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Mechanisms formation of electron-hole trap centers in $LiKSO_4$ crystall

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The mechanisms of creation of electron-hole trapping centers in $LiKSO_4$ have been investigated by the methods of vacuum and thermal activation spectroscopy. It is shown that electron-hole trapping centers are formed during the trapping of electrons by anionic complexes and localization of a hole in the lattice in the form of the radical SO_4^-. The appearance of phosphorescence at 3.0-3.1 eV, 2.6-2.7 eV and 2.3-2.4 eV confirms the creation of electron-hole trap centers.

Keywords: electron, hole, trap centers, sulfates, crystals, luminescence.

Introduction

The $LiKSO_4$ crystall and other lithium containing mixed sulfates of alkali metals activated by various ions are practically used as phosphors, dosimeters and various sensors. To increase the sensitivity of such active crystals, it is necessary to study the recombination processes under excitation process. The regularities of the relaxation processes depend on the energy-band structure of the crystals. Quantum-chemical calculations of the authors of [1-3] showed that the band gap of the crystals $LiKSO_4$, $LiNaSO_4$, and $LiRbSO_4$ is $5.2 \div 5.8$ eV.

The results obtained are in satisfactory agreement with the experimental data for these crystals [4-7]. Calculations have shown that the upper part of the valence band consists of 3 subbands formed from the *2p* state of oxygen of the anionic complex SO_4^- . The conduction band consists of the *s* state of cations, the *3p* state of sulfur, and the *2p* state of oxygen, which are not filled with electrons. During the relaxation of an excited $LiKSO_4$ crystal, holes formed in three subbands of the valence band rise above the top of valence band and are localized in the form of local states. Depending on the crystallographic direction of the *S-O* bond, nonequivalently located holes SO_4^- are formed. When electrons recombine from the conduction band with nonequivalently localized SO_4^- holes, intrinsic emissions arise. By measuring the creation of intrinsic emission, it is possible to determine at what excitation energies effectively created different intrinsic emissions.

The main intrinsic emission at 3.7-3.8 eV appears upon excitation by low-energy photons with energies 5.1–6.2 eV and high-energy photons with energies of 6.9–10.5 eV. It was assumed that the appearance of emission 3.7-3.8 eV is associated with the recombination of electrons in the s state of the conduction band with localized holes relaxed from the first, second and third subbands in the *2p* state of oxygen above the top of the valence band [8].

Along with the intrinsic emission in the irradiated crystals, there appear long-wavelength emissions associated with the creation of electron-hole trapping centers. It was assumed that long-wavelength recombination emissions at 3.0-3.1 eV, 2.6-2.7 eV and 2.3-2.4 eV is associated with the creation of electron-hole trapping centers.

The main task of this work is to study the nature of long-wavelength emission in the $LiKSO_4$ crystal.

Objects and methods of research

Crystals $LiKSO_4$ are grown at a temperature of 50 °C from a saturated aqueous solution by the method of slow evaporation. Plates 3–5 mm thick were cut from the crystal. We have investigated samples of crystals and powders with a chemical purity of 99.99% (Sigma Aldrich) $LiKSO_4$. Crystals $LiKSO_4$ and powders were investigated by the methods of photoluminescence, X-ray luminescence, vacuum-ultraviolet and thermal activation spectroscopy. A deuterium lamp D200VUV (Heraeus Noblelight, Germany) with a photon energy of $6.2 \div 11.5$ eV and an Xenon lamp XBO 150 W (OSRAM, Germany) with a photon energy of $1.5 \div 6.2$ eV were used for excitation in the ultraviolet region. To measure the emission and excitation spectra in the spectral region of $1.5 \div 6.2$ eV, we used the Solar CM 2203 spectrofluorometer. The excitation and emission spectra in the $4 \div 11.5$ eV spectrum were measured on a vacuum monochromator assembled according to the Seya-Namioka scheme in a wide range temperatures of $15 \div 400$ K. Registration of emission was carried out through an MDR-41 monochromator using a photomultiplier (Photomultiplier tube) 1P28 (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral intensity distribution of the

exciting radiation.

The results of the experiment and their discussion

Figure 1 shows the emission spectrum of a $LiKSO_4$ crystal excited by photons with energies of 7.75 eV (curve 1) and 7.3 eV (curve 2) at a temperature of 15 K. From Figure 1 (curve 1, 2) it can be seen that basically, the long-wavelength emission bands at 3.0-3.1 eV, 2.6-2.7 eV and 2.3-2.4 eV are effectively created. It should be noted that this crystal was pre-irradiated with high-energy photons. In a crystal, short-wavelength emission bands at 3.7-3.8 eV and 4.1-4.3 eV are not efficiently excited. Curve 3 shows the emission spectrum of a $LiKSO_4$ crystal irradiated by photons with an energy of 6.2 eV at 300 K. From Figure 1 (curve 3) it can be seen that an emission band appears at 3.7-3, 8 eV and long-wavelength emission bands at 3.0-3.1 eV, 2.7 eV and 2.3-2.4 eV. Compared to short-wavelength emission, long-wavelength emission appears more efficiently. Figure 1 (curve 4) shows the emission spectrum of the $LiKSO_4$ crystal by photons with an energy of 5 eV at a temperature of 80 K. It can be seen from Figure 1 (curve 4) that long-wavelength emission bands mainly appears at 3.0-3.1 eV, 2.7 eV and 2.4 eV. Recombination emissions associated with induced intrinsic defects are efficiently detected from the broad fundamental emission spectra.

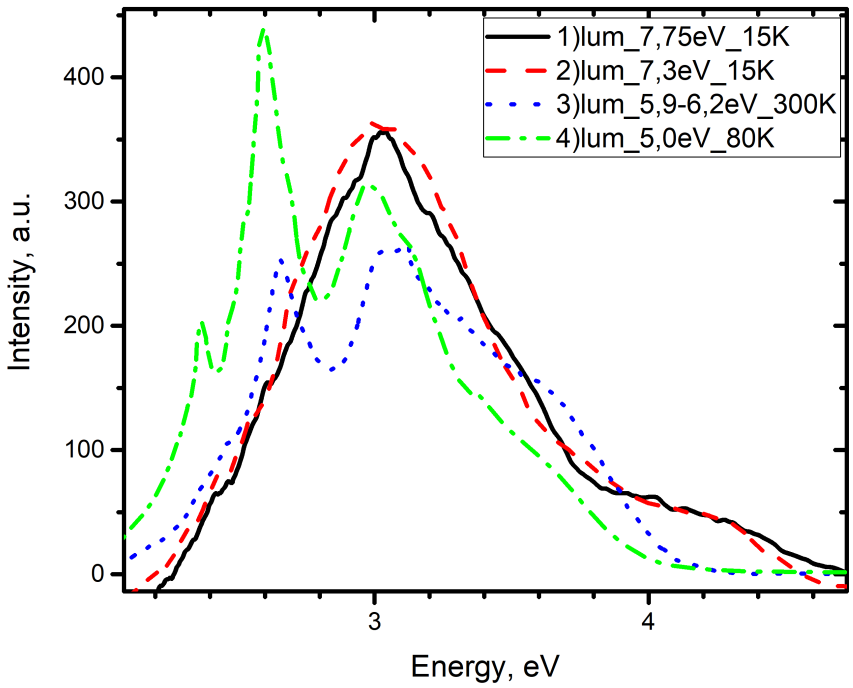

Figure 1. The emission spectrum of the $LiKSO_4$ crystal upon excitation by photons with energies: 1) 7.75 eV at 15 K; 2) 7.3 eV at 15 K; 3) 5.9-6.2 eV at 300 K; 4) 5.0 eV at 80 K.

Figure 2 (curve 1) shows the excitation spectrum for long-wavelength emission at 3.0-3.1 eV. Figure 2 (curve 1) shows long-wavelength emissions at 3.0-3.1 eV

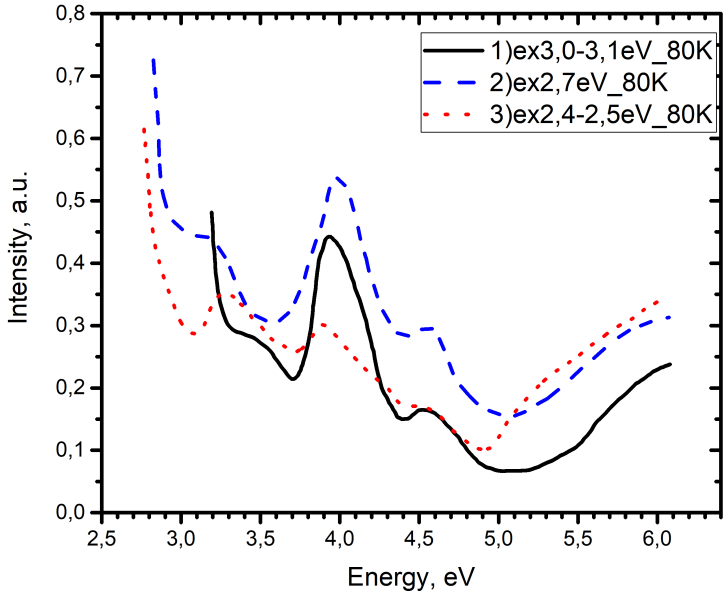

Figure 2. Excitation spectrum for the emission spectrum of the $LiKSO_4$ crystal at 80 K: 1) 3.0-3.1 eV; 2) 2.7 eV; 2.4-2.5 eV.

are excited in the spectral region 3.25-3.5 eV, 3.9-4.0 eV and 4.4-4.5 eV and are created in the spectral region of the crystal, where electron-hole pairs are formed (5.0-6.0 eV). The same Figure 2 (curve 2) shows the excitation spectrum for the emission band 2.7 eV (curve 2). Figure 2 (curve 2) shows that almost the same bands appear at excitation 3.3 eV, 3.9-4.0 eV and 4.5-4.6 eV. Figure 2 (curve 3) shows the excitation spectrum for emission 2.4-2.5 eV. Figure 2 (curve 3) shows a similar excitation spectrum at 3.25-3.3 eV, 3.9-4.0 eV and 4.4-4.5 eV.

Thus, the excitation spectrum of long-wavelength recombination emission bands located in the transparency region of the $LiKSO_4$ crystal. The energy distances between hole and electron trapping centers are 4.5-4.6 eV, 3.9-4.0 eV, and 3.5-3.4 eV, much less than the band gap in the $LiKSO_4$ crystal .To prove the correlation of these excitation spectra of electron-hole trapping centers with recombination emission 3.0-3.1 eV, 2.6-2.7 eV and 2.3-2.4 eV, we measured the emissions under excitation of created electron-hole trap centers. Figure 3 (curve 1) shows the spectrum of recombination emission upon excitation by photons with an energy of 4.0 eV, after the excitation in the fundamental region of the spectrum (6.2-12.4 eV).

Figure 3 (curve 1) it can be seen that the initial recombination emission appears 3.0-3.1 eV, 2.7-2.6 eV and 2.4-2.3 eV (emissions 2.7-2.6 eV and 2 , 4-2.3 eV are detected in the long-wavelength region of the fundamental emission at 3.0-3.1 eV). Thus, excitations of localized electron-hole trapping centers revealed primary long-wavelength recombination emissions of 3.0-3.1 eV, 2.7-2.6 eV, and 2.4-2.3 eV. Figure 3 (curve 2) shows the spectrum of long-wavelength emission upon excitation of trapping centers with photons with an energy of 4.5 eV. Figure 3 (curve 2) shows that the same long-wavelength recombination emissions appear at 3.0-3.1 eV, 2.7-2.6 eV and 2.4-2.3 eV.

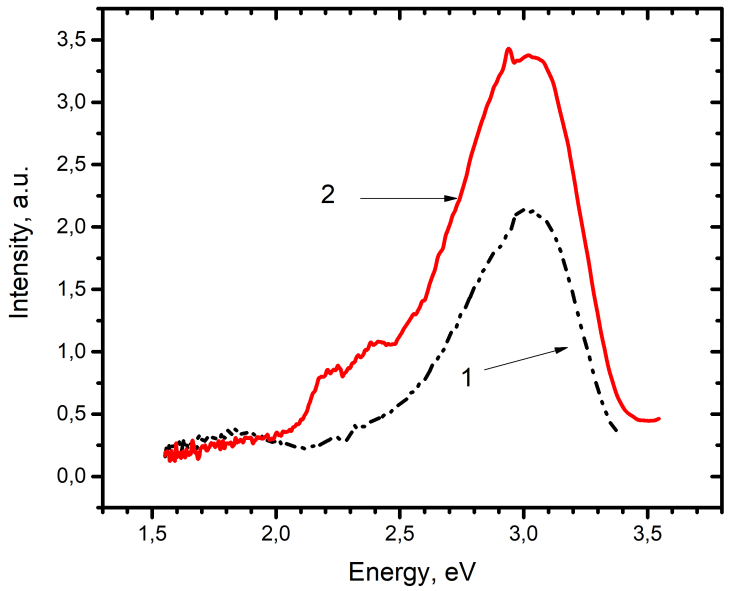

Figure 3. The spectrum of the recombination emission of the $LiKSO_4$ crystal upon excitation by 4.0 eV (curve 1) and 4.5 eV (curve 2).

Thus, we have found for the first time that electron-hole trapping centers are created in irradiated crystals in parallel with the short-wavelength emission bands that arise during the recombination of electrons with localized holes, which appear in the form of long-wavelength tunneling recombination emission of 3.0-3.1 eV, 2.7-2.6 eV and 2.4-2.3 eV.

Figure 4 shows the spectrum of generation of recombination emission 3.0-3.1 eV. Figure 4 shows that recombination emission at 3.0-3.1 eV is generated in the spectral region at 5.9-6.0 eV and above 9-12 eV. Emission of 3.0-3.1 eV is created in the fundamental region of the $LiKSO_4$ crystal, where free electron-hole pairs are created.

Thus, all three bands of recombination emission are excited in the same spectral regions. In our previous publications [9], we assumed that in the photon energy range at 6.0–6.2 eV and 9–12 eV, long-wavelength recombination emission at 3.0–3.1 eV is generated rather than excited. Based on our previous results [9], it can be assumed that the bands of recombination emission in $LiKSO_4$ at 3.0–3.1 eV, 2.7 eV and 2.4 eV upon excitation by photons with energies of 5.5–12, 0 eV are created (Figure 4). And the excitation spectrum at 3.25 eV, 3.9-4.0 eV and 4.4-4.5 eV in $LiKSO_4$ for the recombination emission band at 3.0-3.1 eV, 2.7 eV and 2.4 eV corresponds to an intracenter electronic transition at the trapping centers. As suggested in previous works [9], trapping centers are created when electrons are localized on anionic complexes according to the reaction:

$$SO_4^{2-} + e^- \rightarrow SO_4^{3-}, \quad (1)$$

Holes created in subzones are autolocalized as SO_4^-. Electronic SO_4^{3-} and hole SO_4^- are complementary trap centers. They are created at photon energies of 6.0-6.2 eV and 9-12 eV, where free electron-hole pairs are formed. Accord-

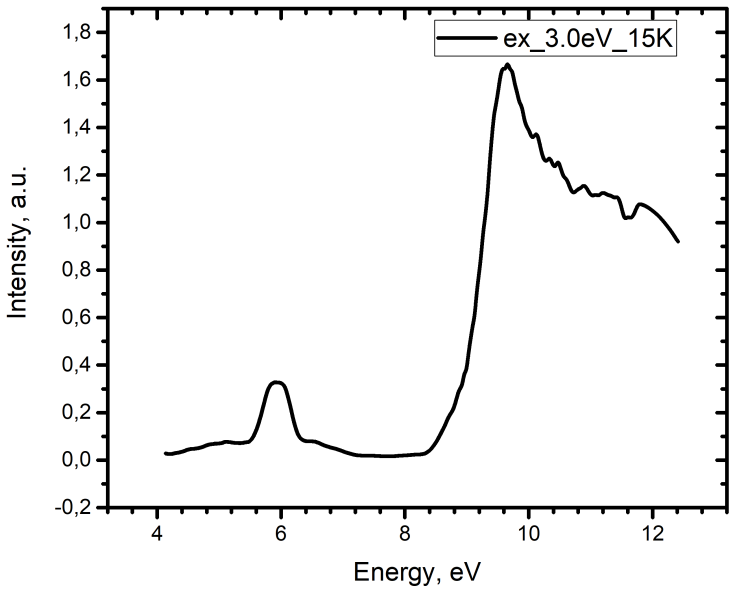

Figure 4. Generation of recombination emission spectrum at 3.0 eV at 15 K.

ing to reaction (1), electron-hole pairs create trapping centers localized in the transparency region of the $LiKSO_4$ crystal. Excited SO_4^{3-} - SO_4^{-} trapping centers, depending on the crystallographic arrangement, emit different recombination or tunneling emissions at 3.0-3.1 eV, 2.7 eV and 2.4 eV.

Figure 5 shows the phosphorescence spectrum of the $LiKSO_4$ crystal measured after the termination of X-ray radiation for 20 min. at 80 K.

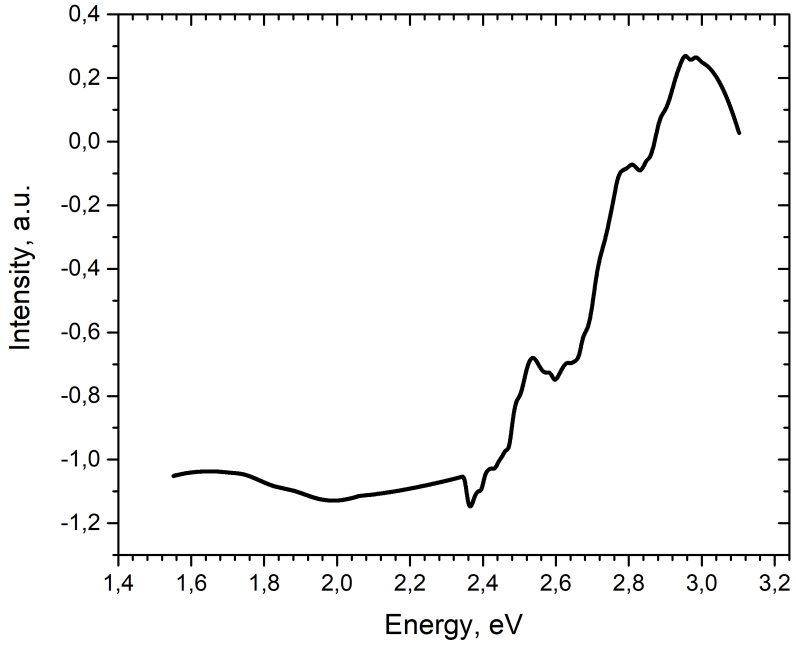

Figure 5. Phosphorescence spectrum of $LiKSO_4$ crystal after termination of X-ray irradiation at 80 K.

It can be seen from Figure 5 that phosphorescence is detected in those spectral regions where we detected recombination emissions at 3.0-3.1 eV, 2.7 eV and 2.4 eV. The appearance of phosphorescence in these long-wavelength ranges proves the existence of electron-hole trapping centers.

Conclusion

In irradiated $LiKSO_4$ crystals, the appearance of long-wavelength recombination emission bands at 3.0-3.1 eV, 2.6-2.7 eV, and 2.3-2.4 eV is associated with the formation of electron-hole trapping centers. The electron-hole trapping centers are formed during the trapping of electrons by the anionic complexes SO_4^{2-} and self-trapping of the hole in the form of the radical SO_4^{-}. The appearance of phosphorescence after the termination of X-ray irradiation proves the existence of electron-hole trapping centers in these spectral regions.

Acknowledgments

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