UDC 1.4.

PHOTOLUMINESCENCE OF $LiKSO_4$ ACTIVATED BY TL^+ IONS

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1. Introduction

The $LiKSO_4$ are crystals with mixed types of the chemical bond: between sub lattice is ionic and in sulfate anion – covalent. These crystals are transparent in wide spectral range. Most of the sulfates are being grown easily which allows setting different tasks in research of qualities of ions with impurity additives of cationic subsystem. Characteristics of mercury-like ions are well studied in cubic crystalline-ion crystals. Therefore, they are good luminescent probes for investigation of different processes in crystals. Crystals of complex lithium and potassium sulfate in temperature range 80-300K have two polymorphic phase-transitions. Parameters of impurity of luminescence's centers can be divided into static and dynamic. Specifications of foreign color centers of fluorescence may be roughly divided into static and dynamic. To static could be attributed for instance the maximal position of the optic stripes [1]. With temperature of liquid nitrogen the maximum of absorption is near 5.55 eV. The typical red displacement generates the heat. The maximum of absorption is being moved towards the big long waves. It allows us to set goals in field of foreign color's characteristics study in different symmetry crystalline without changing chemical composition. The article is dedicated to study spectrally fluorescent characteristics of crystals $LiKS0_4$, activated by ions Tl^+, Sn^{2+}, Pb^+

2. Experiment

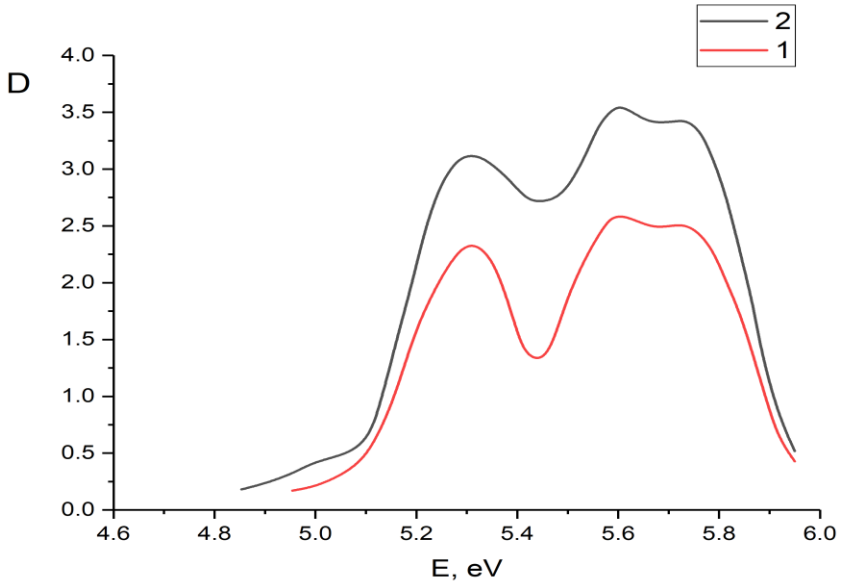
Absorption spectrum of $LiKSO_4$-Tl^+

$LiKSO_4$ crystals (activated by thallium ions) were obtained by adding Tl_2SO_4 and TlCl salts to the initial aqueous solution. It has been established by experiment, which means that when the KCl salt is added to the aqueous absorption bands do not appear in the energy range of 1.5-6.2 eV, i.e. in the region of transparency of the crystal. Optical properties of complex sulfate do not depend on the type of thallium salt used for activation.

Figure 1 shows the absorption spectrum for the $LiKSO_4$-Tl^+ crystal at room temperature. Curve 1 corresponds to the existence of thallium sulfate in the initial solution in the amount of 0.01 mol%, curve 2 - 0.05 mol%. Three optical absorption bands are observed with maxima at 5.3 eV, 5.6 eV, and 5.75 eV. A similar absorption spectrum was obtained when thallium chloride crystals were used for activation. It has been experimentally established that the optical density of the observed absorption bands increases with an increase in the concentration of impurity ions. There are no such absorption bands in non-activated $LiKSO_4$ crystals [2].

Figure 2 shows the absorption spectrum measured at 80K. There are maxima at 5.38 eV, 5.55 eV, and 5.7 eV. It should be noted that, with decreasing temperature, the intracenter processes are characterized by a blue shift by the maximum of the optical bands. In the $LiKSO_4$ crystal, this regularity is violated for the long-wavelength optical band. This is due to the fact that when the

temperature is lowered from 300K to 80K, two polymorphic phase transitions occur in lithium-potassium sulfate [3, 4].



1 - Concentration of impurity ions 0.01 mol %
2 - Concentration of impurity ions 0.05 mol %.
Figure 1 - Absorption spectrum of $LiKSO_4$-Tl^+ crystal at room temperature

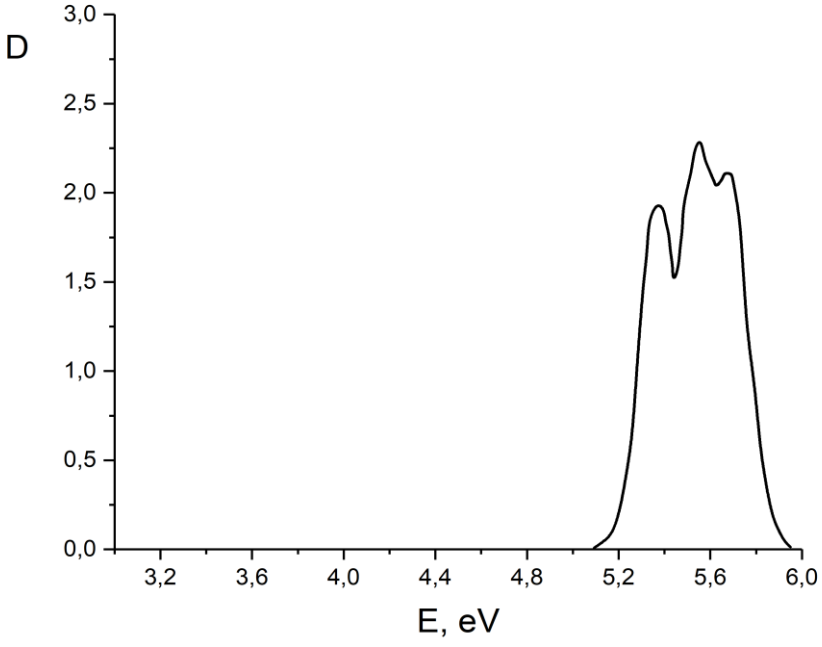
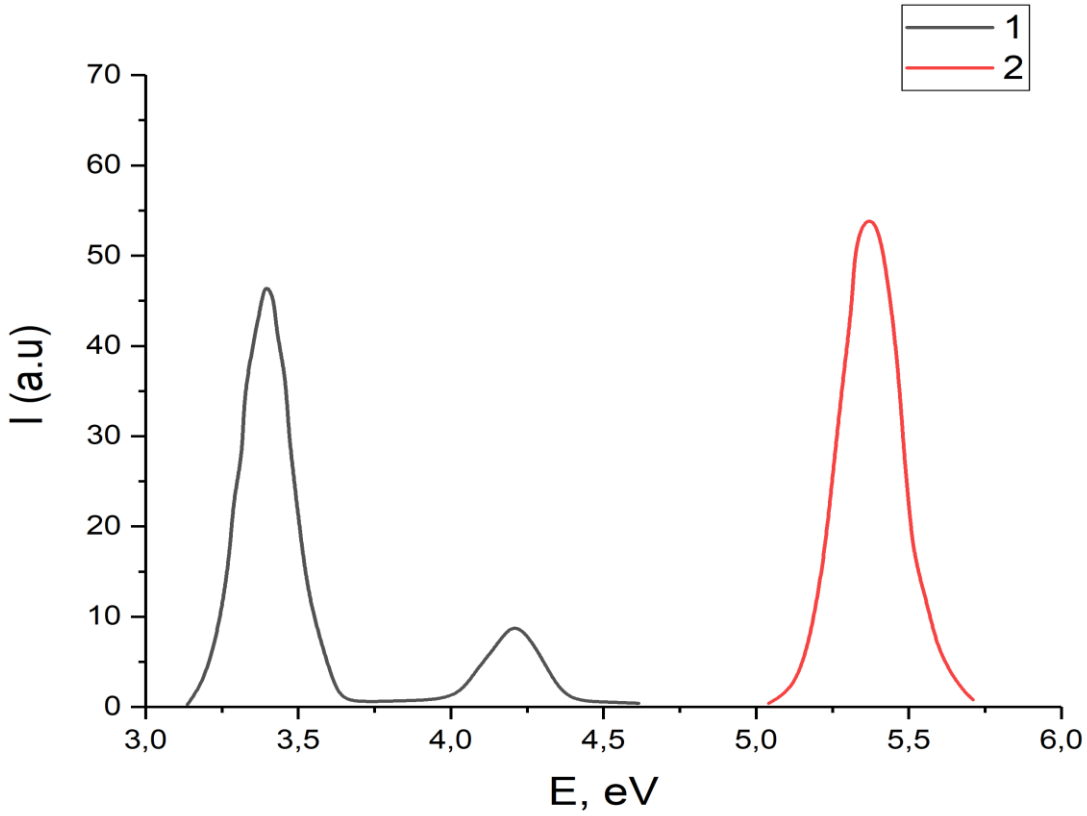


Figure 2 - Absorption spectrum of $LiKSO_4$-Tl^+ crystal at 80K
The concentration of impurity ions is 0.01 mol %

Photoluminescence of $LiKSO_4$-Tl^+

The absorption spectra for the $LiKSO_4$-Tl^+ crystal suggest the formation of two types of impurity centers. This is possible if thallium ions replace potassium and lithium ions in the crystal lattice of this compound. Since the symmetry and coordination numbers of impurity centers in nonequivalent cation sites are different, they should have different luminescence characteristics. Figure 3 shows the emission (curve 1) and excitation (curve 2) spectra for the $LiKSO_4$-Tl^+ crystal measured at room temperature. The emission spectrum was obtained with excitation in the 5.3 eV band. Two emission bands are observed - the main one has a maximum at 3.4 eV, the second, less intense, has a maximum at 4.2 eV. The excitation spectrum represented by curve 2 in Figure 3 was measured for the long-wavelength wing of the emission band with a maximum at 3.4 eV. It has the form of a single band with a maximum at 5.3 eV. Note that, upon excitation of photoluminescence on the long-wavelength wing of the absorption band at 5.3 eV, the luminescence intensity of 4.2 eV decreases.



1 – Excitation spectrum for luminescence 3.4 eV

2 - Emission spectrum upon excitation in the 5.3 eV band

Figure 3 - Emission and excitation spectra for the $LiKSO_4$-Tl^+ crystal at room temperature

Thereby, the three optical absorption bands are divided into two groups in accordance with the observed photoluminescence emission bands. Using the method of moments, it was found that both optical emission bands with maxima at 3.4 eV and 4.2 eV are well approximated by Gaussian curves. The spectral width is 0.21 eV and 0.28 eV, respectively. Deviations from the Gaussian curve become significant at a level below 0.1-0.15 of the maximum radiation intensity. The fact that the optical bands

are well approximated by Gaussian curves makes it possible to use the harmonic approximation for their processing.

3. Conclusion

The analysis of the shape of the photoluminescence emission bands of a lithium and potassium sulfate crystal doped with monovalent thallium ions showed that they are well described by Gaussian curves with an optical width at half maximum of 0.2 eV for the long-wavelength emission band and 0.25 eV for the short-wavelength band.

The emission and excitation spectra show the existence of two types of thallium ion luminescence centers in lithium-potassium sulfate. Based on the obtained experimental results and group-theoretical analysis, it can be argued that the emission band at 3.45 eV and excitation at 5.38 eV are associated with the thallium ion replacing the lithium ion, and the emission band at 4.3 eV and excitation at 5.55 eV and 5.7 eV are associated with the thallium ion replacing the potassium ion.

References

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