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Intrinsic emission and electron-hole trapping centers in crystals Li_2SO_4-Cu

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In the present work, the emission and excitation spectra in Li_2SO_4-Cu crystals have been obtained by the methods of vacuum-ultraviolet and thermoactivation spectroscopy. We have studied the nature of emission from a pressed and annealed sample of Li_2SO_4-Cu powders. It has been revealed that at low temperatures Cu^0-SO_4^- -centers are formed during the trap of electrons by Cu^+ -centers and during localization of SO_4^- -radicals in the form of localized hole centers.

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

Introduction

Lithium sulfates activated by impurities of Cu, Mn, Mg, P and rare-earth ions are widely used as inorganic phosphors, detectors of ionizing radiation, thermoluminescent dosimeters, etc. Such impurities play the role of luminescence centers or traps for electrons and holes. The sensitivity of alkali metal sulphate detectors is dependent on defects formed during irradiation.

In the works of the authors [1, 2] for crystals Li_2SO_4-Cu it is shown that Mg^{2+} and P introduced into the matrix double the intensity of emission Cu^+ at 3.20-2.18 eV (387-389 nm). The authors showed that copper impurities play an important role in increasing the emission intensity. It is possible that these impurities act as sensitizers. Impurities Cu^+ in dosimetric crystals LiF:Mg,Cu,P [3-6], LiF:Mg,Cu,Si [7], and $Li_2B_4O_7$-Cu [8-10] are the main emitter with the development of thermally stimulated luminescence (TSL).

The authors of [11] show the luminescence bands of the copper ion in various crystals, for example, 3.3 eV (375 nm) for $NaMgF_3$, 2.98 eV (415 nm) $KMgF_3$, 2.66 eV (465 nm) ($LiBaF_3$), 3.0 eV (413 nm) (CaS), 2.62 eV (472 nm) (MgS), 2.59 eV (478 nm) (SrS), 2.11 eV (585 nm) (BaS),3.02 eV (410 nm), 2.75 eV (450 nm), 2.58 eV (480 nm), 2.43 eV (510 nm) and 2.29 eV (540 nm) (silicon zeolites), 2.43 eV (510 nm) (silicon glasses), 3.4 eV (360 nm) and 2.95 eV (420 nm) (NaCl) and 3.20 eV (387 nm) (Li_2SO_4-Cu). Studies have shown that the addition of copper increases the thermoluminescence sensitivity of TLD dosimeters to improve monitoring of low radiation background. In the study [12] evaluated the fading of a new copper-doped dosimeter using modern equipment for processing TLD characteristics.

The relevance of this study is due to the fact that Cu^+ in the crystal Li_2SO_4-Cu stimulates the formation of electron – hole trapping centers. In the literature, there is no purposeful study of the mechanism of creation of electron-hole trapping centers in Li_2SO_4-Cu. The influence of the Cu^+ impurity on the stabilization of intrinsic electron – hole traps has not been investigated.

Objects and methods of research

Crystals Li_2SO_4-Cu were grown at a temperature of 50° C from a saturated aqueous solution by the method of slow evaporation. Powdered samples were obtained by the "wet" chemical method from Li_2SO_4 (Sigma-Aldrich) with the addition of 0.01 mol% $CuSO_4$-$5H_2O$ (Sigma-Aldrich). After evaporation at 800 °C for 8 hours, powdered samples Li_2SO_4-Cu are formed. After drying, the sample is annealed at 700° C for 1 hour. After these processes, the powder was pressed with a pressure of 0.5 MPa using a laboratory hand press.For excitation in the ultraviolet region of the spectrum, a source of VUV radiation was used - a hydrogen flow discharge lamp with a photon energy of 6.2-11.5 eV. The spectra of excitation and emission in the spectral region of $4 \div 11.5$ eV were measured on a vacuum monochromator assembled according to the Seya-Namioka scheme in a wide temperature range $15 \div 400$ K. The emission was recorded through an MDR-41 monochromator using a photomultiplier 1P28 (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral distribution of the intensity of the exciting radiation.

The results of the experiment and their discussion

At the initial stage, in a wide spectral region, the efficiency of the formation of intrinsic and impurity emission at temperatures at which the impurity electron – hole trapping centers are not stable is investigated.

Figure 1 shows the emission spectrum of a Li_2SO_4-Cu crystal upon excitation by photons with energies from 6.2 eV to 4.27 eV (curves 1-11) at a temperature of 300 K.

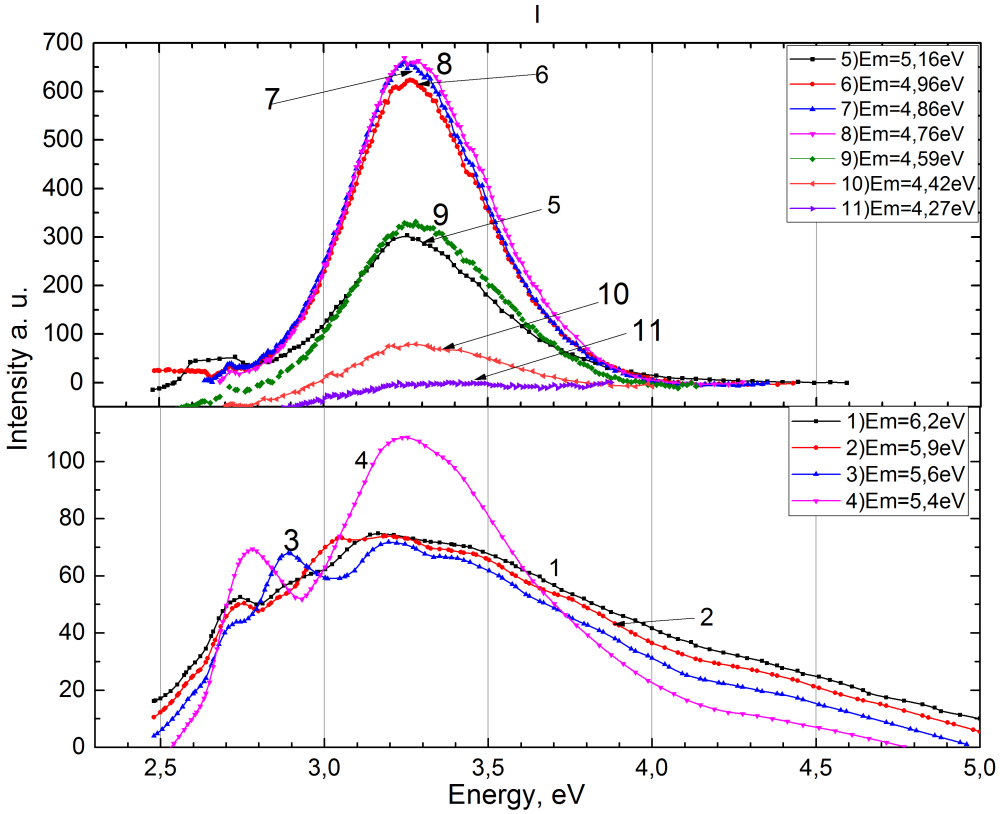

Figure 1. Emission spectrum of highly pure (99.99%) powder Li_2SO_4-Cu, when excited by photons with an energy from 4.27 eV to 6.2 eV at 300 K

It is seen that at a photon energy of 6.2-5.4 eV (curves 1-4), the intensity of intrinsic and impurity emission Cu^+ is weakly observed. Beginning with a photon energy of 5.16 eV (curve 5), the intensity of the impurity emission gradually increases to the value of the exciting photon 4.77 eV (curves 6-8). Then, with a decrease in the photon energy to 4.27 eV, the emission intensity decreases to a minimum value (curves 9-11). The maximum emission appears at 3.26 eV, and the excitation is 4.77-4.86 eV.

Figure 2 shows the emission spectrum of a crystal Li_2SO_4-Cu irradiated by 6.2-4.28 eV at 80 K (curves 1-10). Emission appears with a maximum at 3.18 eV. Figure 2 shows (curves 1-3) the appearance of a weak intrinsic and impurity emission at 4.0-4.3 eV and 3.7-3.8 eV and 3.18 eV, respectively. Beginning with energy of 5.4 eV, the intensity of the impurity emission gradually increases (Figure 2, curves 4-10).

It should be noted that in the long-wavelength part of the main impurity emission at 3.18 eV, an additional emission band appears at 3.0-3.1 eV (curves

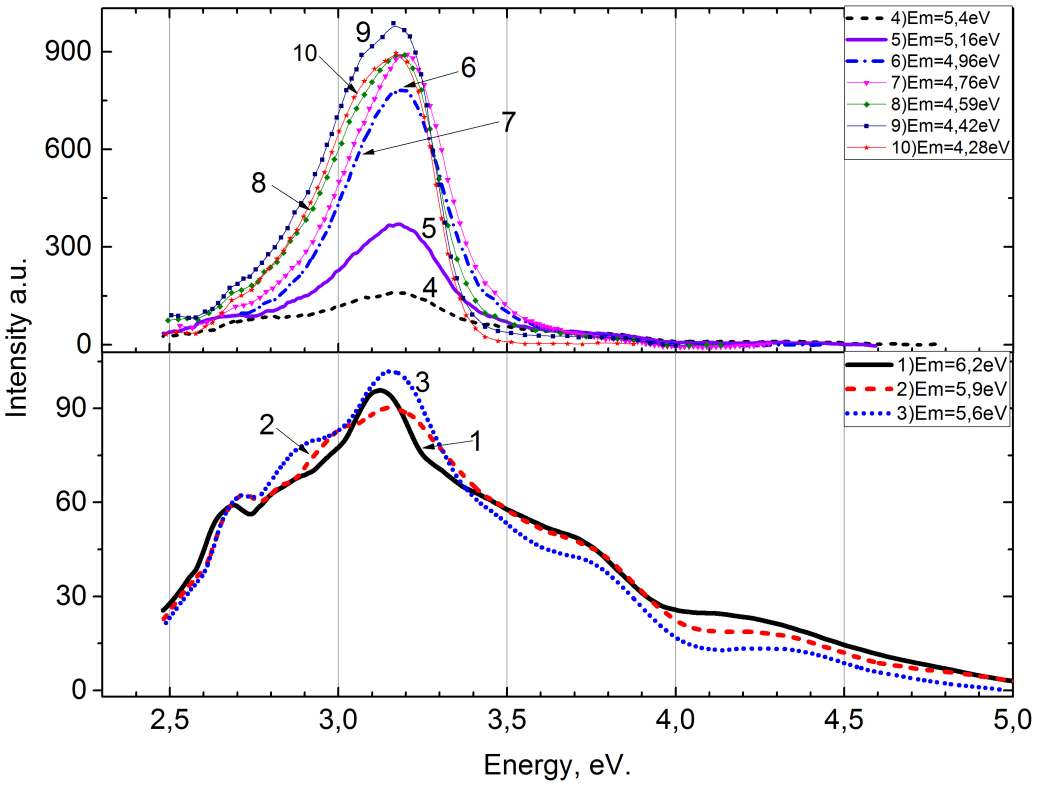

Figure 2. Emission spectrum of highly pure (99.99%) powder Li_2SO_4-Cu, when excited by photons with an energy from 4.27 eV to 6.2 eV at 80 K.

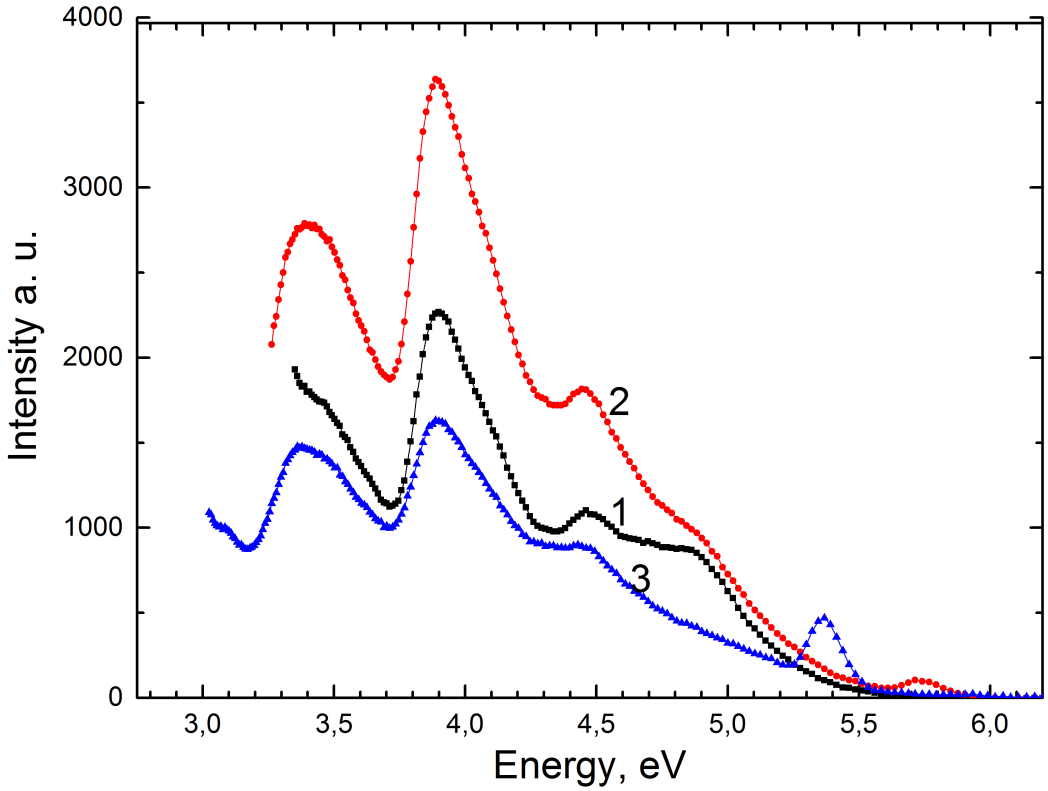

Figure 3. Excitation spectrum Li_2SO_4-Cu for emission bands 1-3,18 eV, 2-3,05 eV, 3-2,84 eV at 80 K.

7-10). Next, we measured the excitation spectrum for the emission band of 3.18 eV (Figure 3, curve 1), for the emission band of 3.05 eV (Figure 3, curve 2) and for

the emission band of 2.84 eV (Figure 3, curve 3). Figure 3 shows that the impurity emission bands of 3.18 eV, 2.84 eV and 3.05 eV are excited by 4.43 eV, 3.87 eV, 3.4 eV. From the Figure 3 it can be seen that the Cu^{+} impurity emission is excited at lower energies but should be excited at 4.77-4.96 eV.

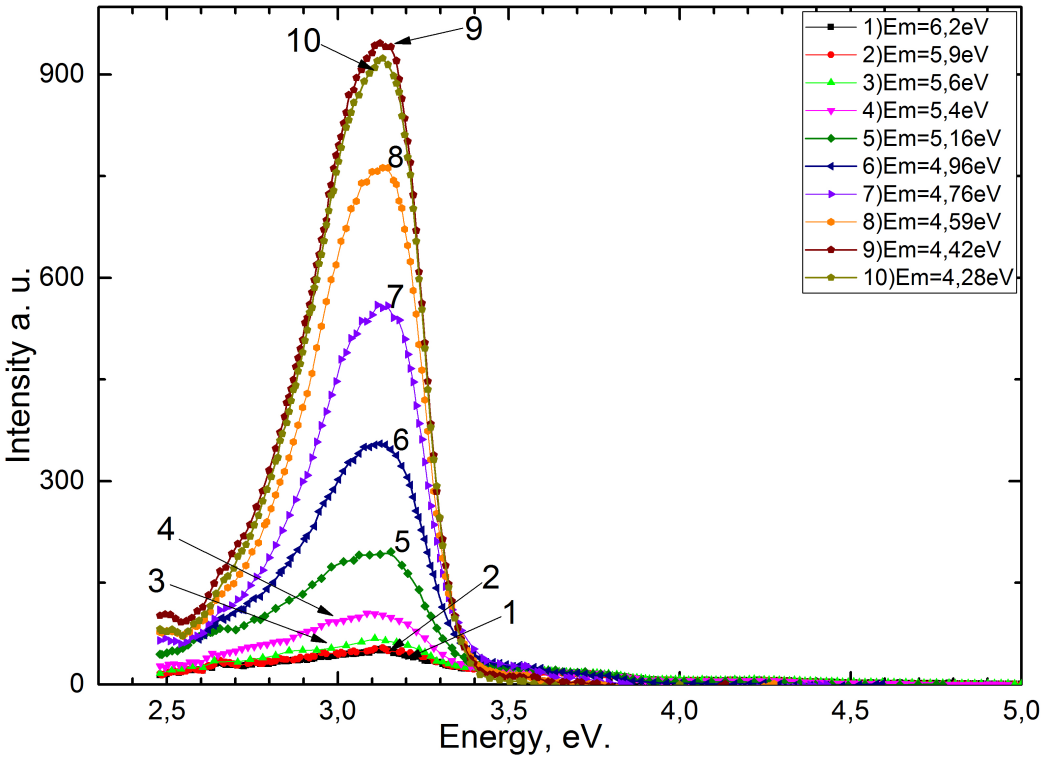

Figure 4. The emission spectra of X-ray irradiated Li_2SO_4-Cu crystal at the excitation by photons from 4.27 eV to 6.2 eV at 80 K.

Figure 4 shows the emission spectrum of a Li_2SO_4-Cu crystal irradiated with photons by 6.2-4.28 eV (curves 1-10) at 80 K. The crystal was pre-irradiated with X-rays for 10 minutes at 80 K. As can be seen from Figure 4, emission appears with a maximum at 3.1 eV. Figure 4 shows that at the initial moment a weak band of impurity and intrinsic emission appears (curves 1, 2). Beginning with an exciting energy 5.4 eV, the intensity of the impurity emission gradually increases to the value of the exciting photon 4.27 eV - 4.43 eV (Figure 4, curves 3-10).

Figure 5 shows the excitation spectrum of the 3.18 eV emission band (curve 1), the 3.05 eV emission band (curve 2) and the 2.84 eV emission band (curve 3). It is seen that the impurity emission bands of 2.84 eV, 3.05 eV, and 3.18 eV are excited by 4.43 eV, 3.87 eV, 3.4 eV. From the experimental fact it follows that the Cu^{+} impurity emission bands are excited at lower energies than should be excited with maximum intensity at 4.77-4.96 eV.

Figure 6 shows the temperature dependence of the emission band 3.13 eV in Li_2SO_4-Cu irradiated with photons with an energy of 4.77-4.96 eV at 80 K. Cu^{+} and Cu^{0}-SO_4^{-} -centers are annealed in the temperature range 200-300 K, in which Cu^{0}-SO_4^{-} -centers are gradually destroyed.

Based on the results obtained in previous works [13], we can conclude that at temperatures in which localization of electron-hole pairs does not occur, for

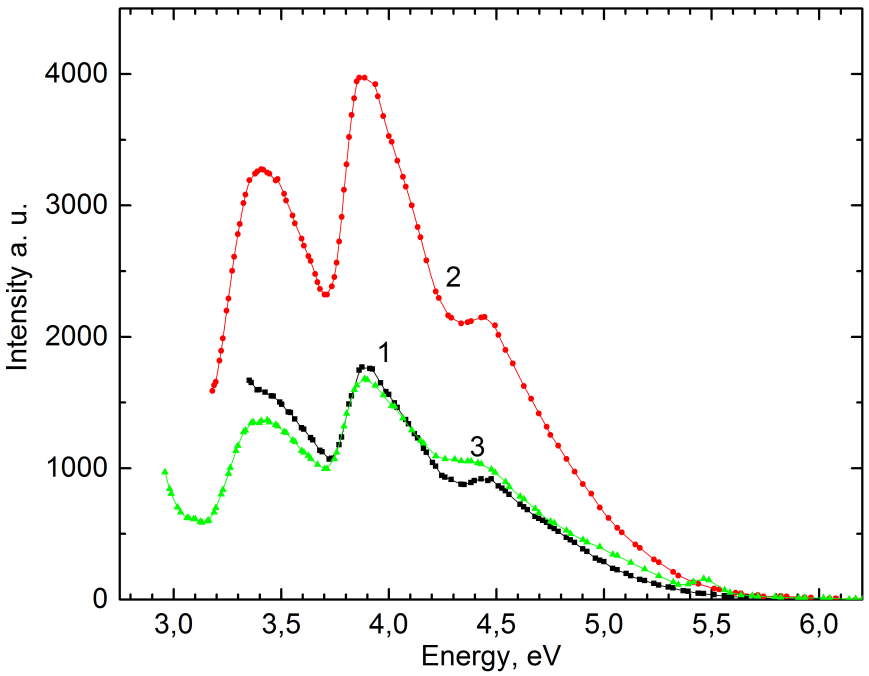

Figure 5. Excitation spectrum of X-ray irradiated crystal Li_2SO_4-Cu : 1-3.18 eV, 2-3.05 eV, 3-2.84 eV at 80 K.

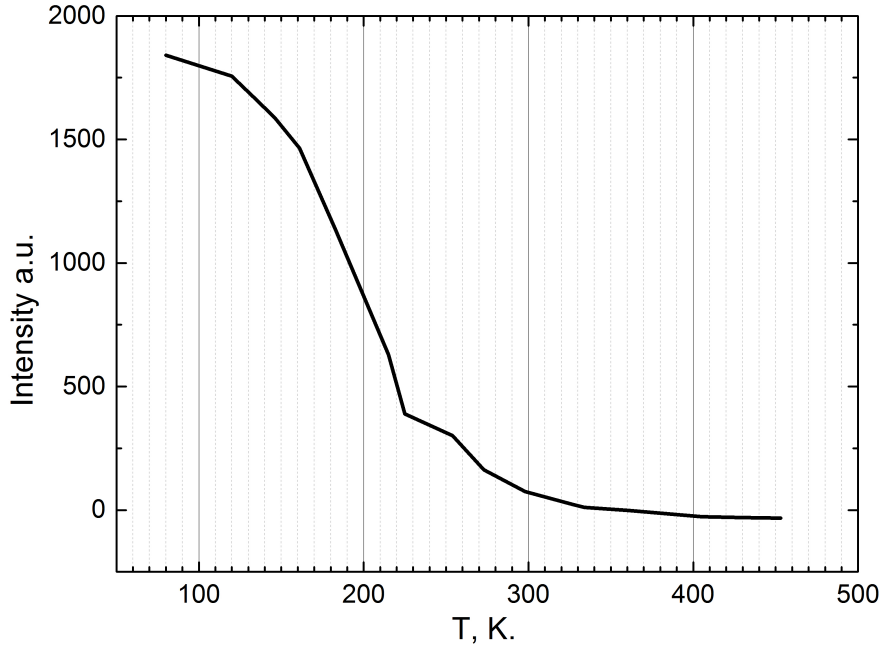

Figure 6. Temperature dependence of the emission band of 3.13 eV of the Li_2SO_4-Cu crystal irradiated with photons with an energy of 4.77-4.96 eV at 80 K.

crystals $LiKSO_4$-Cu and K_2SO_4-Cu we observe the emission and excitation spectrum of an undisturbed impurity ion Cu^+. At low temperatures, Cu^0-SO_4^--centers are formed during the trap of electrons by Cu^+-centers and when the SO_4^--radicals are localized in the form of localized hole centers, the emission of the crystal proceeds by complex mechanism.

In this work, we investigated the emission spectrum of a pressed and annealed sample Li_2SO_4-Cu. As shown in Figure 1 the Cu^+ impurity band in Li_2SO_4-Cu

crystal emits at 3.26 eV, and is excited by 4.77-4.86 eV. At the temperature of liquid nitrogen, the maximum of the emission band appears at 3.18 eV under excitation of 4.77-4.81 eV. With a decrease exciting energy from 4.81 - 4.27 eV, the intensity of the emission band changes insignificantly. In the long-wavelength region of the broad band, an additional band appears at 3.02 - 3.1 eV. Measurements within a wide emission band of the excitation spectrum for emission bands at 2.84 eV, 3.05 eV and 3.18 eV showed that these bands are excited by 4.43 eV, 3.87 eV, 3.4 eV. The excitation energy of Cu^+ emission impurity bands are much less than the optimal value of the excitation energy of an impurity ion at 4.77-4.8 eV.

Preliminary X-ray irradiation of Li_2SO_4-Cu crystals at 80 K shifts the main broad emission band to the long-wavelength region of the spectrum from 3.26 eV to 3.1 eV - 3.14 eV. Measurement of the excitation spectrum at 2.84 eV, 3.05 eV, and 3.18 eV showed that these bands are excited in the same energy ranges at 4.43 eV, 3.87 eV, 3, 4 eV. For pure crystals $LiKSO_4$ and Li_2SO_4 we studied [14] the creation of electron-hole trapping centers. It has been shown experimentally that in pure crystals a long-wavelength recombination emission band at 3.0-3.1 eV is created, but not excited at photon energies of 5.9-6.2 eV and 9-12 eV, at which electron-hole pairs are generated.

It is assumed that electron-hole pairs are created according to reaction (1) during the capture of e^- -by anionic complexes SO_4^{2-}

$$SO_4^{2-} + e^- \rightarrow SO_4^{3-} \rightarrow (SO_3^{2-} - O^-), \quad (1)$$

The hole is localized as SO_4^- -radical. Thus, in pure crystals, electron-hole pairs are created in the form:

$$[SO_3^{2-} - O^-] - SO_4^-, \quad (2)$$

Measurement of the excitation spectra of recombination radiation 3.0-3.8 eV showed that at 80 K they are excited at photon energies 3.9-4.0 eV and 4.4-4.5 eV for $LiKSO_4$ crystals, at 3.9-4.0 eV and 4.6-4.75 eV for Li_2SO_4.

It is assumed that the energy distances of the created electron-hole trapping centers, which irradiate by tunneling at 3.0-3.1 eV, should be 3.9-4.0 eV and 4.6-4.75 eV, for example, for Li_2SO_4.

For the crystal Li_2SO_4-Cu we have created conditions for the traps of electrons Cu^+ by ions and the formation of Cu^0-SO_4^- - electron-hole trapping centers. It is assumed that the energy distance between the electron-hole trapping centers of Cu^0-SO_4^- -centers is 3.87 eV and 4.43 eV. Recombination radiation for Li_2SO_4-Cu occurs at 3.1-3.14 eV.

Measurement of the temperature dependence of the broad 3.13 eV band showed that in the temperature range in which the Cu^0-SO_4^- -centers should be destroyed, the intensity of this band in the temperature $200 \div 300$ K gradually decreases.

Thus, we assume that the excitation of the emission band Cu^+ centers in the energy range 4.43 eV, 3.87 eV, 3.4 eV should be associated with the destruction of electron-hole trapping Cu^0-SO_4^- -centers. The excitation energies of the main bands at 4.43 eV, 3.87 eV, 3.4 eV are the energy distance of the electron-hole

trapping centers Cu^0-SO_4^-. During excitation, the electron of the ionized C^0-center recombines with the SO_4^--radical and the energy of the recombination process excites the Cu^+ ion. In three excitation bands of 4.43 eV, 3.87 eV, 3.4 eV we observe the emission of an impurity ion Cu^+ in Li_2SO_4-Cu.

Conclusion

In the crystal Li_2SO_4-Cu, electron-hole trapping centers with an energy distance of 4.43 eV, 3.87 eV, 3.4 eV have been discovered for the first time. They are formed when the Cu^+ centers trapping the electrons and when the SO_4^- - radical is localized in the form of a hole trapping center SO_4^-. It was found that Cu^0-SO_4^- - centers are stable at temperatures below 200 K.

Acknowledgments

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