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Paper title: Mechanisms formation of electron-hole trap centers in alkali metal sulphates

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Abstract

- The mechanism of creating electron-hole trap centers in $LiKSO_4$ is studied by vacuum and thermoactivation spectroscopy. It has been shown that electron-hole trap centers are formed upon capture of electrons by anionic complexes and the localization of a hole in the lattice in the form of a SO_4^- radical.

Keywords-emission, recombination emission, photon. alkali metal sulphates

Experimental Setup

- Crystals 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). Crystals 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÷11.5 eV and an Xenon lamp XBO 150 W (OSRAM, Germany) with a photon energy of 1.5÷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÷6.2 eV, we used the Solar CM 2203 spectrofluorometer. The excitation and emission spectra in the 4÷11.5 eV spectrum were measured on a vacuum monochromator collected according to the Seya-Namioka scheme in a wide range temperatures of 15÷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.

Figure 1(1)

- Figure 1 shows the emission spectrum of a $LiKSO_4$ crystal excited by photons with an energy of 7.75 eV (curve 1) and 7.3 eV (curve 2) at a temperature of 15 K. Figure 1 (curve 1.2) shows that mainly long-wavelength emission bands are effectively exhibited at 3.0–3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV. It should be noted that this crystal was previously irradiated with high-energy photons. In the crystal, the short-wavelength emission bands at 3.7-3.8 eV and 4.1-4.3 eV are not efficiently excited. Figure 1 (curve 3) also shows the emission spectrum of a $LiKSO_4$ crystal irradiated with 6.2 eV photons at 300 K.

Figure 1 (2)

Figure 1 (curve 3) shows that there are appears an emission band 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-wave emissions, long-wave emissions appear more efficiently. Figure 1 (curve 4) shows the emission spectrum of a $LiKSO_4$ crystal with 5 eV photons at a temperature of 80 K. Figure 1 (curve 4) shows that mainly long-wavelength emission bands appear at 3.0-3.1 eV, 2.7 eV, and 2.4 eV. Recombination emission associated with induced intrinsic defects is effectively detected from a wide main radiation band.

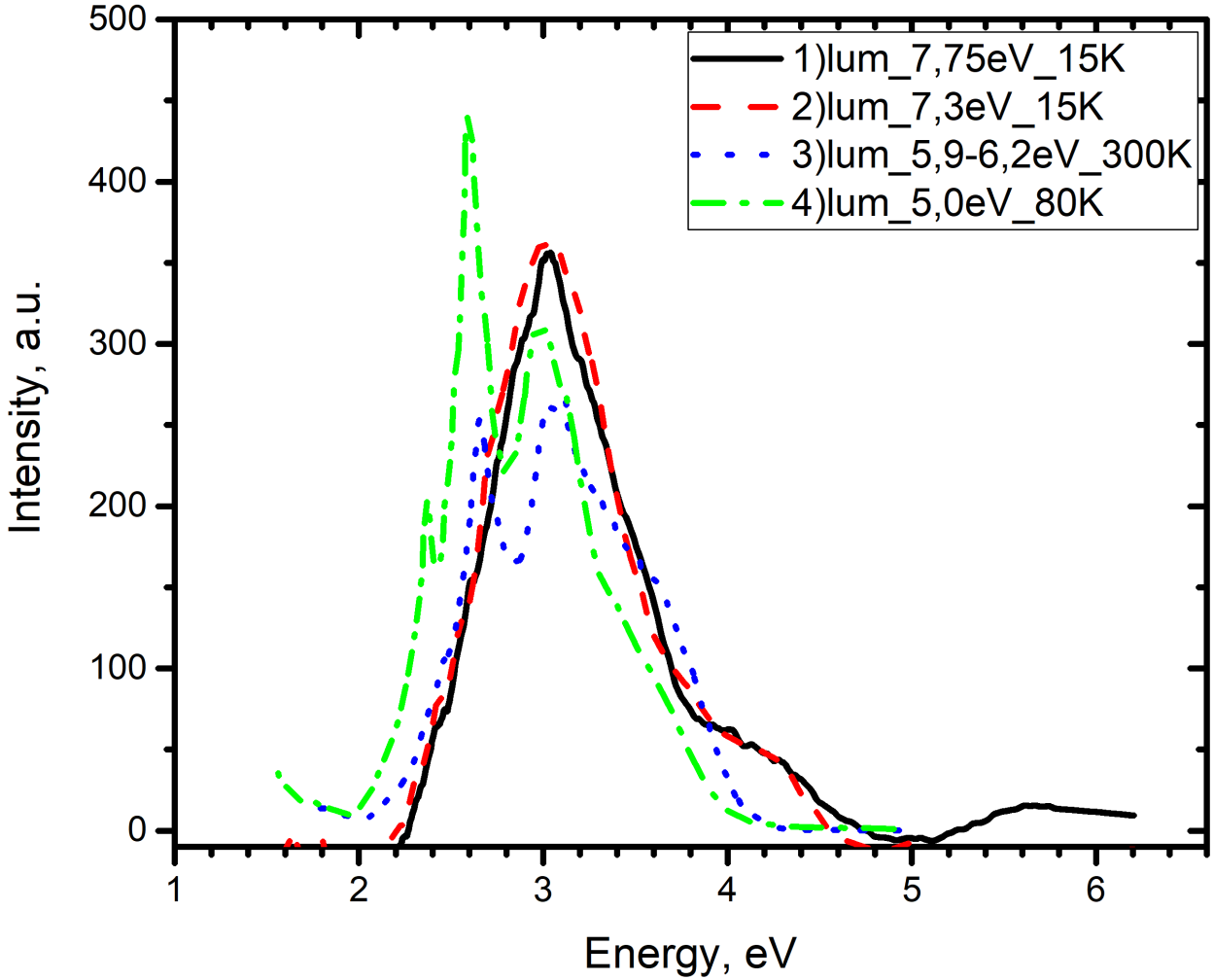

Fig.1. The emission spectrum of a $LiKSO_4$ crystal upon excitation by photons with an energy of: 1) 7.75 eV at 15 K; 2) 7.3 eV at 15 K; 3) 5.9-6.2 eV at 300 K; 4) 5.0 eV at 80 K.

Figure 2

Figure 2 (curve 1) shows the excitation spectrum for long-wave emission at 3.0–3.1 eV. Figure 2 (curve 1) shows long-wavelength emissions at 3.0-3.1 eV are excited in the spectral range 3.25 ÷ 3.5 eV, 3.8 ÷ 4.0 eV and 4.4-4,5 eV and are generated in the spectral region of the crystal where electron-hole pairs are formed. The figure 2 (curve 2) also shows the excitation spectrum for the emission band of 2.7 eV (curve 2). Figure 2 (curve 2) shows that almost the same bands appear at 3.3 eV, 3.9-4.0 eV and 4.5-4.6 eV excitation. Figure 2 (curve 3) shows the excitation spectrum for emission at 2.4–2.5 eV. Figure 2 (curve 3) shows a similar excitation spectrum at 3.25–3.3 eV, 3.4–4.0 eV, and 4.4–4.5 eV.

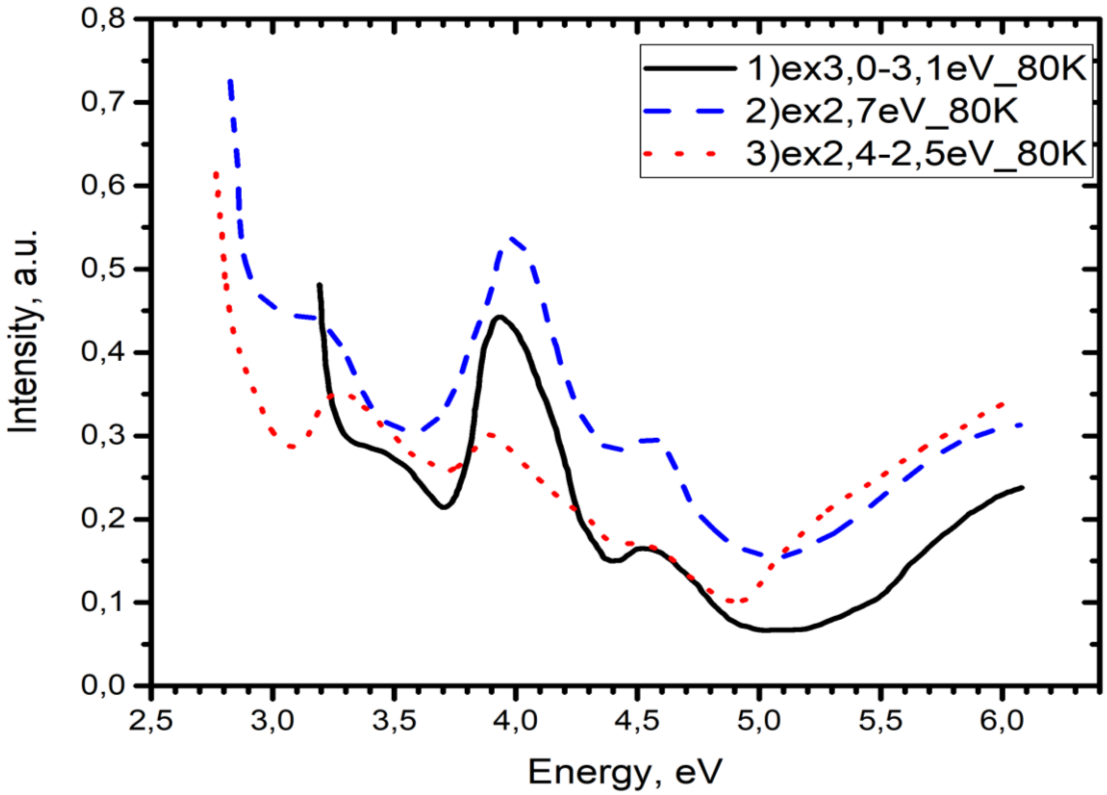

Fig. 2. The excitation spectrum for the emission bands of the $LiKSO_4$ crystal at 80 K: 1) 3.0-3.1 eV; 2) 2.7 eV; 2.4-2.5 eV.

Figure 3

Figure 3 shows the spectrum of the creation of recombination emission of 3.0-3.1 eV. Figure 3 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 generated in the fundamental region of the $LiKSO_4$ crystal, where free electron-hole pairs are created.

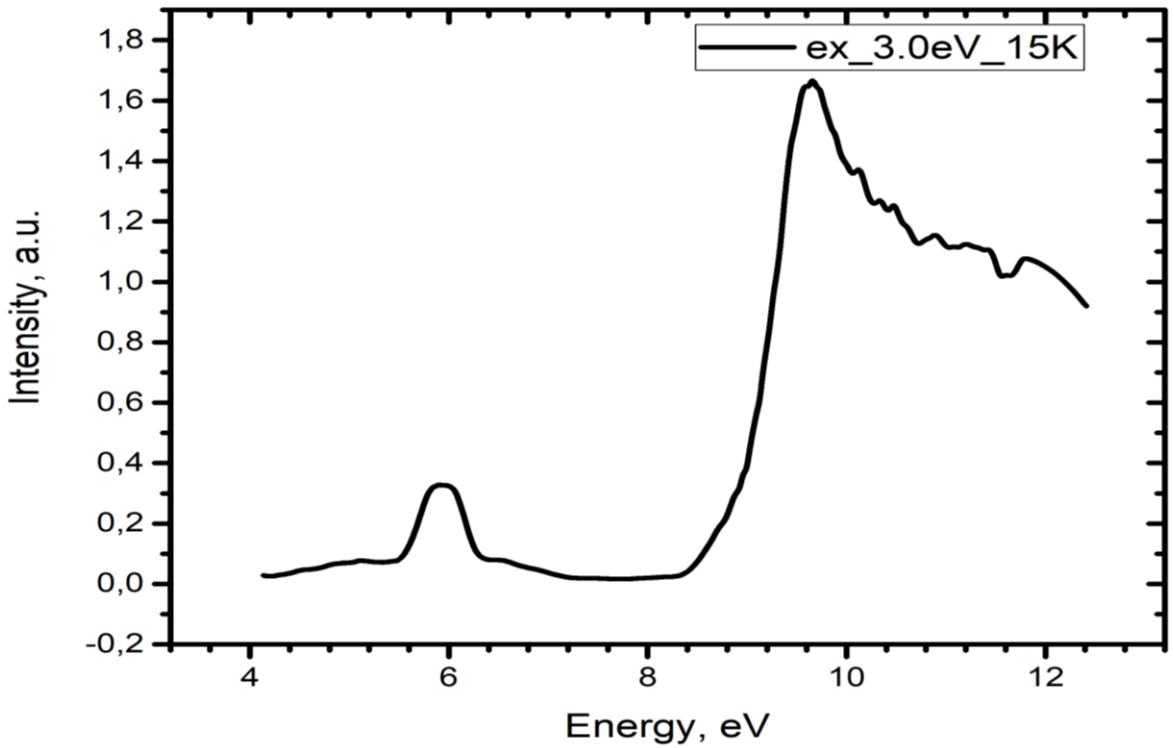

Fig. 3.The creation spectrum for the recombination emission band at 3.0 eV at 15 K.

Discussion

- Thus, all three bands of recombination emission are excited in the same spectral regions. We in our previous publications [8] assumed that in the region of photon energy at 6.0–6.2 eV and 9–12 eV, long-wave recombination emission at 3.0–3.1 eV is generated rather than excited. Based on our previous results [8], we can assume that the recombination emission bands in at 3.0–3.1 eV, 2.7 eV, and 2.4 eV when excited by 5.5–6.0 eV photons, are created (Figure 2, curves 1,2,3). And the excitation spectrum at 3.25 eV, 3.9-4.0 eV and 4.4-4.5 eV in $LiKSO_4$ recombination for the emission band at 3.0-3.1 eV, 2.7 eV and 2.4 eV corresponds to the intracenter electronic transition at the trap centers. As was assumed in previous works [8], trap centers are created when electrons are localized on anion complexes by the reaction:

$$SO_4^{2-} + e^- \rightarrow {}^{3-}_{4} \quad (1)$$

- Holes created on subbands are autolocalizedas SO_4^- . Electronic SO_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. According to reaction (1), electron – hole pairs create trap centers localized in the transparency region of the $LiKSO_4$ crystal.
- Excited SO_3^- SO_4^- trap centers, depending on the crystallographic location, emit different recombination or tunnel emission at 3.0-3.1 eV, 2.7 eV and 2.4 eV.

- Electron-hole trap centers can be created upon the transition of electrons from the valence band to the anti bonding orbitals, $4t_2^*$ and $3a_1^*$ 2p of the oxygen state in the conduction band. In this case, the excited anionic complex dissociates to form Frenkel defects - an interstitial atom or oxygen ion and an oxygen vacancy by the reaction:

$$\left(SO_4^{2-}\right)^* \rightarrow SO_3^- \vartheta_0^+ e^- + O^0 \text{ or } \qquad SO_3^- \vartheta_0^+ + O^-$$

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 trap centers. Electron-hole trap centers are formed upon electron captured by the SO_4^{2-} anion complexes and hole self-trapping in the form of the SO_4^{-} radical, as well as upon dissociation of the excited SO_4^{2-} anionic complex.

REFERENCES

1. I.V. Kityk, J. Kasperczyk, B.V. Andrievskii, Phys. Lett., vol. 216(A) pp. 161–166, 1996.
2. P.A. Shchepanskyi, V.Yo. Stadnyk, M.Ya. Rudysh, R.S. Brezvin, B.V. Andrievskii, Opt. Spectrosc.,vol. 125 (3), pp. 353–357, 2018.
3. V.Yo. Stadnyk, B.V. Andrievskii, L.T. Karplyuk, O.R. Onufriv, Opt. Spectrosc, vol.121 (2),pp. 283–288, 2016.
4. N.K. Madi, M.E. Kassem, M. El-Muraikhi, A.M. El-Khatib, Mater. Lett.,vol. 38,pp. 154–159, 1999.
5. M. El-Muraikhi, Mater. Lett., vol. 51, pp. 19–26, 2001.
6. A. Abu El-Fadl, M.A. Gaffar, M.H. Omar, Physical, vol. 269 (b), pp. 403–408, 1999.
7. S.P. Puppalwar, S.J. Dhoble, J. Lumin. Appl., vol. 137,pp. 245–251, 2013.
8. T.N.Nurakhmetov, A.T.Akilbekov, Zh.M.Salikhodzha, A.M.Zhunusbekov, A.Zh.Kainarbay, B.M.Sadykova, D.H.Daurenbekov, K.B.Zhangylysov, Radiation Measurements, vol. 125, pp. 19–24, 2019.