

Photoluminescence and thermoluminescence in a Li_2SO_4 crystal

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The nature of intrinsic emission and the creation of electron-hole trapping centers in irradiated with ultraviolet and X-rays at 15 K and 300 K was investigated in Li_2SO_4 by methods of spectroscopy. It is shown that in activated Li_2SO_4 with an energy of $6 \div 12.4$ eV, emission appears in a wide spectral range to excite rare earth ions that are used as UV sources. These same photons create electron-hole trapping centers as well.

Keywords: electron; hole; trap centers; sulfates; crystals; luminescence

Introduction

Luminescent materials are popular in using as a main element in lighting (fluorescent lamp, LEDs), medicine for phototherapy, in display devices, thermoluminescent dosimeters. Li_2SO_4 crystals doped by rare earth ions are used as phosphors and dosimeters [1–9]. The sensitivity of a Li_2SO_4 – Dy or Eu crystal as a tissue equivalent ($Z_{ef} = 11.19$) dosimeter is better than that of a commercial dosimeter based on a LiF crystal (TLD-100). Alkali-metal sulfates including crystals Li_2SO_4 activated by rare-earth impurities Ce^{3+} , Tb^{3+} , Cd^{3+} and Eu^{3+}

emit in ultraviolet spectral range from 200 to 400 nm. These emissions are used in medicine to treat various skin diseases, to destroy various bacteria as needed [10–18]. Thus, some alkali metal sulfates, including crystals or powders of Li_2SO_4 activated by rare earth ions, are used as luminescent materials. For such practical applications, we need to study the energy transfer mechanisms from the matrix to various emitters, i.e. rare-earth impurities, and the creation of electron-hole trapping centers. Energy transfers from the matrix to the emitters are carried out by their intrinsic emission. In the case of working as TLD dosimeters, it is needful to know the accumulation of defects. To do this, we need to investigate the nature of intrinsic emission and defect formation in a crystal or in a powder Li_2SO_4 .

Objects and methods of research

The Li_2SO_4 crystal was grown from a saturated aqueous solution by the method of slow evaporation at a temperature of 50°C . Plates of 3–5 mm of thickness and a of 10–15 mm diameter were cut out of the crystal. We have studied samples crystal and powders Li_2SO_4 with a purity of 99.99%.

The objects of study were irradiated using 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 the X-ray photon is 10–15 keV. For excitation in the vacuum ultraviolet region of the spectrum, a H_2 lamp with energy of $6.5 \div 12.4$ eV and an XBO 150W xenon lamp (OSRAM, Germany) with a photon energy of $1.5 \div 6.2$ eV.

Measuring of emission spectra in the spectral region of $1.5 \div 6.2$ eV was done in spectrofluorometer CM 2203. Luminescence and excitation spectra measured in the 4–12 eV spectral region on a vacuum monochromator, established by Seya-Namioka circuit, in $15 \div 300$ K. A photomultiplier 1P28 was used.

The thermally stimulated luminescence (TSL) is one of the basic experimental methods of investigation trapping centers in dielectrics. To obtain TSL curves, the crystal under study is cooled to the liquid nitrogen boiling point of 77 K. Under these conditions, the crystal is excited for some time by UV emission or X-rays. After the termination of excitation, the crystal is heated at a constant rate of 0.2 deg/s and the intensity of thermoluminescent emission is measured as a temperature's function.

Results and discussion

To clarify the intrinsic emissions' nature of the Li_2SO_4 crystal, measuring of luminescence and excitation spectra were performed at photon energies of 6.9 (curve 5) eV, 7.3 eV (curve 4), 7.75 eV (curve 3), 10.3 eV (curve 2) and 12.4 eV (curve 1) at $15 \div 300$ K. The short-wavelength luminescence bands exist in the spectrum at 5.5–5.6 eV, 4.1–4.2 eV, 3.7–3.8 eV and long-wavelength bands at 3.0–3.1 eV, 2.6–2.7 eV, 2.3–2.4 eV (figure 1).

Figure 2 shows that basically the same emission bands appear at 5.5–5.6 eV, 4.1–4.2 eV, 3.7–3.8 eV, as well as long-wavelength bands at 3.0–3.1 eV, 2.6–2.7 eV

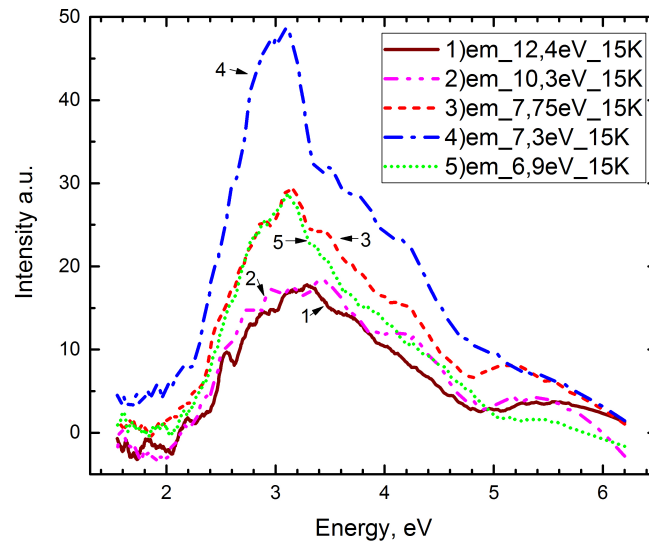


Figure 1. The luminescence spectrum of a Li_2SO_4 crystal during exciting by photons with energy: 1) at 12.4 eV 2) 10.3 eV 3) 7.75 eV 4) 7.3 eV 5) 6.9 eV at 15 K.

and 2.3–2.4 eV. At 15 K, the emission band's intensity is 2–3 times lower than that of the irradiation crystal.

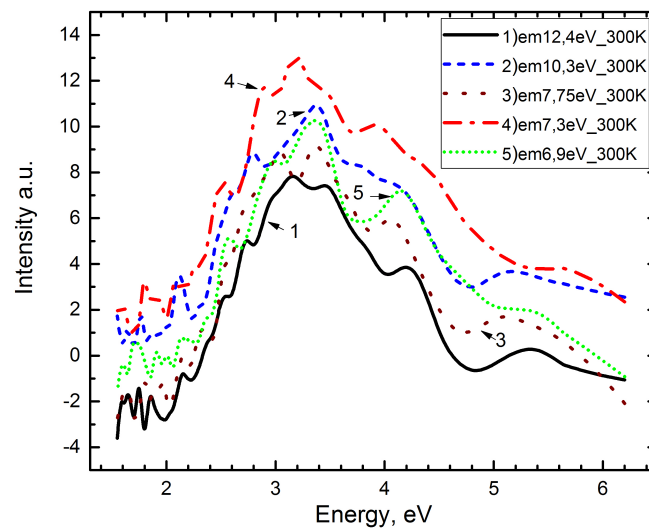


Figure 2. The luminescence spectrum of a Li_2SO_4 crystal during exciting by photons with energy: 1) at 12.4 eV 2) 10.3 eV 3) 7.75 eV 4) 7.3 eV 5) 6.9 eV at 300 K.

Figure 3 shows the excitation spectra of the main emission bands at 3.0–3.1 eV and 3.7–3.8 eV for a crystal and powder Li_2SO_4 . It is obvious that (curves 1.2) emission of 3.0–3.1 eV is produced at photon energies of $8.85 \div 10.3$ eV and $5.6 \div 6.2$ eV. The crystal's excitation spectra for 3.7–3.8 eV emission at 15 K and 300 K (curves 3, 4), respectively. At a temperature of 15 K, the band is excited at photon energies of $8.85 \div 10.3$ eV, 7.3 eV and $4.4 \div 6.2$ eV. Similar results were obtained at room temperature. The emission intensity of 3.7–3.8 eV gradually

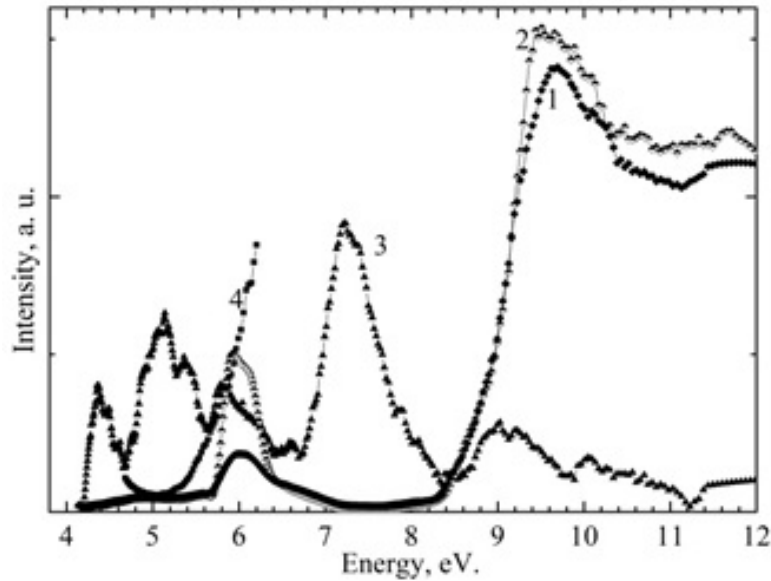


Figure 3. Excitation spectrum of Li_2SO_4 for the 3.1 eV band: 1) crystal; 2) powder with 99.99% purity; 3) for emission $3.7 \div 3.8$ eV at 15 K; 4) for emission $3.7 \div 3.8$ eV at 300 K.

decreases with a reduction in the energy of exciting photons in the range of $4.96 \div 6.2$ eV. At photon energies of 4.96 eV, emission of 3.7–3.8 eV is not detected.

The experiments have shown that high-energy photons more effectively create short-wavelength emission at 3.7–5.6 eV, and low-energy photons, along with the main emission of 3.7–3.8 eV, more effectively create long-wavelength emission bands at 3.0–3.1 eV, 2.6–2.7 eV and 2.3–2.4 eV, which are excited at photon energies of 5.5–6.2 eV.

During relaxation, some of the electrons and holes created by photons can be localized in the crystal lattice. The electron is trapped by the anionic complex SO_4^{2-} , and the hole SO_4^- is autolocalized. Electronic $[\text{SO}_3^{2-} - \text{O}^-]$ [19] and hole SO_4^- trapping centers are formed.

Figure 4 shows the spectrum of TSL Li_2SO_4 irradiated by X-rays at 80 K. The main single TSL peak appears at 150–160 K (curve 4). The same figure 4 shows the temperature dependence of individual X-ray luminescence bands on the temperature of liquid nitrogen from 80 K to 450 K in irradiated Li_2SO_4 at 80 K. The temperature dependence in three emission bands at $4.1 \div 4.2$ eV (curve 1), $3.7 \div 3.8$ eV (curve 2) and $3.05 \div 3.1$ eV (curve 3) almost identical. The intensity of all three bands has a maximum value in the temperature range $150 \div 160$ K, at this temperature the emission intensity increase. The main TSL peaks for Li_2SO_4 are in this temperature range $150 \div 160$ K.

Thus, upon excitation by high-energy photons from 6.9–12.4 eV, as well as upon excitation by X-rays [20–24], a broad band of intrinsic emission appears in Li_2SO_4 sulfates of alkali metals.

The shift of the maxima of individual short-wavelength emission bands within a wide band is associated with the crystallographic arrangement of electron and hole trapping centers. Electronic and hole trapping centers are formed during the radiolysis of SO_4^{2-} -radicals. Local states corresponding to localized holes SO_4^-

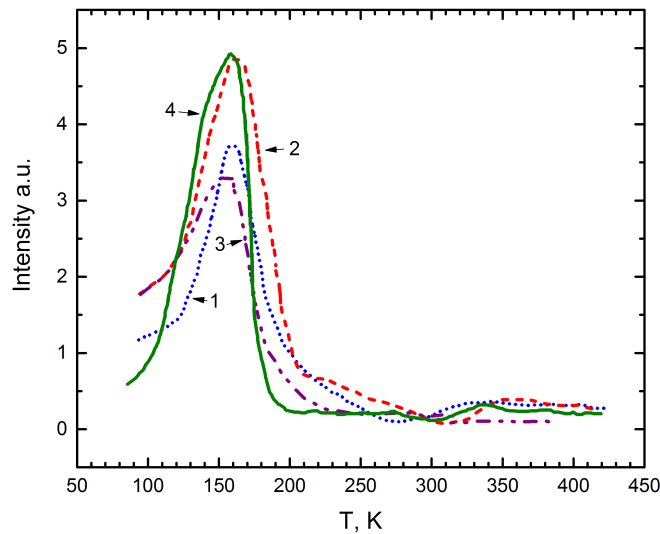


Figure 4. Temperature dependence of individual X-ray luminescence bands from 80 K to 450 K in a Li_2SO_4 crystal. at $E = 4.1 - 4.2$ eV; 2) at $E = 3.65 - 3.7$ eV; 3) at $E = 3.0 - 3.2$ eV; 4) Thermally stimulated luminescence of a Li_2SO_4 crystal irradiated at 80 K.

in different crystallographic directions will have different energy distances from the maximum of the valence band's highest point [25–26]. Hence, the maxima of the emission bands arising during the recombination of electrons at the trapping centers will differ.

An analysis of published works [20–24] showed that the intensity of the short-wavelength emission band 3.7–3.8 eV changes insignificantly with increasing exposure time or absorbed dose, the intensity of all long-wavelength emission bands gradually increases with exposure time.

The appearance of short-wavelength emission bands at 3.7–3.8 eV, 4.1–4.2 eV, 5.2–5.6 eV as well as long-wavelength emission bands 3.0–3.1 eV, 2.6–2.7 eV and 2.3–2.4 eV and measuring their temperature dependence shows that during irradiation, part of the electron-hole pairs recombine radiatively, and the other part accumulates in the form of defects in lattice structure. The experimental fact of the appearance of TSL and the buildup of recombination emission at 150–160 K confirms our assumption.

Knowing the spectral position of its intrinsic emission in Li_2SO_4 makes it possible to choose an activator to obtain the desired wavelength of emission when using them in production or medical application.

The nature of the recombination luminescence originating at trapping centers was determined by measuring the temperature dependence of individual emission bands.

The rising of the intensity of recombination luminescence in the Li_2SO_4 crystal is associated with the appearance of additional photons during the recombination of pre-accumulated trapping centers in addition to stationary photoluminescence and X-ray luminescence. Stationary photoluminescence and X-ray luminescence occur during the recombination of electrons in a local state with localized hole trapping centers. If the lifetime of electrons in the local state is long, then electron

and hole pairs of trapping centers are formed in the system. During relaxation, the electron lifetime in the local state will be less than a certain value, we observe stationary photoluminescence and X-ray luminescence. Thus, the increasing intensity of recombination emission is associated with the delocalization of accumulated defects at a certain temperature and the appearance of additional emission. Namely, during the delocalization of accumulated defects at a certain temperature, TSL peaks appears. At the same temperature, an increase in X-ray and photoluminescence is observed. Delocalization of hole or electronic trapping centers at a temperature of 150–160 K is associated with the phase transition of the Li_2SO_4 crystal in this temperature range [25–27].

Conclusion

Experiments have shown that when Li_2SO_4 is bombarded with ultraviolet photons with energies ranging from 6 to 12.4 eV, emission occurs in a wide spectrum range, exciting rare-earth ions, which are used as UV sources. It is shown that UV photons create long-wavelength emission at 3.0–3.1 eV, 2.6 eV, which create electron-hole trapping centers responsible for the formation of defects in lattice structure.

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