Electron-hole capture centers in an irradiated $K_2SO_4$-Cu crystal

T.N. Nurakhmetov$^{*,1}$, Zh.M. Salikhodzha$^1$, R.Z. Bakhtizin$^2$, A.M. Zhunusbekov$^1$, A.Zh. Kainarbay$^1$, D.H. Daurenbekov$^1$, B.M. Sadykova$^1$, K.B. Zhangylyssov$^1$, B.N. Yussupbekova$^1$

$^1$L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan
$^2$Bashkir state university, Ufa, Russia

E-mail: nurakhmetov_tn@enu.kz

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The methods of vacuum-ultraviolet and thermal activation spectroscopy were used to measure the excitation spectra of impurity radiation in the fundamental absorption band of $K_2SO_4$-Cu crystals at 15 K and 300 K. An energy transfer was detected from the base to Cu$^{+}$ impurities. The band gap of crystals $K_2SO_4$ was estimated. In $K_2SO_4$-Cu crystals, recombination radiation bands were detected at 2.95 ÷ 3.0 eV corresponding to electron-hole capture centers.

Keywords: photon, electron, hole, tunnel luminescence, recombination, band gap.

Introduction

Sulfates of alkali and alkaline earth metals activated by various impurities are widely used in thermoluminescent dosimeters (TLD) and scintillators. Sulfates are radiation sensitive materials. Therefore, they are mainly used as TLD dosimeters. The sensitivity of TLD dosimeters depends on the concentration of defects generated during irradiation. Specially introduced activators increase the concentration of defects in sulfates of alkali and alkaline earth metals in several times. Defects in activated sulfates are created by several mechanisms: during irradiation the created electron-hole pairs are localized on matrix ions or activators; creation of Frenkel pairs of defects in the electronic excitations decay; anionic or cationic
vacancies are formed near the impurity to compensate charge, which are stabilize the defects.

In the early works of the authors of [1], it was assumed that in the K$_2$SO$_4$-Tl crystal under ionizing radiation, electronic Tl$^0$ and hole Tl$^{2+}$ capture centers are created, during localization process of electrons near the impurity Tl$^+$ and by holes SO$_4^{2-}$.

The authors of [2, 3] showed that in the K$_2$SO$_4$ crystal activated by ions Ce$^{3+}$, Eu$^{3+}$, Ca$^{2+}$, Na$^+$ and Al$^{3+}$ after irradiation, high-temperature peaks of thermally stimulated luminescence (TSL) and recombination emission bands are created, which mean the generation of radiation defects. Defects are detected by heating or optical stimulation irradiated impurity in K$_2$SO$_4$ crystals. It is assumed that during irradiation, energy is stored in the form of electron-hole capture centers.

The authors of [4-6] investigated lithium-containing alkali metal sulfates, such as LiNaSO$_4$ and Li$_2$SO$_4$ activated by rare-earth ions Eu$^{3+}$, Ce$^{3+}$, Sm$^{3+}$, La$^{3+}$, Tb$^{3+}$ which are tissue-equivalent TL dosimeters. In these sulfates, low-temperature (350 ÷ 450 K) and high-temperature (500 ÷ 650 K) TSL peaks are created. The spectral composition of TSL peaks reveals the content of impurity emission associated with intracenter transitions at the corresponding impurity ions.

Alkali metal sulfates K$_2$SO$_4$, CsSO$_4$ and Rb$_2$SO$_4$ with an admixture of Cu$^+$ were studied by the authors [7]. It was shown that impurity emission of Cu$^+$ at 2.7 ÷ 2.9 eV and it is excitation in 4.7 ÷ 4.8 eV at 300 K.

The authors of [8] suggest that LiNaSO$_4$ crystals with impurities Cu$^+$, Mg$^{2+}$ can be used as TL dosimeters. The authors showed that the sensitivity of dosimeters based on LiNaSO$_4$-Cu, Mg is comparable to commercial dosimeters TLD-100 or CaSO$_4$-Dy. In irradiated LiNaSO$_4$-Cu and LiNaSO$_4$-Cu, Mg crystals, the authors found TSL peaks at 160 °C and 166 °C, respectively. The authors of [8] associate the manifestation of TSL with the formation of electron – hole capture centers near the Cu$^+$ impurity.

The main objective of this work is to elucidate the nature of intrinsic and impurity emission and the mechanisms of formation of electron-hole capture centers in the K$_2$SO$_4$-Cu crystal.

**Objects and research methods**

K$_2$SO$_4$-Cu crystals grown at a temperature of 50 °C from a saturated aqueous solution by slow evaporation. 3-5 mm thick plates were cut from the crystal. We studied samples of crystals and powders (chemical purity 99.99%) K$_2$SO$_4$-Cu. Samples were studied by photoluminescence, x-ray luminescence and vacuum-ultraviolet spectroscopy. Excitation in the ultraviolet is performed by VUV radiation source by using flowing hydrogen lamp with a photon energy 6.2 ÷ 11.5 eV. To measure the emission and excitation spectra in the spectral range of 1.5 ÷ 6.2 eV, the Solar CM 2203 spectrofluorimeter was used. The spectra of excitation and emission in the spectral region of 4 ÷ 11.5 eV were measured on a vacuum
monochromator assembled according to the Seya-Namioka scheme in a wide temperature range 15 ÷ 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

Figure 1 shows the emission spectrum of a compressed powder K₂SO₄ -Cu when excited by photons with an energy of 6.5 eV (curve 1), 6.2 eV (curve 2), 5.9 eV (curve 3), 5.64 eV (curve 4), 5.4 eV (curve 5), 5.16 eV (curve 6), 5.06 eV (curve 7), 4.77 eV (curve 8) at 300 K. Figure 1 shows that when excited by photons with an energy of 6.5 eV, intrinsic emission at 3.65 eV, long-wavelength emission at 3.0 ÷ 3.4 eV and an impurity luminescence band at 2.6 ÷ 2.7 eV is appear. These emission bands also appear upon excitation by photons of 6.2 eV (Figure 1, curve 2). The results obtained mean that the energy of the electron – hole pair in K₂SO₄ excites the impurity ion Cu⁺. When excited by photons with energies of 5.64 eV and 5.4 eV, the emission intensity of the impurity ion and intrinsic luminescence is minimal. At these energies, the intrinsic and impurity emission bands are not excited.

The authors determined the band gap in the energy range \( E_g = 5.64 ÷ 5.9 \text{ eV} \). A further decrease in the energy of the exciting photon from 5.64 ÷ 5.06 eV increases the intensity of impurity emission. Since impurity emission is effectively excited in the photon energy range 4.77 ÷ 5.06 eV. Thus, the emission of the Cu⁺ impurity in K₂SO₄ is excited both in the fundamental absorption region of the crystal and in the absorption band of the Cu⁺ ion in the matrix.

Figure 2 shows the excitation spectrum of impurity emission at 2.65 ÷ 2.7 eV. Figure 2 shows that the impurity emission is excited at a photon energy of 4.77 ÷ 5.06 eV and 5.9 ÷ 6.05 eV.

Figure 3 shows the emission spectrum of K₂SO₄ powders (curve 1) upon excitation by photons with an energy of 4.9 ÷ 5.0 eV at 80 K. From Figure 3 it is seen that emission bands of 3.0 ÷ 3.1 eV and a wide emission band of 2.90 ÷ 2.70 eV is appear. At the next stage, the emission spectrum was measured at 300 K under excitation by photons with an energy of 4.9 ÷ 5.0 eV (curve 2). Figure 3 (curve 2) shows that the emission band of 3.0-3.1 eV falls to a minimum, the band of 2.9-2.7 eV stands out as a separate emission band. It can be seen that the emission band of 3.0-3.1 eV is unstable at room temperature, due to the delocalization of electrons or holes from the capture centers.

Figure 4 shows the emission spectrum of K₂SO₄ -Cu when excited by photons with an energy of 7.75 eV at 300 K. Figure 4 (curve 1) shows that intrinsic short-wavelength emission band of 5.0 eV, 4.2 ÷ 4.3 eV, 4.0 eV, 3.7 ÷ 3.8 eV and the long-wavelength band at 2.7 ÷ 2.9 eV and 2.5 ÷ 2.4 eV is appear. The intense emission band of 2.7 ÷ 2.9 eV should correspond to the impurity Cu⁺. At the next stage, the K₂SO₄ crystal is irradiated by photons with an energy of 7.75 eV at 15 K. In addition to the short-wavelength emission bands from 3.64 eV to 5.0
Figure 1. The emission spectrum of a compressed powder K$_2$SO$_4$-Cu at 300 K when excited by photons with an energy of 1) 6.5 eV, 2) 6.2 eV, 3) 5.9 eV, 4) 5.64 eV, 5) 5.4 eV, 6) 5.16 eV, 7) 5.06 eV, 8) 4.77 eV.

Figure 2. The excitation spectrum of K$_2$SO$_4$-Cu powders for emission band of 2.65 ÷ 2.7 eV at 300 K.

Figure 3 (curve 3) shows the excitation spectrum of the emission band at 3.0 ÷ 3.1 eV is excited in the transparency region of the K$_2$SO$_4$ crystal at 4.43 eV and 3.87 eV.
Figure 3. The emission spectrum of the K$_2$SO$_4$-Cu powder upon excitation by photons with an energy of: 1) 4.9 eV at 80 K; 2) 4.9 eV at 300 K; 3) 3.0 ÷ 3.1 eV at 80 K.

Figure 4. The emission spectrum of K$_2$SO$_4$-Cu when excited by photons with an energy of 7.75 eV 1) at 300 K; 2) at 15 K.

For irradiated K$_2$SO$_4$-Cu crystals at 80 K, TSL spectra were measured (Figure 5). Figure 5a shows that TSL peaks appear at 180-200 K, 240-250 K, and 310-330 K. Measurement of the spectral composition of TSL peaks of the K$_2$SO$_4$-Cu crystal irradiated at 80 K showed that in TSL peaks at 180 ÷ 200 K and 240 ÷ 250 K there are emission bands with maxima of 2.6 eV and 2.65 eV, respectively, and in addition
broad emission band with maxima of $2.95 \div 3.0$ eV appears in the TSL peaks at $310 \div 330$ K (Figure 5b). This wide band also contains long-wavelength emission bands of $2.6 \div 2.65$ eV (Figure 5b).

Under stationary X-ray excitation at 80 K of $\text{K}_2\text{SO}_4$ -Cu crystals, emission bands arise at $2.6$ eV and $2.95 \div 3.0$ eV (Figure 6a, curve 1). A study of the temperature dependence of the emission $2.6$ eV and $2.95 \div 3.0$ eV of the $\text{K}_2\text{SO}_4$ -Cu crystals showed that the intensity of the band at $2.95 \div 3.0$ eV increases in the temperature region where the TSL peaks of the $\text{K}_2\text{SO}_4$ -Cu crystal were detected after irradiation at 80 K. The emission intensity increases at the TSL peak of 310-330 K is tens of times more intense than at the peak at 180-200 K. After the cessation of irradiation, tunnel luminescence was measured. As it was found out, the maxima of the tunnel luminescence bands coincide with the X-ray luminescence band (Figure 6a).

**Discussion**

In alkali metal sulfates activated by impurities $\text{Cu}^+$ sulfates, an emission band was detected in the spectral region $2.7 \div 2.9$ eV. This band is excited by photon energy of $4.7 \div 4.8$ eV at 300 K [7]. Additional impurities introduced into alkali metal sulfates activated by $\text{Cu}^+$ ions increase the high-temperature dosimetric peaks of TSL. From an analysis of the authors’ works [4-6] it follows that two types of dosimetric TSL peaks are created in irradiated crystals with impurities. Low-temperature TSL peaks (350-450 K) associated with the delocalization of electrons and holes from impurity capture centers created by localization of
Figure 6. X-ray luminescence spectrum, temperature dependence, and tunnel luminescence of the K$_2$SO$_4$-Cu crystal: a) X-ray and tunnel luminescence spectra: 1 - X-ray luminescence spectrum of the K$_2$SO$_4$-Cu crystal; 2 - spectrum of tunnel luminescence of the K$_2$SO$_4$-Cu crystal; b) temperature dependence of the intensity of the X-ray luminescence band with a maximum of 2.95 eV.

electrons and holes on impurities. High-temperature TSL peaks (500-650 K) are mainly dosimetric TSL peaks of unknown nature.

In accordance with the main objective of this work, we investigated the mechanism of the formation of electron-hole trapping centers in a K$_2$SO$_4$-Cu crystal by the methods of thermally activated and vacuum-ultraviolet spectroscopy. When a K$_2$SO$_4$-Cu crystal is excited by photons with an energy of 6.5 eV at 300 K, intrinsic emission appears at 3.65 eV, 3.0 ÷ 3.4 eV and impurity emission at 2.65 ÷ 2.7 eV. Measurement of the excitation spectrum of the impurity emission showed that 2.65 ÷ 2.7 eV emission is excited by photon energies of 4.77 ÷ 5.06 eV and 5.9 ÷ 6.05 eV. Thus, impurity emission is excited in the spectral region corresponding to the absorption of the Cu$^+$ ion in the matrix K$_2$SO$_4$ [7]. The absorption and emission in the Cu$^+$ ion corresponds to the electronic transition $3d^{10} \leftrightarrow 3d^9 4s$ [7]. In addition, it can be seen from Figure 2 that the impurity Cu$^+$ is excited at photon energies of 5.9-6.05 eV. In our previous works [9, 10], it was shown that in this energy region of 5.9-6.05 eV in crystals K$_2$SO$_4$, as well as in other sulfates, an intrinsic emission band is excited and radiation defects are created. This fact means that defects and emission bands are created by intrinsic electronic excitations of alkali metal sulfates. An experimental fact means that the impurity Cu$^+$ is excited by its intrinsic electronic excitations. The energy of electron-hole pairs is transferred to impurities.

The following experiment showed that upon excitation of the high-energy part of the impurity excitation or on the tail of the fundamental absorption band 4.9 ÷ 5.0 eV of the K$_2$SO$_4$ crystal, apart from the impurity emission of 2.7 ÷ 2.9
eV, short- wavelength emission at $3.0 \pm 3.1$ eV at 80 K (Figure 3, curve 1). This short-wavelength emission band is excited in the spectral transparency region of the K$_2$SO$_4$ crystal at 3.87 eV and 4.43 eV (Figure 3, curve 3). The same emission bands are created upon excitation of the K$_2$SO$_4$ crystal by photons with an energy of 7.75 eV (Figure 4, curve 2) at 15 K. At 300 K, a new emission band is quenched at $3.0 \pm 3.1$ eV (Figure 4 curve 2 and Figure 3 curve 2). The excitation of the emission band at $3.0 \pm 3.1$ eV in the transparency region of the crystal means that electronic transitions occur at the induced electron – hole capture centers. To clarify the nature of this emission band, the TSL spectrum of the irradiated K$_2$SO$_4$-Cu crystal was measured. It was shown that in the spectral composition of the TSL peaks of the irradiated K$_2$SO$_4$-Cu crystal, in addition to impurity emission of $2.6 \pm 2.65$ eV, it also contains a emission band at $2.95 \pm 3.0$ eV. Measurement of the temperature dependence of the emission band $2.95 \pm 3.0$ eV showed that the intensity of this band increases significantly in the temperature range where there are TSL peaks of $240 \div 250$ K and $310 \div 330$ K (Figure 6b). The increases of the emission intensity at $2.95 \div 3.0$ eV in 3 times showed in the TSL peak $240 \div 250$ K, and a dozen times in the peak $310 \div 330$ K.

It is known that increase in intensity of an individual band of recombination emission at a certain temperature means the delocalization of electrons or holes from the induced capture centers with their subsequent recombination. Based on experimental facts, it is assumed that the emission $2.95 \pm 3.0$ eV (under x-ray excitation) or $3.0 \pm 3.1$ (when excited by photons with an energy of $4.9 \pm 5.0$ eV, 7.75 eV) related with recombination decay of electron-hole capture centers.

The occurrence of phosphorescence coinciding with the band of impurity emission Cu$^+$ and recombination emission of $2.95 \pm 3.0$ eV indicates the existence of induced electron-hole color centers (Figure 6a). It is assumed that the appearance of phosphorus after the cessation of X-ray irradiation at 80 K is associated with a tunneling electron transition at electron-hole capture centers. In tunneling transitions, $2.95 \div 3.0$ eV emissions appear at the capture centers, and when this energy is transferred to Cu$^+$ impurities, intracenter emissions of the Cu$^+$ impurity are observed at $2.6 \div 2.65$ eV.

**Conclusion**

In the present work, on the basis of new experimental data and task, the following conclusions are made:

In K$_2$SO$_4$-Cu crystals, the transfer of energy from electron-hole pairs to Cu$^+$ impurities was experimentally detected.

Based on the data on measuring the excitation spectrum of the Cu$^+$ impurity in the fundamental region of the K$_2$SO$_4$ crystal, the band gap of the energy is estimated.

In the K$_2$SO$_4$-Cu crystal, a recombination emission band at $2.95 \div 3.0$ eV corresponding to the electron-hole capture centers was experimentally detected for the first time.
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