

Intrinsic emissions and formation of electron-hole trapping centres in excited Li_2SO_4

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Vacuum ultraviolet and thermal activation spectroscopies were used to study the nature of intrinsic emission and the mechanisms of the formation of electron and hole trapping centres in irradiated Li_2SO_4 powders and crystals. The obtained results along with excitation spectra showed that recombination emission at 3.8–4.2 eV and 4.5–5.5 eV occurs when an electron passes from the second and third sub-bands of the valence band formed from the $2p$ state of oxygen to the conduction band. It has been determined that Li_2SO_4 electron and hole trapping centres are created when electrons are trapped in the SO_4^{2-} anionic sites. The holes are localised in the form of SO_4^- radicals. The spectral position and intensity of individual emission bands are dependent on the crystallographic arrangement of localised holes.

Keywords: Li_2SO_4 , emission, hole trapping centres, thermal activation spectroscopy

INTRODUCTION

Lithium containing mixed alkali metal sulphates activated by rare earth ions are used as phosphors and highly sensitive thermoluminescent dosimeters [1–4]. Emissions observed in sulphates of

alkali and alkaline earth metals are associated with the recombination of electrons with localised holes [5–10]. The spectral position of emission in such processes mainly depends on the crystallographic arrangement of localised holes (as SO_4^- radicals). Experimental and theoretical calculations [11] have shown that the orbital

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energy of an unpaired electron in the ground state of the SO_4^- radical differs in different crystallographic directions of anisotropic crystals. Therefore, during the recombination of an electron from the conduction band or the local state of the electron trapping centre with holes SO_4^- emission should appear in a certain spectral range [5–10].

In many sulphates in the studied temperature range, there are phase transitions associated with rearrangement of the crystal lattice. The rearranged lattice is mainly related to the orientation of the anion complex SO_4^- [11]. In some cases, the detected high-temperature EPR signals corresponding to the SO_4^- radicals can expand in the low-temperature region. In irradiated LiKSO_4 with Tl^+ impurities, Tl^{2+} centers appear when holes are trapped by the ground state of the Tl^+ impurity. The EPR method showed that Tl^{2+} in two temperature ranges of 183 and 203 K, where phase transitions occur, are reoriented. The reorientation is associated with a change in the crystallographic direction of holes SO_4^- near the impurity Tl^+ [12]. The spectral position of the emission centre of specially introduced impurities of rare-earth ions and copper changes insignificantly before and after phase or polymorphic transitions [13–16].

In the present work, the recombination emission at trapping centers in Li_2SO_4 in wide spectral (from 2 to 12 eV) and temperature (15–500 K) ranges has been investigated. Regularities of the localisation of electron and hole trapping centres relative to the energy bands of the crystal were studied.

EXPERIMENTAL

Lithium disulphate (Li_2SO_4 ; Sigma Aldrich, 99.99%) powders were used for the investigation of the nature of intrinsic emission. Powders were used in the form of tablets, pressed with a pressure of 5 to 6 MPa. The Li_2SO_4 crystals were grown from a saturated aqueous solution by slow evaporation at a temperature of 55°C. Plates 3–5 mm thick and 10–15 mm in diameter were cut from the crystal.

The objects of study were irradiated by a BSV-23 X-ray tube with a copper anode, the tube current was 10 mA, and the voltage was 40 kV. The energy of X-ray photons was 10–15 keV. For excitation in the UV region a D200VUV deuterium lamp

(Heraeus Noblelight, Germany) with photon energy of 6.2–11.5 eV and an XBO 150W xenon lamp (OSRAM, Germany) with photon energy of 1.5–6.2 eV were used. To measure the emission spectra in the spectral region of 1.5–6.2 eV, a Solar CM 2203 spectrofluorimeter was used. Measurements of the excitation and emission spectra in the spectral region of 4–12 eV were carried out on a vacuum monochromator assembled according to the Seya–Namioka scheme in a wide temperature range of 15–300 K. When studying in the high-energy energy range of 7.3–12 eV, our experimental setup allowed the measurements at temperatures from 15 K. It should be noted that in this setup it is possible to keep the temperature of 15 K constant. Registration of crystal emission was carried out through an MDR-41 monochromator using a PMT (Photomultiplier tube) 1P28 (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral distribution of the intensity of excitation emission. Absorption spectra were obtained on a Jasco V-770 spectrophotometer with an integrating sphere attachment (ISN-923), which allows measurements in the range from 190 to 2700 nm. The integrating sphere makes it possible to measure the reflectance spectrum of opaque solid samples with uneven surfaces. The resulting reflection spectrum is converted into an absorption spectrum by the Kramers–Kronig method. Powder X-ray diffraction data were collected on a Rigaku miniFlex II diffractometer operating in Bragg–Brentano ($\theta/2\theta$) geometry, using Ni-filtered $\text{Cu K}\alpha$ radiation. The morphology of the samples was studied using a field-emission scanning electron microscope (FE-SEM) Hitachi SU-70.

RESULTS AND DISCUSSION

The XRD pattern of the pressed to the pellet Li_2SO_4 sample is presented in Fig. 1. The XRD pattern shows that all detected diffraction peaks correspond to the standard XRD pattern of Li_2SO_4 (#96-101-0468), and no peaks attributable to the side phases could be detected. Therefore, no possible crystalline impurity phases during the mechanochemical treatment of Li_2SO_4 have formed [17].

To study the nature of emission in pressed to the pellets Li_2SO_4 powders, the emission spectra

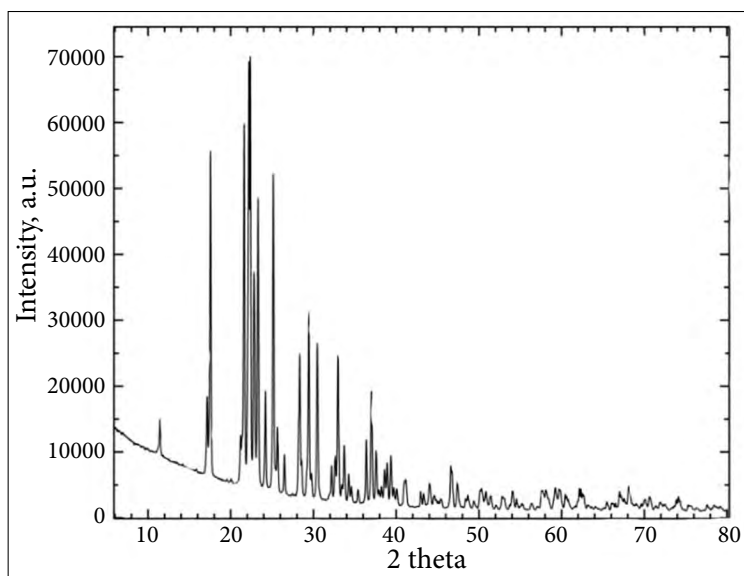


Fig. 1. The XRD pattern of the pressed to the pellet Li_2SO_4 sample

at different temperatures (80 and 300 K) were studied (Fig. 2). The samples were excited by 6.2 eV–5.64 eV. Emission observed in a region of 3.7–3.8 eV at 300 K is associated with the recombination of an electron with a non-equivalently located hole above the valence band [7–10]. Emission bands determined in regions of 3.1–3.17 eV, 2.6–2.7 eV and 2.3–2.4 eV (only at 80 K) are associated with electron-hole trapping centres [10]. Besides, no emission at 80 K was observed in a region of 3.7–3.8 eV. Figure 3 shows analogous emission spectra of the pressed Li_2SO_4 powders at 15 and 300 K when excited by high-energy photons from 7.3 to 12.4 eV. When working with energies of 7.3–12 eV, the samples were cooled to a temperature of 15 K. The similar bands but with a higher intensity are seen. Short-wavelength recombination bands at 3.8–4.0 eV and long-wavelength bands at trapping centres with a spectral shift were observed in comparison to low-energy excitations. The intensity of all bands increases by 3–4 times.

To compare the obtained results, the emission spectra of the single crystal were also studied (Fig. 4). The obtained results of the single Li_2SO_4 crystal at 15 and 300 K showed that when excited by photons from 7.3 eV–12.4 eV, the same long-wavelength bands appear at 3.0–3.1 eV, 2.6–2.7 eV and 2.3–2.4 eV at both temperatures. A specific feature of the single crystal is the appearance of short-wavelength emission bands at 4.0–4.2 eV and 5.0–5.6 eV. The intensity of all bands decreased several times.

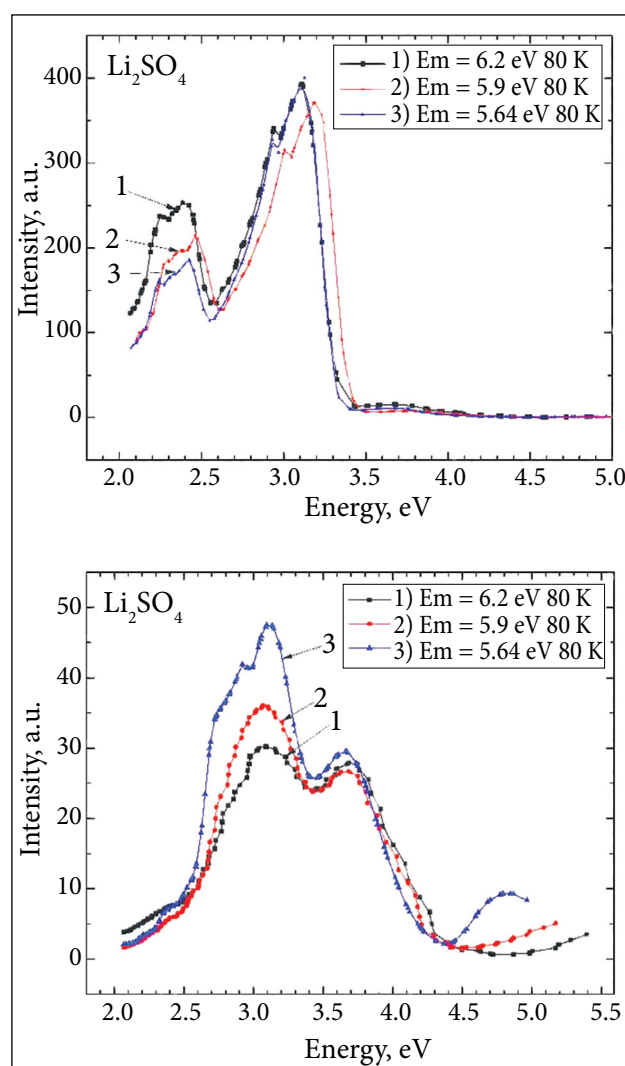


Fig. 2. Emission spectra of Li_2SO_4 powders excited by low-energy photons at 80 K (top) and 300 K (bottom): excited by 1–6.2 eV, 2–5.9 eV and 3–5.64 eV

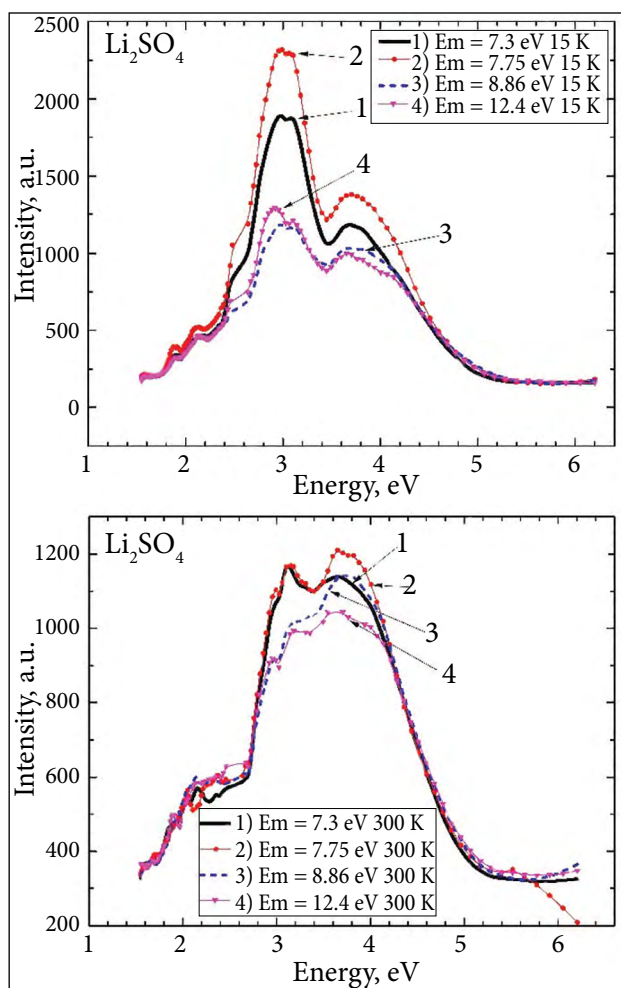


Fig. 3. Emission spectra of Li_2SO_4 powders excited by high-energy photons at 15 K (top) and 300 K (bottom): excited by 1–7.3 eV, 2–7.75 eV, 3–8.86 eV and 4–12.4 eV

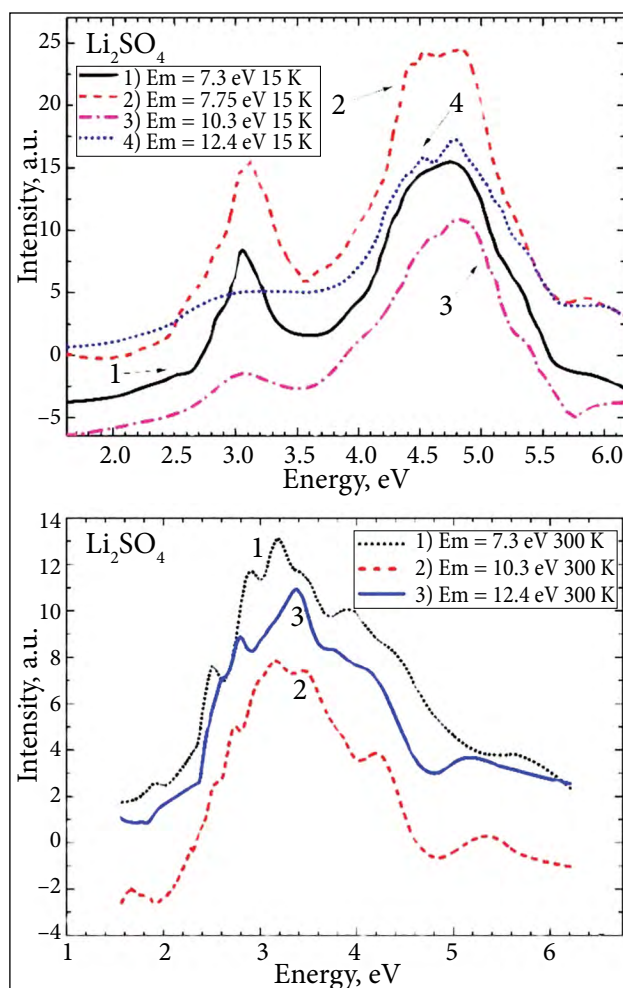


Fig. 4. Emission spectra of the Li_2SO_4 single crystal excited by high-energy photons at 15 K (top) by 1–7.3 eV, 2–7.75 eV, 3–10.3 eV and 4–12.4 eV and 300 K (bottom) when excited by 1–7.3 eV, 2–10.3 eV and 3–12.4 eV

This cannot be associated with surface morphology, since both pelletised powders and single crystals show similar morphological features (see Fig. 5).

Figure 6 shows the excitation spectra of the main short-wavelength emissions of Li_2SO_4 powders for the band at 4.3 eV (curves 1 and 2 at 15 and 300 K,

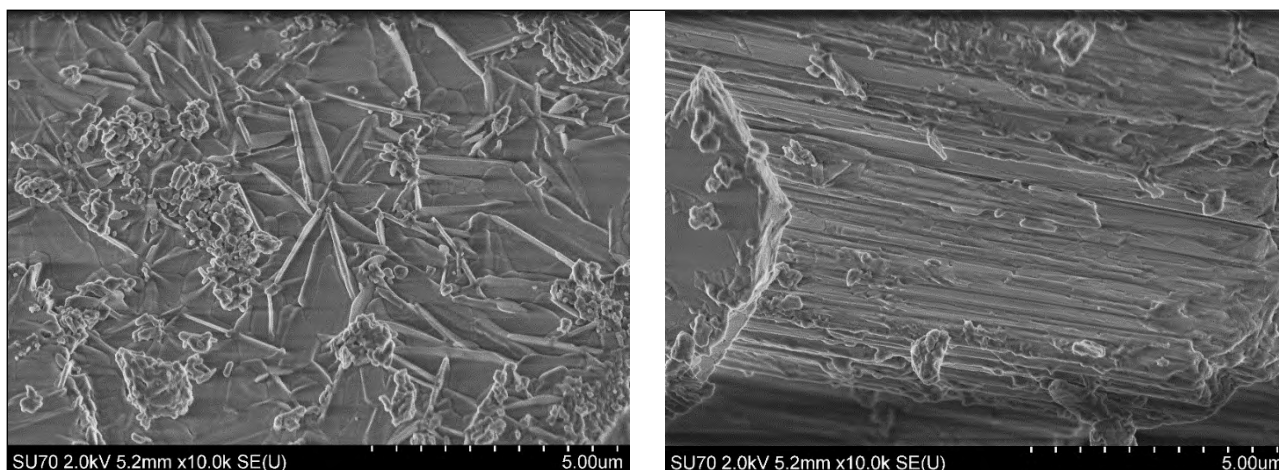


Fig. 5. SEM micrographs of Li_2SO_4 pellets (top) and single crystal (bottom)

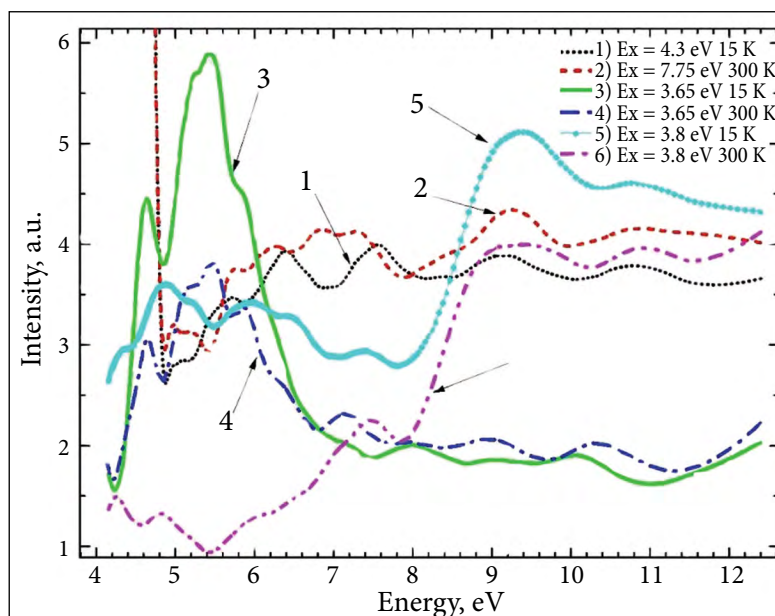


Fig. 6. Excitation spectra of the powder for the emission band 4.3 eV (curves 1–2), 3.65 eV (curves 3–4) and 3.8 eV (curves 5–6)

respectively), at 3.65 eV (curves 3 and 4 at 15 and 300 K, respectively) and at 3.8 eV of the Li_2SO_4 single crystal (curves 5 and 6 at 15 and 300 K, respectively). It can be seen that short-wavelength bands at 3.65 and 4.3 eV in pellets and 3.8 eV in crystal samples are excited at a photon energy of 5.9–6.2 eV, 6.9–7.2 eV, 7.8–8.0 eV and 10–11 eV in the spectral region corresponding to electronic

transitions from three sub-bands of the valence band to the conduction bands found in the theoretical calculations of the authors [18–21].

Figure 7 shows the excitation spectra of long-wavelength recombination emission at 3.1 eV for the crystal sample (curves 3 and 4 at 300 and 15 K, respectively) and for the 2.95 eV band of powder sample (curves 1 and 2 at 300 and 15 K, respectively).

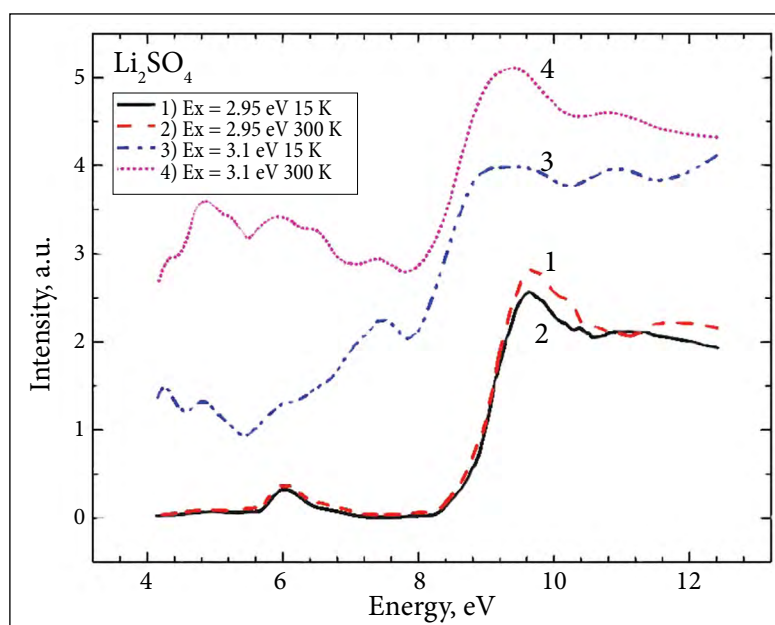


Fig. 7. Excitation spectra of the emission bands of Li_2SO_4 powder and crystal: 1 for the 2.95 eV emission band at 300 K, 2 for the 2.95 eV emission band at 15 K, 3 for the 3.1 eV emission band at 300 K and 4 for the 3.1 eV emission band at 15 K

The results obtained show that the long-wavelength band of recombination or tunnelling emission at 3.1 and 2.95 eV for the powder and crystal are excited in the same way at photon energies of 5.8–6.1 eV and 8.85–12 eV, where free electron-hole pairs arise in the fundamental region [8, 9].

To reveal the electronic structure and local position relative to the top of the valence band of emerging electron and hole trapping centres, we studied the excitation spectra of long-wavelength emission at 3.1, 2.95, 2.6–2.7 and 2.3–2.4 eV. Figure 8 shows the excitation spectra of the Li_2SO_4 powders for long-wavelength bands at 2.95 eV (curves 1 and 2 at 300 and 80 K, respectively) and 3.1 eV (curves 3 and 4 at 300 and 80 K, respectively). Figure 8 shows that long-wavelength bands at 2.95 and 3.1 eV are excited at photon energies of 4.5

and 3.95 eV in the matrix transparency region, in addition, in the fundamental region of the Li_2SO_4 powders, where free electron-hole pairs arise, as a result of which new electron and hole trapping centres are created. The emission spectra of the powder Li_2SO_4 pre-irradiated with UV photons in the fundamental region upon excitation by photons with energy of 4.5 eV (curve 1 at 300 K and curve 2 at 80 K) and 3.95 eV (curve 3 at 300 K and curve 4 at 80 K) are also presented in Fig. 8. It follows from the previous experimental data that in the powders with induced electron-hole captures, by exciting photons with energy of 4.5 or 3.95 eV equal to the excitation energy of the trapping centres, it is possible to create primary long-wavelength recombination or tunnelling emission at induced traps at 3.1 and 2.95 eV [7–10].

Thus, it has been shown that electron-hole trapping centres are formed in Li_2SO_4 powders upon irradiation with the energy exceeding the band gap. The trapping centres are located in the spectral region of the matrix transparency. Energy distances of local levels between electron and hole trapping centres are 4.5–4.6 eV and 3.9–4.0 eV, which is less than the band gap. It has been experimentally shown that long-wavelength recombination emissions of 3.1–3.0 eV, 2.6–2.7 eV and 2.3–2.4 eV are created in irradiated crystals in parallel with their intrinsic emission. These long-wavelength emissions are associated with the formation of electron-hole trapping centres.

Figure 9 shows the thermally stimulated luminescence of Li_2SO_4 powders irradiated with X-rays at 80 K. TSL for the Li_2SO_4 powder (curve 4) and the temperature dependence of the X-ray luminescence intensity Li_2SO_4 crystal for 3.9 eV (curve 1), 3.6–3.8 eV (curve 2) and 3.1 eV (curve 3) bands are in the same temperature region. This temperature range of 150–160 K corresponds to the delocalisation of electrons from electron trapping centres. The delocalisation process is associated with a polymorphic transition as a result of the reorientation of localised SO_4^- holes located near the electronic trapping centre. The emission bands (1–3, Fig. 9) flare up in the temperature region where TSL of the irradiated powder occurs at 80 K (curve 4). Also, for the Li_2SO_4 powder, electron-hole trapping centres were created with energy of 6.2 eV. The emission band at 3.1 eV at 80 K slightly flares up at higher temperatures of

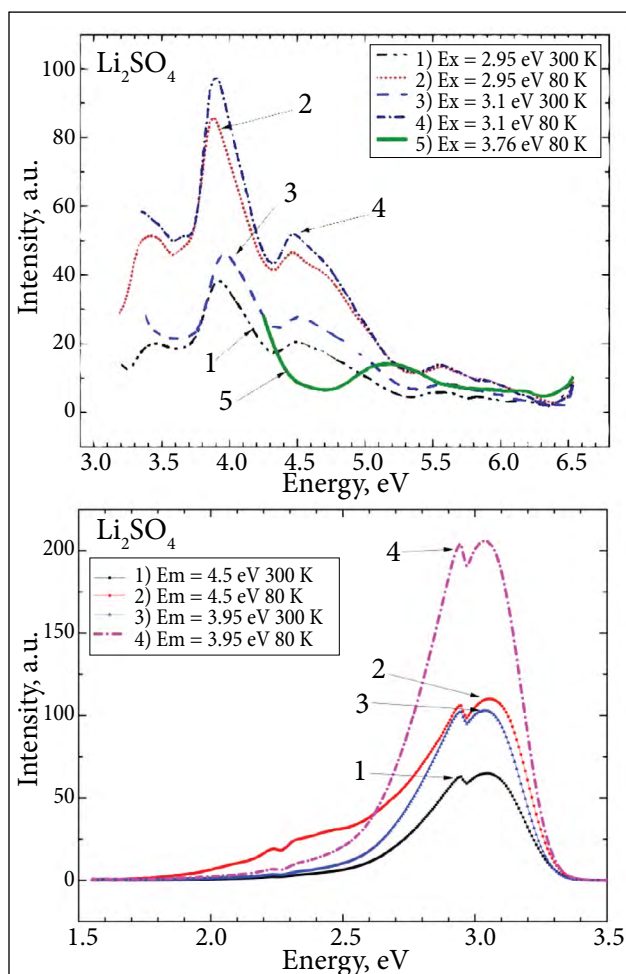


Fig. 8. Excitation spectra (top) of long-wavelength emission bands: 1 for 2.95 eV at 300 K, 2 for 2.95 eV at 80 K, 3 for 3.1 eV at 300 K, 4 for 3.1 eV at 80 K and 5 for 3.76 eV at 80 K. Emission spectra (bottom) when excited by 4.5 eV at 300 K (1), 4.5 eV at 80 K (2), 3.95 eV at 300 K (3) and 3.95 eV at 80 K (4)

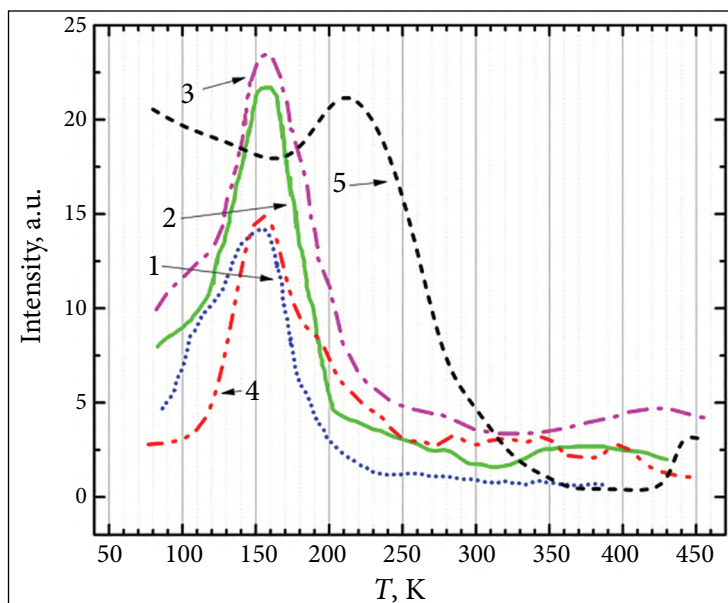


Fig. 9. Temperature dependence of X-ray luminescence for bands: 1) 3.9 eV, 2) 3.6–3.8 eV, 3) 3.1 eV and 4) TSL powder Li_2SO_4 irradiated with X-rays at 80 K within 5 min. (5) Temperature dependence of the emission band 3.1 eV

180–200 K and, as in the crystal, decreases exponentially to 350 K (curve 5).

CONCLUSIONS

In this work, the irradiated pressed Li_2SO_4 powders and crystals showed short-wavelength emission bands at 3.7–3.8 eV, 4.2–4.5 eV and 5.0–5.6 eV which are associated with the recombination of electrons with nonequivalently located holes. The 3.7–4.2 eV emission band excited by photons with energies of 5.16–6.2 eV and 7.3–7.4 eV is associated with electron transitions from the middle and first sub-bands to the conduction band. Based on the measurement of the excitation spectra for the recombination emission at 3.0–3.1 eV, it was determined that they are excited at photon energy of 3.9–4.0 eV and 4.5–4.6 eV. In the irradiated Li_2SO_4 hole SO_4^- trapping centres emitting recombination emission at 3.0–3.1 eV are formed. Upon excitation of the trapping centres created by UV irradiation with energy of 4.0 and 4.5 eV, a new long-wave tunnel emission at 3.0–3.1 eV was observed. The spectral positions and intensity of individual emission bands depend on the crystallographic arrangement of localised holes.

Received 28 July 2023
Accepted 17 August 2023

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VIDINĖ EMISIJA IR ELEKTRONŲ-SKYLIŲ GAUDYMO CENTRŲ SUSIDARYMAS SUŽADINTAME Li_2SO_4

Santrauka

Vakuuminė ultravioletinė ir terminės aktyvacijos spektroskopija buvo naudojamos vidinės emisijos pobūdžiui ir elektronų bei skylių gaudymo centrų susidarymo mechanizmams tirti apšvitintuose Li_2SO_4 milteliuose ir kristaluose. Gauti rezultatai kartu su sužadavimo spektrais parodė, kad 3,8–4,2 eV ir 4,5–5,5 eV rekombinacinė emisija atsiranda, kai elektronas pereina iš valentinės juostos, susidariusios iš $2p$ deguonies būsenos, antrosios ir trečiosios pojuostės į laidumo juostą. Nustatyta, kad Li_2SO_4 elektronų ir skylių gaudymo centrai susidaro, kai elektronai yra įstrigę SO_4^{2-} anjoninėse vietose. Skylės yra lokalizuotos SO_4^- radikalų pavidalu. Atskirų emisijos juostų spektrinė padėtis ir intensyvumas priklauso nuo lokalizuotų skylių kristalografinio išsidėstymo.