Electronic excitations and luminescence of SrAlF₅ crystals doped with Ce³⁺ ions

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ABSTRACT

This paper reports the results of a time-resolved photoluminescence and energy transfer processes study in Ce³⁺ doped SrAlF₅ single crystals. Several Ce³⁺ centers emitting near 4 eV due to 5d–4f transitions of Ce³⁺ ions substituting for Sr²⁺ in non-equivalent lattice sites were identified. The lifetime of these transitions is in the range of 25–35 ns under intra-center excitation in the energy region of 4–7 eV at $T = 10$ K. An effective energy transfer from lattice defects to dopant ions was revealed in the 7–11 eV energy range. Both direct and indirect excitation channels are efficient at room temperature. Excitons bound to dopants are revealed at $T = 10$ K under excitation in the fundamental absorption region above 11 eV, as well as radiative decay of self-trapped excitons resulting in luminescence near 3 eV.

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1. Introduction

SrAlF₅ (SAF) crystals have recently become promising candidates for the realization of all-solid-state lasers and other non-linear optical applications which operate in the ultraviolet and vacuum ultraviolet (VUV) spectral range. It has been shown that SAF is highly transparent down to the cutoff wavelength near 150 nm. The SAF band gap was estimated to be 12 eV (Villora et al., 2005; Vink et al., 2002). However, there are only few works devoted to the spectroscopical properties of rare earth ions in SrAlF₅ host lattice. Namely, photon cascade emission in the Pr³⁺:SrAlF₅ system (Potapov et al., 2005), the properties of Ce³⁺ ions (Dubinskii et al., 1998) and Sm²⁺ ions by (Penhouet and Hagemann, 2008) have been investigated. Previously we have studied lattice defects and electronic excitations in pure SrAlF₅ crystals (Pustovarov et al., 2008, in press). The main goal of the present work is the investigation of luminescence under direct intra-center excitation of Ce³⁺ ions and through energy transfer processes from the host to dopants by electronic excitations resulting from absorption of VUV photons. A preliminary report on the present research was published in (Omelkov et al., in press).

2. Experiment details

The time-resolved and steady-state photoluminescence (PL) spectra in the 1.5–6.0 eV region, time-resolved PL excitation spectra

(3.7–20.0 eV), and PL decay kinetics were recorded using synchrotron radiation excitation (SR) at the SUPERLUMI station (Beam-line I of HASYLAB at DESY) (Zimmerer, 2007). The 0.3 m ARC SpectraPro-308i spectrometer equipped with a R6358P (Hamamatsu) photomultiplier was used. Simultaneously with time-integrated luminescence, spectra in two time windows with a length of Δt and delayed by δt relative to the exciting SR-pulse were registered. The fast component had the following parameters: $\delta t_1 = 10$ ns and $\Delta t_1 = 21$ ns; the slow component was recorded with $\delta t_2 = 123$ ns and $\Delta t_2 = 35$ ns. The time resolution of the whole detection system was ~ 1 ns (FWHM). The convolution method was used to analyze fast components of the PL decay kinetics. The error of the obtained decay time values was less than 2%.

Crystals have been grown using the Bridgman technique. AlF₃ (99.99) and SrF₂ (99.99) were taken as starting reagents. CeF₃ (99.99) was added as a dopant with concentration of 0.5 mol%. The SrAlF₅ crystals belong to the tetragonal symmetry group (the point symmetry group is C_{4h}, the space symmetry is I41/a or C64 h) (Kubel, 1998).

3. Results

The PL spectra of SrAlF₅:Ce at $T = 10$ K, when excited by photons with energy below 6 eV, do not show any significant differences if compared with the ones measured at $T = 90$ K (Pustovarov et al., 2008). The spectra contain a number of bands around 4.0 eV, and their shape strongly depends on the excitation wavelength (see Fig. 1). The increase of exciting photon energy to the VUV region (8.2 eV) results in the appearance of an additional intense broad

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Fig. 1. Time-integrated PL spectra of SrAlF₅:Ce at $T = 10$ K: $E_{\text{exc}} = 4.6$ eV (1); $E_{\text{exc}} = 5.2$ eV (2); $E_{\text{exc}} = 8.2$ eV (3); $E_{\text{exc}} = 11.2$ eV (4).

luminescence band centered at 2.9 eV. At room temperature, this band shifts to 3.1 eV (Fig. 2). Such behavior was also found for an analogous band in the nominally pure crystal (Pustovarov et al, in press). Practically the same shift was observed at $T = 10$ K, when the excitation energy was increased to 11.2 eV (Fig. 1, curve 4), which corresponds to the excitonic region of SAF crystals. The decay kinetics of this emission contains only slow components. The excitation spectra of different emissions show specific features (see Figs. 3 and 4). The studied spectral range can be divided into three regions. In the low energy region the shape of the spectra is strongly dependent on the excitation wavelength, and short decay times ($\tau = 25$ –35 ns, see inset at Fig. 2) were recorded, which depend on the selected emission (see Table 1).

In the second region (7–11 eV), excitation spectra of UV emissions near 4 eV are similar, only the one at 2.9 eV shows a complementary behavior, i.e. its maxima coincide with the minima of other emissions. The decay kinetics of all emissions becomes slightly shorter. In the intrinsic excitation region (above 11 eV) the decays contain a weak fast component superimposed to the slow processes forming a notable background. A similar phenomenology was observed at $T = 290$ K (see Fig. 5) for the low energy regions. In the fundamental absorption region the luminescence bands near 4.0 eV are practically quenched, and for band-

Fig. 2. Time-integrated PL spectra of SrAlF₅:Ce at $T = 295$ K, $E_{\text{exc}} = 8.05$ eV (1); $T = 10$ K $E_{\text{exc}} = 8.2$ eV (2) and PL spectra of nominally pure crystal $E_{\text{exc}} = 7.7$ eV (3) from Pustovarov et al. (2008). Inset: decay curves of the 3.85 eV emission, $E_{\text{exc}} = 4.60$ eV, (4) and of the 3.99 eV emission, $E_{\text{exc}} = 5.16$ eV (5) at $T = 10$ K.

Fig. 3. Time-integrated PL excitation spectra for different emission bands of SrAlF₅:Ce at $T = 10$ K: $E_{\text{em}} = 3.8$ eV (1), $E_{\text{em}} = 3.95$ eV (2), $E_{\text{em}} = 4.2$ eV (3), $E_{\text{em}} = 2.9$ eV (4).

to-band transitions the luminescence intensity is ~ 25 times weaker than at 10 K.

4. Discussion

As reported in Pustovarov et al. (2008), the UV emission bands in the PL spectra of SrAlF₅:Ce are assigned to 5d–4f transitions of Ce³⁺ ions substituting Sr²⁺ ions in 4 non-equivalent sites of the host crystal lattice. The revealed peaks in the 4.2–5.8 eV energy range in the UV PL excitation spectra (Fig. 5) correspond to inter-configurational transitions from the 4f ground level to 5d configuration of the Ce³⁺ ions. The transitions to higher 6s and 6p states are forbidden and their contribution in the excitation spectra is negligible. In the second spectral region the efficient excitation of PL of Ce³⁺ ions points to the energy transfer channel from the lattice defects to dopant centers. This statement is supported by the fact that the PL excitation spectra of luminescence from defects and Ce³⁺ centers are competing (Fig. 3). A resonance energy transfer mechanism is mostly probable, because in nominally pure SAF crystals an emission band has been found at 4.5 eV (Fig. 2, curve 3), overlapping with the absorption of Ce³⁺ ions. This emission originates from PL of lattice defects (Pustovarov et al., 2008, in press). Another defect emission band in nominally pure SAF crystals peaks at 2.9 eV, when excited in the second spectral region (7–11 eV). These bands are tentatively assigned to the same lattice defect, and

Fig. 4. Time-resolved PL excitation spectra of the 3.95 eV emission band of SrAlF₅:Ce at $T = 10$ K.

Table 1

The PL decay time (in ns) of SrAlF₅:Ce crystals at selected excitation and emission energies ($T = 10$ K).

Excitation energy E_{exc} , eV	Emission energy E_{em} , eV			
	3.79	4.02	4.27	4.47
4.62	35	–	–	–
5.14	–	26	–	–
8.2	30	27	24	24
9.7	30	27	24	24
10.4	29	26	23	23
11.3	28	24	21	19
12.7	18	21	17	13

Fig. 5. Time-integrated PL excitation spectra for different emission bands of SrAlF₅:Ce at $T = 295$ K: $E_{\text{em}} = 3.77$ eV (1); $E_{\text{em}} = 4.0$ eV (2); $E_{\text{em}} = 4.25$ eV (3).

correspond to radiative transitions from its singlet and triplet excited states to the ground state. The competing excitation spectra of these luminescence bands support our viewpoint. The low intensity of the 4.5 eV band, the short decay time and strong temperature quenching point to a high probability of depopulation from the corresponding singlet level. In Ce-doped crystals the resonant energy transfer to the Ce³⁺ ions is obviously the main depopulation channel, because this process is continuously efficient even at $T = 290$ K, while in pure SrAlF₅ the 4.5 eV PL band is totally quenched at such high temperature. In pure SrAlF₅ the self-trapped exciton (STE) emission has not been revealed earlier (Pustovarov et al., 2008). However, in the present study the broad luminescence band at 3.1 eV (Fig. 1, curve 4), observed under excitation by 11 eV photons, is tentatively interpreted as radiative decay of STE. The presence of STE emission was also identified in the SAF crystals doped with other rare-earths like Pr³⁺ (Vink et al., 2002). The decay kinetics, measured on the shoulder of this broad 3.1 eV band in the Ce³⁺ emission region, contain, in addition to the main microsecond-range decay component, a fast component ($\tau \approx 13$ –20 ns) typical for Ce³⁺ luminescence. This is assigned to fast energy transfer from impurity bound excitons, indirectly proving their creation. However, at $T = 10$ K the probability of such

a process is significantly smaller than that of STE creation. Taking into account the need for charge compensation due to extra charge of rare earth ions through lattice defects, bound excitons can be created not only at Ce³⁺ ions, but also at lattice defects even with a smaller probability. At room temperature all the excitonic processes do not play a significant role in energy transfer because of the highly probable thermal dissociation of excitons.

5. Conclusion

The PL and energy transfer processes in Ce³⁺ doped SrAlF₅ single crystals were investigated. The 5d → 4f luminescence of Ce³⁺ ions was revealed. The resonance energy transfer mechanism from the lattice defects to Ce³⁺ ions was identified. At low temperatures, excitation in the fundamental absorption region results in the creation of self-trapped and bound excitons. The efficiency of excitation of various Ce³⁺ centers depends on the exciting photon energy and differs for the intra-center, excitonic and band-to-band excitation regimes.

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