The luminescence of Gd\(^{3+}\) ions in SrAlF\(_5\) host crystal

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Our report presents results of the study of the electronic excitation dynamics, radiative relaxation and energy transport in the Gd\(^{3+}\)-doped SrAlF\(_5\) (SAF) single crystals. The SAF crystals have a high potential for applications as non-linear UV/VUV optical material [1, 2]. Properties of undoped SAF crystals have been studied earlier and the value of energy gap is found to be \(\sim 12.7\) eV [3]. The luminescence and energy transport in Ce\(^{3+}\)-doped SrAlF\(_5\) crystal were also studied [4]. The present study was carried out by the means of time-resolved luminescence spectroscopy in VUV region.

![Figure 1: Time-integrated PL emission spectra (left) and PL excitation spectra (right) of SAF:Gd at T=10 K.](image)

![Figure 2: Time-resolved PL excitation spectra \(E_{\text{em}}=5.63\) eV of SAF:Gd at T=10 K (left) and at various emission energies at T=290 K (right). The fast time window length was 9 ns, delay relative to the exciting SR-pulse – 1.5 ns. Reflection spectrum of undoped SAF crystal is presented for reference from [3]. Inset: PL emission spectra at \(E_{\text{exc}}=10.7\) eV at T=290 K.](image)

Time-resolved and integrated photoluminescence (PL) spectra (in the range of 2-6 eV), PL excitation spectra (in the range of 6-20 eV), and the decay kinetics of PL were recorded for SAF:Gd crystals at the SUPERLUMI station (Beamline I). The 0.3 m ARC SpectraPro-308i spectrometer equipped with the CCD camera for PL spectra recording and R6358P (Hamamatsu) PMT for PL excitation spectra were used as registration system. The PL excitation spectra were corrected using sodium salicylate as a standard. All the examined single crystals were grown from the corresponding metal fluorides at the Institute of Geology & Mineralogy (Novosibirsk, Russia). The Gd\(^{3+}\) concentration (in melt) was 0.5 mass \%.
PL emission spectra of SAF:Gd at T=10 K are presented at Fig.1, and at T=290 K in the inset of Fig. 2. The well-known 312 nm (3.95 eV) emission of Gd$^{3+}$ ions due to the $^6P_{7/2}$ – $^8S_{7/2}$ radiative transition in 4f$^7\text{ configuration is clearly observed in spectra. However, its direct excitation efficiency is negligible below 7 eV. At low temperatures, broad luminescence band peaked at 5.63 eV was revealed, which can be excited through higher lying 4f transitions (Fig.2, left). While excitation energy is increased above 8 eV, the fast components ($\tau_1=2.5$ ns, $\tau_2=10$ ns at $E_{exc} = 11$ eV) appear in the PL decay curve of this band. The wide band around 11 eV in the excitation spectrum is assigned to the $^{4}f^{7} – ^{4}f^{5}d^{1}$ interconfigurational transition of Gd$^{3+}$, because its energetic position is in agreement with the estimate according to the methodology [5] using the data on Ce$^{3+}$ 4f-5d transitions in SAF reported in [4]. Moreover, this energy is below exciton creation region (see reflection spectrum on Figure 2). The interpretation of the band at 9.5 eV needs additional studies. Either it can be due to transitions to high lying levels in 4f$^7$ configuration or it is the charge transfer transition, which is well-known for Eu$^{3+}$ doped compounds [5]. Data about such transitions for various rare earth ions is collected in Ref [5], but due to high expected charge transfer transitions energies for Gd$^{3+}$, so far no solid evidences have been listed. It is not fully excluded that host defect absorption may play also role in the formation of this excitation band. The 5.63 eV emission is practically not excited by any energy transfer mechanisms in the intrinsic absorption of SAF.

The strong 312 nm emission of Gd$^{3+}$ ions appears only when exciting photon energy is in the range of absorption of lattice defects (7-11 eV). The emission bands in the region of 2.7 - 3.0 eV are the result of the luminescence of defects of host, and the excitation spectra of these bands and that of 312 nm emission are in good correlation. This points to the mechanism of resonance energy transfer from the lattice defects to dopant ions, in the similar manner as it was proposed for Ce$^{3+}$ [4]. Despite that there is no strong evidence for the direct transitions $^5S_{7/2} – ^1I_7$ of Gd$^{3+}$ ions (in the energy range of 4.35 – 4.45 eV) in the excitation spectra, the absorbed energy can be transferred to these levels from the excited state of defects. It has been shown in [3] that undoped SAF has a broad band emission peaked at 4.5 eV, which overlaps with above mentioned 4f$^7$ states of Gd$^{3+}$.

The self-trapped exciton (STE) emission was not identified in pure SAF [3]. STE luminescence band was found in SAF:Ce, partly overlapped with Ce$^{3+}$ emission [4], what caused a problem in its exact spectral positioning. In Gd-doped SAF these difficulties vanished, and the band with maximum at 3.7 eV can be confidently assigned to STE. Its excitation spectrum is presented on Figure 1 (right) demonstrating the best excitation efficiency in the intrinsic absorption of SAF. However, this broad luminescence has a sufficient overlap with the defect emission, resulting in respective excitation features in the transparency range of the host from 7 to 11 eV. The Gd$^{3+}$ lines are absent in the emission spectrum excited by 12.65 eV photons at T=10 K (Figure 1, left), so energy transfer to Gd$^{3+}$ is inefficient at low temperatures. However, at T=290 K, when STE emission is quenched and where is no overlap with Gd$^{3+}$ absorption, the excitation spectrum of 3.97 eV shows rise of intensity in the band-to-band transitions region (>12 eV). Thus, energy transfer processes populate the $^3P_{7/2}$ level of Gd$^{3+}$, wherefrom 312 nm emission takes place.

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References