A luminescence spectroscopy study of scintillation crystals SrI_2 doped with Eu^{2+}

V. A. Pustovarov^a, I. N. Ogorodnikov^{a,*}, A. A. Goloshumova^b, L. I. Isaenko^b,
A. P. Yelissev^b

^a*Ural Federal University, 19, Mira Street, 620002 Ekaterinburg, Russia*

^b*Institute of Geology and Mineralogy of Siberian Branch of RAS, 43, Russkaya Street, 630058, Novosibirsk, Russia*

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 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 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 SrI_2 . The pronounced manifestation of the effect of multiplication of electronic excitations was revealed in the energy range above $2E_g$.

Keywords:

luminescence spectroscopy, luminescent materials, scintillation crystals, strontium iodate, europium

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

*Corresponding author

Email address: i.n.ogorodnikov@gmail.com (I. N. Ogorodnikov)

for gamma-ray detection include: a high light yield of $(9\div 12)\times 10^4$ 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 Sr^{2+} ($r = 0.12434$ nm) and Eu^{2+} ($r = 0.11696$ nm in monoclinic and $r = 0.11107$ nm in rhombic positions) are practically identical, therefore the Eu^{2+} ion substitutes easily the host isovalent ion 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 SrI_2 and EuI_2 (melting points 515 and 580°C, respectively) were prepared in a dry chamber by dissolving SrCO_3 (99.99%) and Eu_2O_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 $\varnothing 15 \times 40$ mm³. Samples were cut from a clean part of crystal boule which was 25 mm, Fig. 1. In the present study we used single crystals of Sr_{0.97}Eu_{0.03}I₂ which are further labeled as SrI₂:Eu²⁺. 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 SrI₂.

Because of hygroscopic nature of SrI₂:Eu²⁺, 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 hours 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

Figure 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 Eu^{2+} ions. These transitions were observed in the same spectral region in various hosts doped with 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 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 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 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 Eu^{3+} ions at about 600 nm is not observed neither in the PL emission spectra, nor in the XRL spectra.

Figure 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 10 eV ($E_{\text{ex}} > 2E_g$) there is a sharp increase in the photoluminescence yield which is associated with the manifestation of the multiplication of electronic excitations and it characterizes the generational stage of the scintillation pulse formation. The effect is pronounced, and it is a necessary attribute of an effective scintillator. From the results of the calculation [7] it follows that the width of the valence band $E_v < E_g$, so that generation of secondary electron-hole pairs is due to the scattering of photoelectrons, and the threshold for multiplication effect should occur at slightly higher energy than experimental value of $2E_g$ [11].

The PL decay kinetics measured at $T = 295$ K is monoexponential in shape for both the intracenter ($E_{\text{ex}} = 4.26$ eV) and interband ($E_{\text{ex}} = 13$ eV) excitations. According to our data the PL decay kinetics, measured at $E_m = 2.4$ and 2.85 eV, exhibit no appreciable differences. The measured time constant of the PL decay kinetics was always equal to $\tau = 0.36 \mu\text{s}$. This value is noticeably different from the time-constants obtained with other types of excitations: $\tau = 1.2 \mu\text{s}$ for single pulse of YAG:Nd laser with $E_{\text{ex}} = 4.66$ eV [8] and $\tau = 1.1 \mu\text{s}$ for ^{137}Cs -gamma radiation [2]. However, it is not surprising. Glodo et al. revealed that the decay time-constant of the $\text{SrI}_2:\text{Eu}^{2+}$ radioluminescence depends on the dopant concentration. It happens because of radiation trapping, at which the scintillation light is multiple time absorbed and consequently emitted by the dopant [12]. With that, the 1650 ns decay time-constant, observed for a 10% Eu sample, decreases to 620 ns for a 0.5% Eu sample [12]. In our opinion, the further ‘shortening’ of the decay time-constant occurs due to the high repetition frequency (5.21 MHz) of excitation pulses used in our measurements. In fact, the use of synchrotron pulses of high repetition frequency for sample excitation may cause the overlaying of emission decay pulses excited by present and multiple past excitation pulses. This dynamical phenomenon usually leads to ‘shortening’ of the observed decay kinetics [13].

To determine the influence of the products of interaction with the atmosphere on the PL spectra of hygroscopic crystals SrI_2 we carried out several measurements of the photoluminescence at different time intervals under identical experimental conditions, Fig. 5. During the time of crystal confinement at $T = 295$ K in oil-free vacuum better than 10^{-4} Torr the PL band near 2.2 eV increases in intensity. This may be due to the following reasons. The 10^{-4} Torr vacuum is not very deep vacuum. The residual gases can interact with the crystal surface. Cherepy et al. showed that the main products of this interaction are in the form of hydrates [14]. If the 2.2 eV luminescence is due to the hydrates, then its intensity should correlate with concentration of these hydrates. One would expect not only desorption of the products from the surface, but adsorption of the residual gases

on the crystal surface as well. This is possible reason why the intensity of the emission band is related to hydrates increases as the time of crystal staying in vacuum. At $T = 90$ K the effect in the PL spectra is recorded much better, Fig. 6. Two possible reasons can be suggested. Firstly, the luminescence intensity increases at cooling. This will be discussed below. Secondly, the thermally stimulated process of desorption will be frozen at low temperature and the adsorption rate will increase. Therefore, the 2.2 eV PL emission band can correspond to appearance of crystal hydrates which are products of interaction between the $\text{SrI}_2:\text{Eu}^{2+}$ surface and water. The forming of such hydrates was confirmed by independent X-ray diffraction studies [14].

The PL emission spectra at $T = 90$ K depend on the excitation energy, Fig. 7. Photoexcitation of $\text{SrI}_2:\text{Eu}^{2+}$ at $E_{\text{ex}} = 5.5$ eV and $T = 90$ K produces PL emission with the maximum at 3.3–3.4 eV as it was observed at $T = 9$ K, Fig. 3. Fig. 8 shows the PL excitation spectra for $E_{\text{m}} = 2.85$ and 3.4 eV. As follows from Fig. 8, the cooling to 90 K causes the 0.22 eV blue shift of the high-energy peak of the PL excitation spectrum measured for $E_{\text{m}} = 2.85$ eV. The similar shift can be observed in the PL excitation spectra presented on Fig. 4. At the same time, the 3.4 eV emission band can not be excited at $E_{\text{ex}} < 5.2$ eV, whereas at $E_{\text{ex}} > 5.2$ eV the PL excitation spectrum of this band demonstrates a sharp increase in intensity with a maximum near 5.5 eV.

On the basis of the obtained experimental data, the 2.85 eV emission band can be assigned to inter-configurational radiative $d \rightarrow f$ transitions in the Eu^{2+} ions. An Eu^{2+} ion can occupy one of the 8 equivalent Sr^{2+} positions in the elementary cell of SrI_2 crystal. The luminescence occurs due to electronic transition in Eu^{2+} ion from the lowest level of $4f^65d^1$ -configuration onto the $^8S_{7/2}$ -level of $4f^7$ configuration. The 3.9–4.4 eV excitation bands in the PL excitation spectra (Fig. 4 and Fig. 8) correspond to $f \rightarrow d$ transitions and their energy positions do not depend on temperature. At the same time the 5.02 eV narrow excitation band demonstrates blue shift under cooling. These features match well the known properties of the exciton localized near an impurity defect. The blue shift of the excitation band of this exciton correlates usually with a temperature shift of the low-energy tail of fundamental absorption band [11, 15–17]. The excitons localized near Eu^{2+} -ions were previously revealed and studied in many dielectric materials, see e.g. [15, 16]. On the basis of these facts the 5.02 eV excitation band in SrI_2 should be assigned rather to creation of excitons, localized at the Eu^{2+} impurity centers, than to intracenter excitation of an Eu^{2+} ion.

The low-temperature emission band at 3.4 eV can be excited only in the fundamental absorption region of a crystal and its decay kinetics is characterized by

the micro- and millisecond time-constant. In this connection the 3.4 eV band can be assigned to the intrinsic emission due to radiative annihilation of triplet self-trapped excitons. The emission of such excitons has been revealed even at room temperature in many haloids of the alkali and alkaline-earth metals, see e.g. [5, 11, 15–17]. The PL excitation spectrum of the 3.4 eV emission allows us to refine an estimate of the bandgap value for the $\text{SrI}_2\text{:Eu}^{2+}$ crystal. The theoretical consideration for this estimation has been carried out by Belsky and Krupa [18]. On the basis of their theory we derived from the PL excitation spectra (curve 3 on Fig. 8) the value of $E_g = 5.7\text{--}5.8$ eV. Moreover, from [18] it follows that the low-energy slope of the PL excitation band of the STE emission should match the low-energy tail of fundamental absorption. This allows us to refine an estimate of the cutoff energy for fundamental absorption (the fundamental absorption edge). From the PL excitation spectra (curve 3 on Fig. 8) it follows that the cutoff energy at 90 K should be located in the energy range of 5.0–5.2 eV. This corresponds to the cutoff wavelength of 240–250 nm.

Figure 9 shows the temperature dependence of the PL intensity, measured for the 2.2 and 3.5 eV emission bands, as well as the temperature dependence of the XRL intensity, measured for the 2.85 eV emission band. According to the Mott law, we estimated roughly the activation energies for appropriate processes of temperature quenching: $E_a = 0.14, 0.10$ and 0.27 eV for curves 1, 2 and 3, respectively, Fig. 9.

4. Conclusion

Thus, the UV and VUV spectroscopy technique was used to study luminescent properties of scintillation crystals $\text{SrI}_2\text{:Eu}^{2+}$ over the temperature range from 9 to 450 K. The main essential results are following.

1. The bandgap of SrI_2 crystals at 90 K was estimated as $E_g = 5.7\text{--}5.8$ eV. The pronounced manifestation of the effect of multiplication of electronic excitations was revealed in the energy range above $2E_g$. This effect characterizes the generational stage of the scintillation pulse formation and it is a necessary attribute of an effective scintillator.

2. Photoluminescence of the Eu^{2+} ions was studied under both the intracenter and interband excitations including an X-ray excitation. The 2.85 eV emission band was assigned to inter-configurational $d \rightarrow f$ transitions of Eu^{2+} .

3. In the temperature range below 100 K the intrinsic luminescence at 3.4 eV was revealed, and this emission band was assigned to the luminescence of self-trapped anionic excitons in SrI_2 .

4. The 2.2 eV emission band corresponds to appearance of crystal hydrates which are products of interaction between the $\text{SrI}_2:\text{Eu}^{2+}$ surface and water.

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