $T = 8.8$ K: $E_{\text{exc}} = 10.96$ eV, $E_{\text{em}} = 3.0$ eV (6) and 4.5 eV (7).

Fig. 2. Time-resolved PL excitation spectra of pure SAF crystals, $E_{\text{em}} = 3.0$ eV, $T = 8.8$ K: (1) time-integrated spectrum, (2) fast component, (3) slow component; (4) reflection spectrum.

ity of the fundamental absorption edge and in the energy range of the band-to-band transitions (Fig. 2, 3). It is notable, that from the reflection spectrum (Fig. 2, curve 4) it follows that the SAF energy gap can be estimated at about $E_g = 12.3$ eV, whereas the 11.76 eV

peak, apparently, should be assigned to the excitonic states. This assessment of E_g is in line with that of other investigators [2].

X-rays exposure leads to creation of the luminescence centers, which form emission bands in the low-

Fig. 3. Time-resolved PL excitation spectra of pure SAF crystals, $E_{em} = 4.5$ eV, $T = 8.8$ K: (1) time-integrated spectrum, (2) fast component, (3) slow component; (4) reflection spectrum.

temperature PL spectra at 1.95 and 2.54 eV (Fig. 1). Their PL excitation spectra differ entirely from that discussed above (Fig. 2, 3). These centers do not manifest themselves in the PL emission spectra at excitation energies $E_{exc} > E_g$. Under irradiation with X-rays, the luminescence spectrum coincides in profile with the PL emission spectrum of the undoped SAF crystal. In addition, the effective thermally stimulated luminescence (TSL) peaks at 235, 320 and 405 K (activation energies of 0.36, 0.67 and 1.08 eV, respectively) appears on heating the SAF crystal irradiated previously with X-rays at 90 K.

Ce:SrAlF₅. The Ce^{3+} ions do not manifest themselves in the optical absorption spectra. Under X-ray excitation at 300 K, several new luminescence bands appear in the ultraviolet energy range, having maxima in the region 3.7–4.5 eV. These bands dominate also in the PL emission spectra (Fig. 4). The intensities of the ultraviolet PL emission bands depend only slightly on a temperature over the range 90–450 K. The new 2.72 eV emission band appears in the PL spectrum at $T = 90$ K and a specific structure of the spectrum profile becomes more remarkable. Each UV emission band has its own specific PL excitation spectrum, Fig. 5 provides several examples of such spectra. At the same time, PL excitation spectrum of the 2.72 eV band differs sufficiently from the other bands and it demonstrates broad weak bands and an increase of intensity towards the VUV range. Under electron beam excitation the luminescence decay kinetics of the UV-bands in the 3.7–4.5 eV region does not depend on a temperature over the range from 90 to 300 K. The decay kinetics involves only the fast component with

$\tau = 60 \pm 5$ ns and it does not demonstrate any slow components of the microsecond range.

Figure 6 represents the glow curves measured on heating after an exposure with X-rays at 90 K. The curves for pure and doped crystals show different sets of the peaks appeared at 108–115, 182–195, and 422–430 K. It should be noted that the emission spectra of the TSL peaks in doped Ce:SAF crystals appear in the energy range peculiar to an emission of the Ce^{3+} ions (Fig. 6, curve 2).

4. RESULTS DISCUSSION

From the above mentioned it follows that the undoped SAF crystals exhibit the PL on photoexcitation mainly in the optical transparency band at $E_{exc} < E_g$ (Fig. 2, 3). In doing so, the PL spectrum profile does not depend on the exciting photon energy. In this connection, the 2.9 and 4.5 eV emission bands in the PL spectrum should be assigned to a luminescence of the lattice defects, created during the crystal growth process. In the PL spectra no self-trapped excitonic states is revealed. All the differences in the PL spectra of the fast and slow components as well as the shape and parameters of the PL decay kinetics points to the manifestations of the radiative transitions from the singlet and triplet excited states of two luminescence centers. However, the observed excitation at $E = 2.95$ eV and, in particularly, 4.5 eV bands with photons over the excitonic energy range (peaks at 11 eV in the PL excitation spectrum, Figs. 2, 3) suggest that the lattice defect emission at low temperatures can be excited not only directly by photons of $E_{exc} < E_g$, but through creation of the bound excitons as well. Moreover, the lumi-

Fig. 4. PL spectra of Ce:SAF (0.5 at %), $T = 90$ K, $E_{\text{exc}} = 4.64$ eV (1), 4.9 eV (2), 5.78 eV (3).

Fig. 5. PL excitation spectra of Ce:SAF, $T = 90$ K, $E_{\text{em}} = 3.68$ (1), 4.52 (2) and 2.72 eV (3).

nescence of these defects can be effectively excited through the electron-hole recombination process.

The SAF crystals exhibit low lattice stability under action of an ionizing radiation, an exposure with X-rays leads to a creation of new lattice defects

through the ionizing mechanism of a defect creation. New luminescence centers, based on the radiation-induced defects, manifest themselves in the low energy part of the PL spectra (emission bands at 1.92 and 2.54 eV). As the fluoride ions have a lowest binding

Fig. 6. Thermoluminescence glow curves of Ce:SAF crystals, irradiated by X-rays at $T = 90$ K: integrated emission registered in the range $E = 2.0\text{--}6.0$ eV (1), emission registered through monochromator in the bands 4.5 eV (2), and 2.9 eV (3).

energy, a creation of such defects can be dominant in the anion sublattice of SAF.

All the features and parameters discussed above for the UV emission of the Ce:SrAlF₅ crystals match exactly that known for the Ce³⁺ ion luminescence in various host lattices, and allow to interpret the UV emission as luminescence of the Ce³⁺ ions substituting the cations in the host lattice. The Ce³⁺ ion luminescence in Ce:SAF results from the interconfigurational $5d\text{--}4f$ transitions in the Ce³⁺ ion. Because of significant difference between the ionic radii of the isovalent Al³⁺ and Ce³⁺ ions, the Ce³⁺ impurity ion should substitute the Sr²⁺ host ion. This suggestion is based on [5], where it was found for the SAF crystals that the Sm and Pr impurity ions substitute namely the Sr²⁺ host ion. In addition, on the basis of the crystallographic investigations in [5] it was also shown that the Sr²⁺ ions occupy four nonequivalent positions in the unit cell of the SAF crystal lattice. All above mentioned allow us to assign the UV bands in the PL spectra of Ce:SAF as an emission of the substituting Ce³⁺ ions situated in various nonequivalent sites of the crystal lattice. In doing so, the peaks in the 4.2–5.8 eV energy range in the UV PL excitation spectra (Fig. 6) are due to the interconfigurational transitions from the $4f$ level onto levels of the mixed $4f^{n-1}5d$ configuration of the Ce³⁺ ions. It should be noted that these PL excitation spectra correspond in profile to the optical absorption spectra of Ce³⁺:SAF reported in [4].

However, even in the simplest case, a creation of the cation vacancies of the V_c^{2+} or V_c^{3+} types should accompany the Ce³⁺ $\rightarrow$ Sr²⁺ substitution to ensure a local electro neutrality of a crystal. The additional

2.72 eV emission band appearing only in the low-temperature PL spectra of the doped Ce:SAF crystals might be tentatively assigned to the emission of such cation vacancies.

In conclusion it should be noted that the typical emissions of the Ce³⁺ ions manifest themselves in the luminescence spectra not only under excitation with X-rays, but it appears on heating in the TSL spectra as well. From this it follows that the Ce³⁺ impurity emission on heating appears due to recombination of a delocalized electron with a hole trapped at the impurity ion, i.e. Ce⁴⁺, according to the following reaction: $\text{Ce}^{4+} + e^- \rightarrow (\text{Ce}^{3+})^* \rightarrow \text{Ce}^{3+} + h\nu$.

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