

# A luminescence spectroscopy study of scintillation crystals $\text{SrI}_2$ doped with $\text{Eu}^{2+}$

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## ABSTRACT

We report experimental study of luminescent properties of modern scintillation material  $\text{SrI}_2:\text{Eu}^{2+}$  carried out over the temperature range from 9 to 450 K by the means of the ultraviolet and vacuum ultraviolet spectroscopy with a time resolution. Photoluminescence of the  $\text{Eu}^{2+}$  ions at 2.85 eV was studied under both the intracenter and interband excitations, including an X-ray excitation. The bandgap of the  $\text{SrI}_2$  crystal has been estimated on the basis of the obtained results. In the temperature range below 100 K the intrinsic luminescence at 3.4 eV was revealed and this emission band was assigned by its properties to the luminescence of self-trapped anionic excitons in  $\text{SrI}_2$ . The pronounced manifestation of the effect of multiplication of electronic excitations was revealed in the energy range above  $2E_g$ .

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## 1. Introduction

Since 1968, when Hofstadter has patented a scintillator  $\text{SrI}_2:\text{Eu}^{2+}$  [1], this material has continued to attract increasing attention due to its remarkable scintillation properties. Some properties of the  $\text{SrI}_2:\text{Eu}^{2+}$  scintillator that make it desirable for gamma-ray detection include: a high light yield of  $(9\text{--}12) \times 10^4$  photons/MeV, an excellent light yield proportionality, an energy resolution of  $<2.7\%$  FWHM at 662 keV,  $Z = 50$ , a monoexponential decay kinetics with  $\tau = 1.2 \mu\text{s}$ , an emission band of 410–450 nm (2.7–3.0 eV) that is well-matched to bialkali PMTs and no intrinsic radioactivity [2–5]. The orthorhombic crystal structure, space group *Pbca*, contains 24 atoms per unit cell with eight equivalent Sr atoms and two inequivalent sets of eight I atoms. Ionic radii for  $\text{Sr}^{2+}$  ( $r = 0.12434$  nm) and  $\text{Eu}^{2+}$  ( $r = 0.11696$  nm in monoclinic and  $r = 0.11107$  nm in rhombic positions) are practically identical, therefore the  $\text{Eu}^{2+}$  ion substitutes easily the host isovalent ion  $\text{Sr}^{2+}$  [6,7].

Cherepy et al. showed that  $\text{SrI}_2:\text{Eu}^{2+}$  crystals with high Eu contents can have performance rivaling or exceeding that of  $\text{LaBr}_3:\text{Ce}^{3+}$  both in terms of a light yield and a proportionality [8]. Although scintillation properties of these crystals are rather actively studied in recent years, their spectroscopic properties, the physics of the scintillation process and the transfer of electron excitation energy remain largely unclear due to the lack of luminescence studies in the vacuum ultraviolet (VUV) region of the spectrum over wide temperature and energy ranges. In addition, there is no

reliable estimate of the bandgap of these crystals. This is largely determined by the high hygroscopicity of crystals that makes even an elementary measurement of the absorption spectra quite problematic.

The main goal of this paper is to study the luminescent properties of scintillation crystals  $\text{SrI}_2:\text{Eu}^{2+}$  over a broad temperature range (9–450 K) using the method of the luminescence ultraviolet (UV) and VUV spectroscopy with a time resolution.

## 2. Experimental details

All the examined crystals were grown at the Institute of Geology and Mineralogy SB RAS (Novosibirsk) by the vertical Bridgman method. The starting materials  $\text{SrI}_2$  and  $\text{EuI}_2$  (melting points 515 and 580 °C, respectively) were prepared in a dry chamber by dissolving  $\text{SrCO}_3$  (99.99%) and  $\text{Eu}_2\text{O}_3$  (99.99%) in hydriodic acid, HI (99.99%). Crystalline hydrates  $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{EuI}_3 \cdot n\text{H}_2\text{O}$  were obtained. To remove water from crystalline hydrates and to make the transition  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  sure the prolonged stepwise heating in vacuum with the selected temperature modes was used. Obtained iodides were purified using the two-step directional crystallization. The mixture of strontium iodide and 3% europium iodide was placed to a silica ampoule which then was evacuated, sealed and placed in a two-zone furnace. The resulting composition was heated to 580 °C and then was brought to 540 °C. The crystal growth began with spontaneous nucleation. To ensure a flat crystallization front the optimal pulling speed and vertical temperature gradient in the growth zone were 1 mm/h and 15°/cm, respectively. The size of grown crystals was  $\varnothing 15 \times 40$  mm<sup>3</sup>. Samples were cut from a clean part of crystal boule which was 25 mm, Fig. 1. In

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Fig. 1. Photograph of the sample.

the present study we used single crystals of  $\text{Sr}_{0.97}\text{Eu}_{0.03}\text{I}_2$  which are further labeled as  $\text{SrI}_2:\text{Eu}^{2+}$ . The concentration of the activator was chosen less than the optimum value to make its luminescence comparable in intensity with the other emission bands of  $\text{SrI}_2$ .

Because of hygroscopic nature of  $\text{SrI}_2:\text{Eu}^{2+}$ , any contact with the atmospheric air leads to degradation of the sample surface that becomes cloudy due to the formation of crystalline hydrates. In all our experiments the samples were cleaved in an atmosphere of a dry hot air and immediately mounted in a cryostat with a fast vacuum pumping. In the VUV experiments the crystals were kept in a cryostat for 20 h at  $T = 110$  K in a vacuum better than  $10^{-6}$  Torr.

The present study was carried out by the means of the low-temperature luminescence VUV spectroscopy. Photoluminescence (PL) spectra in the energy range from 1.2 eV to 6.2 eV, PL excitation spectra in the broad energy range from 3.7 eV to 40 eV (0.32 nm resolution) were measured at 9 and 295 K for these crystals at the SUPERLUMI experimental station of HASYLAB [9] using synchrotron radiation. The 0.3 m ARC Spectra Pro-300i monochromator and the R6358P (Hamamatsu) photomultiplier were used as a registration system. The PL excitation spectra were corrected to an equal number of photons incident on the sample using sodium salicylate.

The PL characteristics under excitation in the UV spectral region from 3.0 to 6.0 eV were measured in the temperature range from 90 to 480 K at the laboratory of Solid State Physics of Ural Federal University. The 400 W deuterium discharge lamp with a continuous UV emission spectrum and the primary DMR-4 monochromator were used as an excitation source. The secondary DMR-4 monochromator and the R6358P (Hamamatsu) photomultiplier were used in registration system. The PL emission spectra are shown without correction. The PL excitation spectra were normalized to an equal number of photons incident on the sample using yellow lumogen with the energy-independent quantum yield over the studied spectral range.

Spectra of the X-rays induced luminescence (XRL) were studied in the temperature range from 90 to 480 K by the means of a BSW2:Cu X-ray tube (40 kV, 10 mA), a MDR-23 monochromator and a FEU-106 photomultiplier, operating in a photon counting mode.

### 3. Experimental results and discussion

Fig. 2 shows the optical transmission spectrum of the  $\text{SrI}_2:\text{Eu}^{2+}$  crystal at 295 K. The broad dip observed in the spectral region of 350–420 nm is associated with an optical absorption caused by the  $f \rightarrow d$  intracenter transitions in  $\text{Eu}^{2+}$  ions. These transitions were observed in the same spectral region in various hosts doped with  $\text{Eu}^{2+}$ , see e.g. [2]. With decreasing wavelength down to 300 nm, the optical transmission decreases rapidly and becomes undetectable below 280 nm, Fig. 2. As the direct measurements of the Urbach's rule for  $\text{SrI}_2$  are still unavailable, the value of 280 nm (4.42 eV) can be taken as a long-wavelength limit for estimate of the transmission cutoff wavelength for this crystal at 295 K. The real cutoff wavelength value is probably located at a shorter wavelength. The bandgap value should be somewhat larger than the cutoff energy. Unfortunately, the experimental bandgap value for  $\text{SrI}_2$  was also unavailable because of the lack of experimental research in this area. The results of calculations of the electronic states density of  $\text{SrI}_2$ , carried out in [7], give the calculated bandgap value of  $E_g = 4.5$  eV. However, we must use this value with caution. It has to be taken into account that the states density calculations based on the linearized augmented planewaves method typically underestimate the bandgap value up to 1 eV or more, see e.g. [10]. Although the calculated value of  $E_g$  is not inconsistent with the transmission spectrum (Fig. 2) we should expect that the band-to-band transitions will appear in the PL excitation spectra rather at near 5.5 eV than at 4.5 eV. It follows from [7] that these low-energy electronic transitions correspond to the transfer of an electron from  $2p$ -states of iodine, forming the valence band top, onto the metal unoccupied states, forming the conduction band bottom.

Photoexcitation of  $\text{SrI}_2:\text{Eu}^{2+}$  at photon energies  $E_{\text{ex}} = 5\text{--}30$  eV at  $T = 295$  K produces broad-band PL emission with a maximum at 435 nm (2.85 eV) and a shoulder at 520 nm (2.4 eV), Fig. 3. The observed PL spectrum is consistent with published data [2,3,8]. The XRL spectrum has the same shape. Cooling down to 9 K leads to a narrowing of the PL emission band width and to an increase in the luminescence yield by 4–5 times. In addition, a new band in the region at 370 nm (3.4 eV) appears in the PL spectrum, Fig. 3. Notably, the characteristic  $f \rightarrow f$  emission of  $\text{Eu}^{3+}$  ions at about 600 nm is not observed neither in the PL emission spectra, nor in the XRL spectra.

Fig. 4 presents the PL excitation spectra of  $\text{SrI}_2:\text{Eu}^{2+}$  measured at 9 and 295 K for monitored bands  $E_m = 2.4$  and 2.85 eV. In the low-energy region of the PL excitation spectrum there are two pronounced peaks at 5.26 eV ( $E_m = 2.4$  and 2.85 eV) and 4.26 eV ( $E_m = 2.85$  eV). In the energy range of exciting photons more than

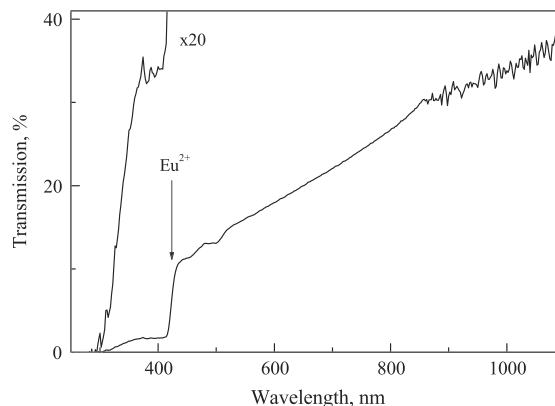


Fig. 2. Optical transmission spectrum of the  $\text{SrI}_2:\text{Eu}^{2+}$  crystal at 295 K. The short-wavelength part of the spectrum is shown with a zoom.

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