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Influence of Cu⁺ impurity on the efficiency of creation of electron hole trapping centers in irradiated Na₂SO₄-Cu crystals

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Influence of Cu^+ impurity on the efficiency of creation of electron-hole trapping centers in irradiated $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals

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The mechanisms of creation of impurity and intrinsic electron-hole trapping centers in $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals have been investigated by spectroscopic methods. It is shown that impurity and intrinsic electron-hole trapping centers in the crystal lattice $\text{Na}_2\text{SO}_4 - \text{Cu}$ are created in the same energy distances approximately 3.87-4.0 eV and 4.43-4.5 eV. During the annealing of electron-hole trapping centers, the energy of the recombination processes is transferred to impurities.

Keywords: alkali metal sulfates, electron-hole pairs, glow centers, phosphorescence, recombination emission, impurity, TSL.

Introduction

Sulfates of alkali and alkaline earth metals, activated by various ions, are usually used in thermoluminescent dosimeters, scintillators, detectors and phosphors [1-13]. The sensitivity of devices depends on the concentration of generated defects. The introduced impurities are the centers of recombination processes and emitters. The sensitivity of the devices is estimated from the intensity of emission

from the luminescence centers during the recombination processes. In our recent works [14], the fundamental processes of the creation of trapping centers in pure $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals were investigated.

During the excitation of pure $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals two types of emission appears: intrinsic short-wavelength emission at 3.7-3.8 eV associated with the recombination of electrons with nonequivalently located holes SO_4^- ; 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. Earlier, in our works [14-16], the nature of the recombination long-wavelength emission bands was purposefully investigated. Based on measurements of the excitation spectra for long-wavelength emission, it is shown that these recombination tunneling emissions arise at electron-hole trapping centers.

The trapping centers are created when electrons are localized by the anionic complexes SO_4^{2-} and holes are localized in the form of SO_4^- radicals. The trapping centers in the transparency region of Na_2SO_4 correspond to local states. The energy distance between the local states for the trapping of electrons and holes is 4.45-4.5 eV, 3.9-4.0 eV, and 3.35-3.5 eV. These values are estimated from the excitation spectra of long-wavelength recombination emission at 3.0-3.1 eV, 2.6-2.7 eV, and 2.3-2.4 eV. The intensity of tunneling luminescence determines the concentration of electron-hole trapping centers in dosimetric crystals. During the accumulated light sum of the TSL dosimetry peaks, the concentration of defects generated by irradiation is determined. It is known that the impurities introduced into alkali metal sulfates increase the light sum of the dosimetric TSL peaks by several times, i.e. increase the concentration of impurity trapping centers. For example, in alkali metal sulfates with an admixture of the Cu^+ , impurity trapping centers $\text{Cu}^0 - \text{SO}_4^-$ are created, which are responsible for the formation of an impurity dosimetric TSL peak in TLD dosimeters [14-16].

In the present work, the correlation between intrinsic and impurity trapping centers in the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal will be investigated.

Objects and methods of research

Crystals $\text{Na}_2\text{SO}_4 - \text{Cu}$ were grown at a temperature of 55°C from a saturated aqueous solution by the method of slow evaporation. Powdered samples were obtained by the wet chemical method from Na_2SO_4 (Sigma-Aldrich) with the addition of 0.1 mol% $\text{CuSO}_4 - 5\text{H}_2\text{O}$ (Sigma-Aldrich). After evaporation at 800°C for 8 hours, powdered samples $\text{Na}_2\text{SO}_4 - \text{Cu}$ 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 ÷ 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

As in pure Na_2SO_4 crystals [14], for sample $\text{Na}_2\text{SO}_4 - \text{Cu}$ the short-wavelength intrinsic emission spectrum and impurity emission was measured, as well as long-wavelength recombination emission upon excitation in the fundamental and absorption region of the impurity Cu^+ . The emission spectrum of a crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$ at 300 K excited by photons in the spectral region from 6.5 eV to 4.27 eV is shown in Figure 1. In Figure 1 it is shown that upon excitation in the fundamental region of the crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$, short-wavelength intrinsic emission bands appear (curves 2, 5), intense long-wavelength recombination emission 3.0-3.1 eV (curves 1, 2, 3), as well as impurity emission (curves 1, 2, 3, 4). In the energy range of the exciting photon 5.4-4.27 eV, impurity emission (curves 5-8) is effectively created at 2.8 eV at 300 K.

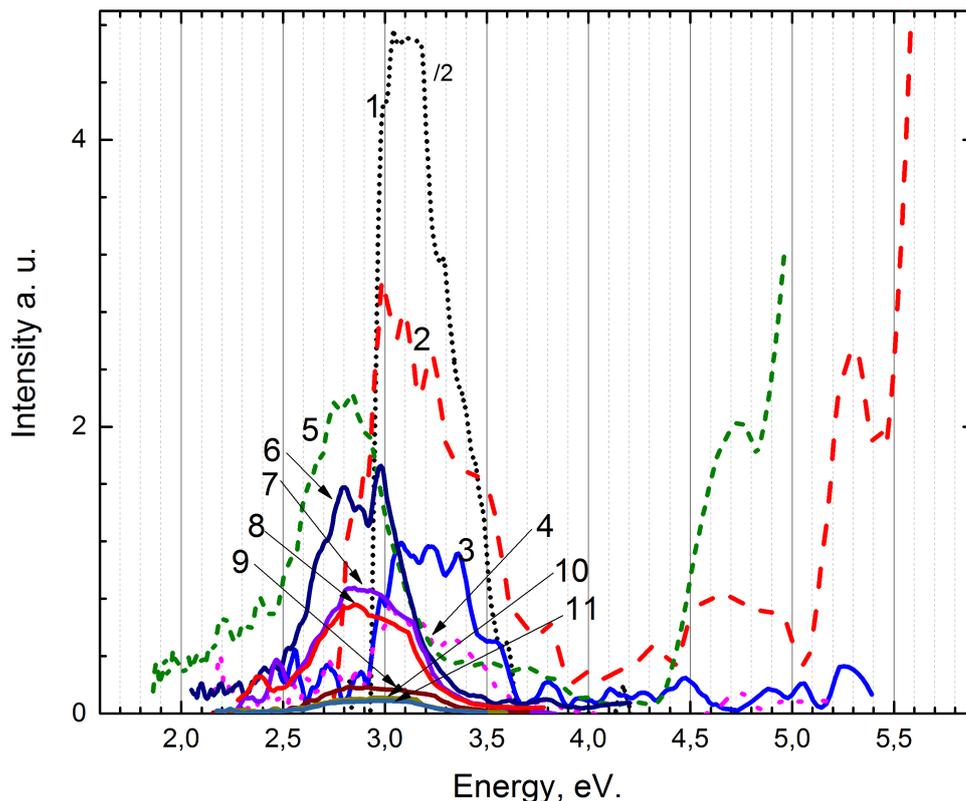


Figure 1. The emission spectrum of powder samples $\text{Na}_2\text{SO}_4 - \text{Cu}$ upon excitation by photons with energies from 4.27 eV to 6.5 eV at 300 K.

The excitation spectra of impurity emission at 2.8-2.90 eV (curves 2, 3) is shown in Figure 2. In Figure 2 it is shown that impurity emission at 2.8-2.90 eV is excited in the absorption region of the impurity ion at 4.9-5.1 eV, and also impurity emission is excited in the fundamental region of the crystal Na_2SO_4 at 5.5-5.6 eV, 5.8-6.05 eV.

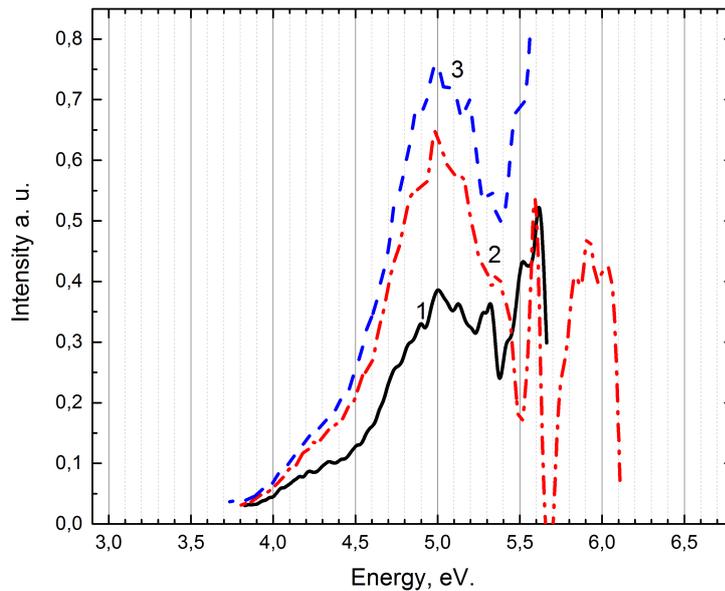


Figure 2. Excitation spectrum of powder samples $\text{Na}_2\text{SO}_4 - \text{Cu}$ for emission bands of 1-3.1 eV; 2-3.0 eV; 3-2.99 eV at 300 K.

The emission spectrum of the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal at 80 K upon excitation by photons with energies from 6.5 eV to 4.27 eV is shown in Figure 3. In Figure 3 it is shown that, upon excitation by photons with an energy of 6.2 eV, impurity and intrinsic recombination emission from 2.70 eV to 3.0-3.1 eV appears in the fundamental region of the matrix. At photon energies of 5.64 eV, 5.9 eV, the emission intensity decreases significantly. At a photon energy of 5.4 eV, impurity and intrinsic recombination emission appears from 2.70 to 3.0-3.1 eV (curve 4) at 80 K. A further change in the photon energy from 5.16 eV to 4.27 eV leads to a constant increase in the intensity of the band 3.0-3.1 eV (curves 6-8) and 3.17 eV (curves 9-10).

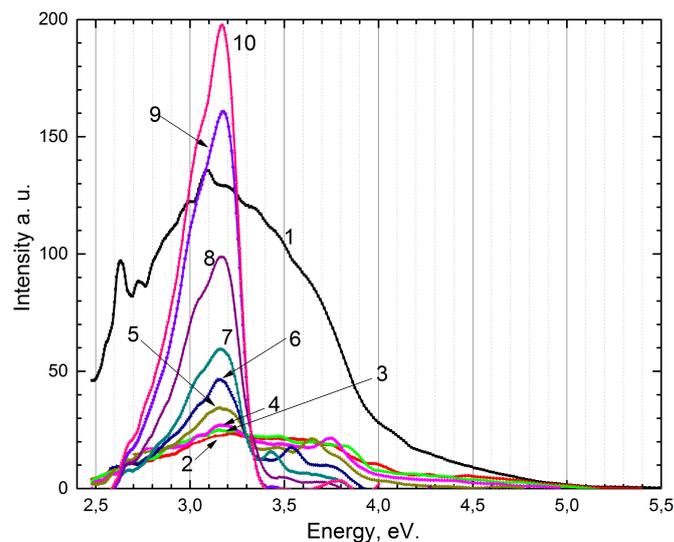


Figure 3. The emission spectrum of powder samples $\text{Na}_2\text{SO}_4 - \text{Cu}$ upon excitation by photons with energies from 4.27 eV to 6.5 eV at 80 K.

The excitation spectrum for the emission band 3.17-3.18 eV is shown in Figure

4. In Figure 4 it is shown that the induced emission band is excited at photon energies 4.33-4.4 eV and 3.77-3.8 eV in the transparency region of the crystal Na_2SO_4 .

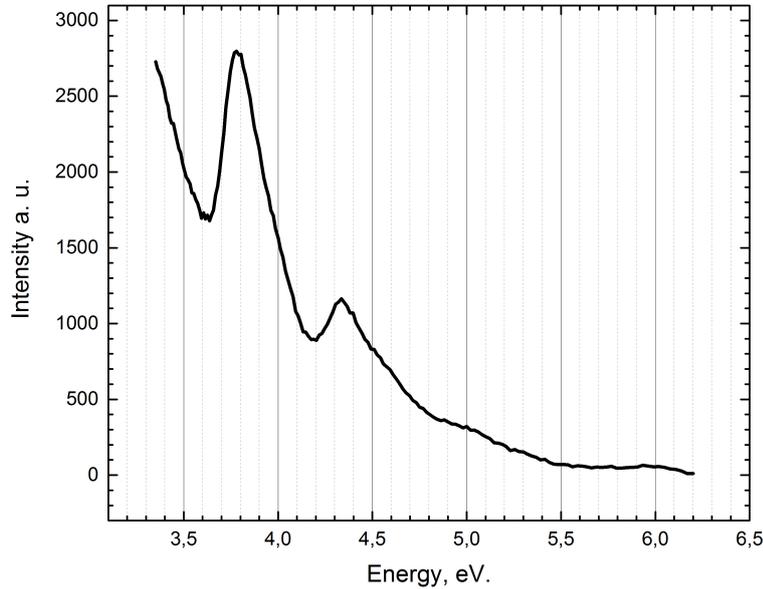


Figure 4. Excitation spectrum for emission 3.17-3.18 eV at 80 K.

The emission spectrum of the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal after a preliminary 10-minute irradiation of the crystal with X-rays at 80 K and excited by photons with energies from 4.27 eV to 6.2 eV is shown in Figure 5. In Figure 5 (curves 1, 2, 3) it is shown that upon excitation by photons with energies from 5.4 eV to 6.2 eV, weak impurity and intrinsic recombination emissions appear in the spectral range from 2.70 eV to 3.2 eV. At energies of the exciting photon in the range from 4.27 eV to 5.16 eV, the intensity of the recombination intrinsic emission of the matrix at 3.0-3.1 eV and the induced impurity emission at 3.22 eV increases several times compared with unirradiated crystals of $\text{Na}_2\text{SO}_4 - \text{Cu}$ (curves 5,6,7,8,9,10).

The spectrum of excitation of the induced emission bands at 3.22 eV (curve 1) and 3.17 eV (curve 2) of $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals at 80 K is shown in Figure 6 (curves 1, 2). In Figure 6 it is shown that the emission bands are excited in the transparency region of the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal at 3.87 eV and 4.4-4.45 eV with a certain intensity.

The emission spectrum of the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal annealed at 450 K and excited in the absorption band of the Cu^+ impurity at 4.96 eV at 300 K is shown in Figure 7. It can be seen from Figure 6 that these emission bands at 2.88 eV should correspond to the recombination emission of intrinsic electron-hole trapping centers formed after annealing of impurity trapping centers of the type $\text{Cu}^0 - \text{SO}_4^-$.

The excitation spectrum for the emission band 2.88 eV and 3.14 eV of the irradiated crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$ after annealing to 450 K is shown in Figure 8 (curves 1, 2). Band excited at a photon energy of 4.96 eV correspond to impurities Cu^+ in the powder $\text{Na}_2\text{SO}_4 - \text{Cu}$. Impurity emission bands of Cu^+ are also excited in the fundamental absorption region of the crystal Na_2SO_4 at 5.6-5.7 eV

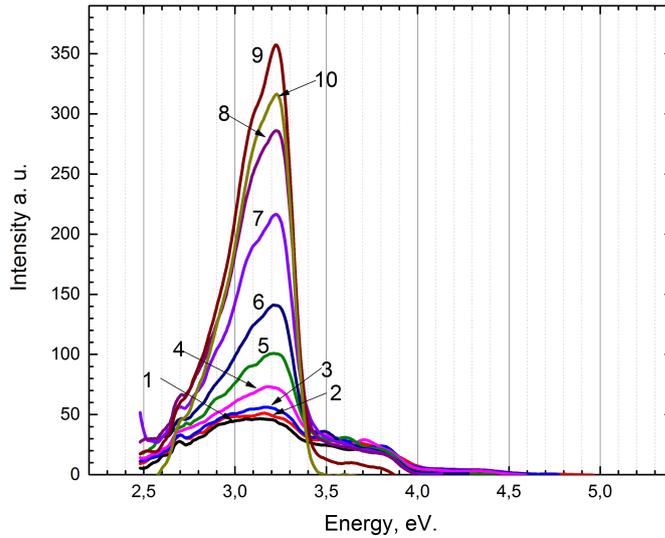


Figure 5. The emission spectrum of an irradiated crystal upon excitation by photons with energies from 4.27 eV to 6.2 eV at 80 K.

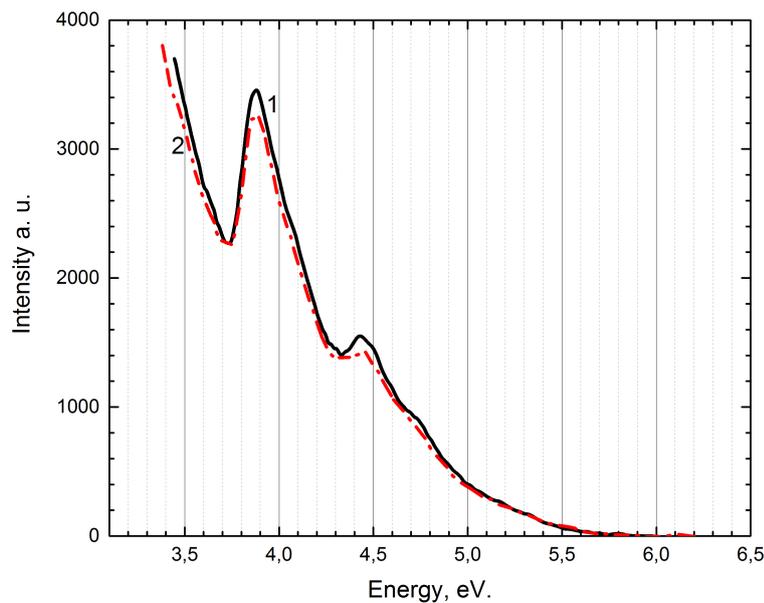


Figure 6. Excitation spectrum of the induced emission bands at 1-3.22 eV; 2-3.17 eV at 80 K after X-ray irradiation of the crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$.

and 5.85-5.95 eV.

The phosphorescence or tunneling luminescence spectrum of the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal after X-ray irradiation for 3 minutes (curve 1), 6 minutes (curve 2), and 10 minutes (curve 3) at 80 K is shown in Figure 9.

Thus, as in other sulfates of alkali metals activated by impurities Cu^+ in the crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$ at 300 K, an emission band appears at 2.8 eV, which is effectively excited in the absorption band of the impurity Cu^+ in Na_2SO_4 , as well as in the fundamental absorption region at 5.6 eV and 5.9 eV.

At a temperature of 300 K, in addition to impurity emission, long-wavelength recombination emission bands of 2.65-2.7 eV and 3.0-3.1 eV are created, which correspond to the induced electron-hole trapping centers in the pure matrix Na_2SO_4 .

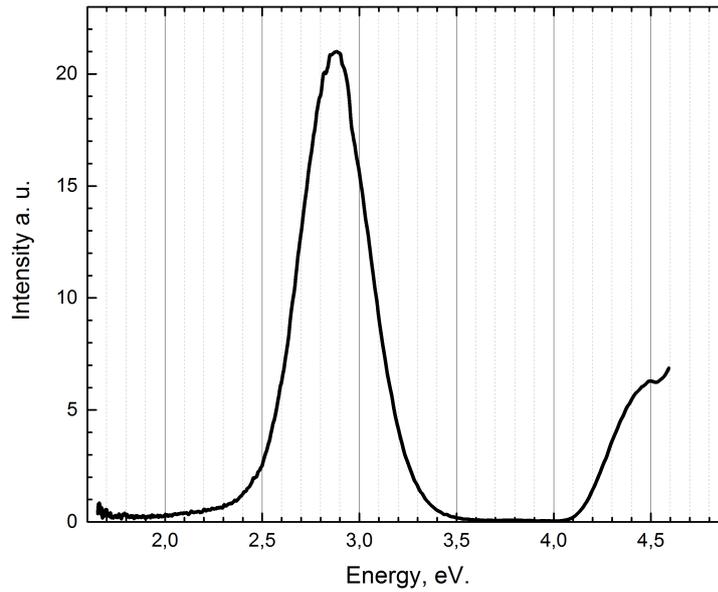


Figure 7. The emission spectrum of the annealed crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$ up to 450 K upon excitation by photons at 4.96 eV at 300 K.

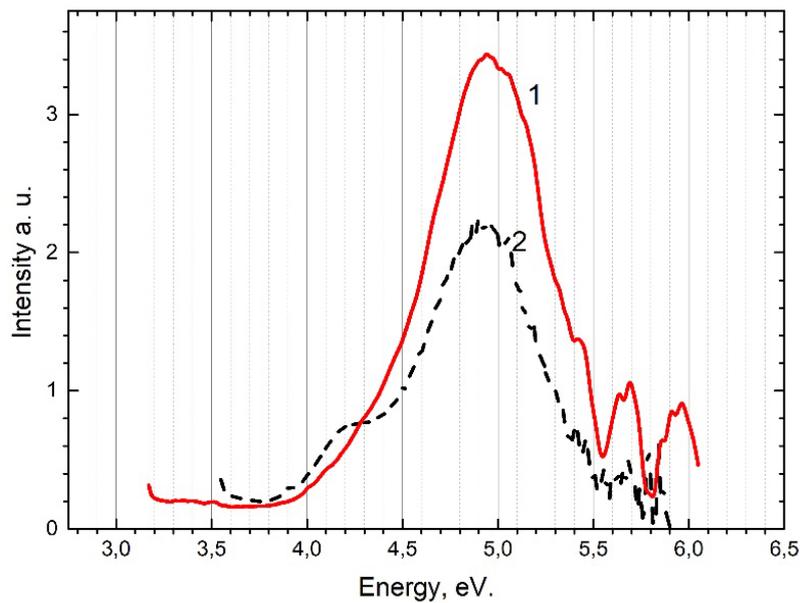


Figure 8. Excitation spectrum for the emission band 2.86 eV and 3.14 eV of the irradiated crystal $\text{Na}_2\text{SO}_4 - \text{Cu}$ after annealing to 450 K.

At 77 K, as in other sulfates of alkali metals with impurities Cu^+ , two main emission bands arise: corresponding to the impurity recombination emission at the trap centers $\text{Cu}^0 - \text{SO}_4^-$ and to the intrinsic recombination emission at the centers of trapping $\text{SO}_4^{3-} - \text{SO}_4^-$, which are created upon excitation in the fundamental region Na_2SO_4 by photons with an energy of 6.2 eV. Recombination emission corresponding to impurity trapping centers at 3.17 eV, and the intrinsic trapping center at 3.0-3.1 eV. Irradiation with X-rays at 80 K for 10 minutes increases the intensity of the impurity and intrinsic recombination emission at the trapping

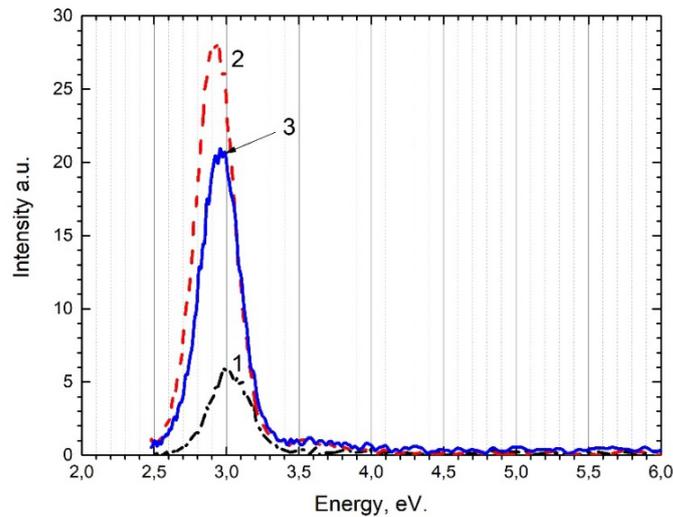


Figure 9. Phosphorescence after the termination of irradiated $\text{Na}_2\text{SO}_4 - \text{Cu}$ with X-rays for 1-1 min; 2-6 minutes; 3-10 minutes.

centers approximately 2 times, the maxima of the emission bands shift to the short-wavelength region to 3.22 eV from 3.1-3.05 eV, respectively. Measurement of the excitation spectra of long-wavelength recombination emission for pure Na_2SO_4 and $\text{Na}_2\text{SO}_4 - \text{Cu}$ showed that they are approximately in the same spectral positions: for pure Na_2SO_4 [14] at 3.9 eV for $\text{Na}_2\text{SO}_4 - \text{Cu}$ at 3.87 eV.

As a result of research in determining the energy distance between the centers of trapping $\text{SO}_4^{3-} - \text{SO}_4^-$ and $\text{Cu}^0 - \text{SO}_4^-$ showed that in activated crystals $\text{Na}_2\text{SO}_4 - \text{Cu}$ intrinsic electron-hole trapping centers are created near impurities, where impurity trapping centers are formed. Measurements of the intensity of intrinsic and impurity emission and its excitation after annealing the crystals to 450 K showed that the bulk of the induced trapping centers are annealed. After annealing, impurity emission is observed at 2.87 eV and its excitation band at 4.95 eV.

Thus, in $\text{Na}_2\text{SO}_4 - \text{Cu}$ at low temperatures, where the impurity electron centers Cu^0 are stable, impurity electron-hole trapping centers are created, which are responsible for the amount of light sum in thermoluminescent dosimeters.

Conclusion

For the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystals, it was shown that impurity electron-hole trapping centers $\text{Cu}^0 - \text{SO}_4^-$ are created during electron trapping by impurities Cu^+ and hole localization in the form radical SO_4^- .

It is shown for the first time that impurity and intrinsic electron-hole trapping centers are created in the transparency region of the crystal at the same energy distances, approximately equal to 3.87-4.0 eV and 4.43-4.5 eV.

During the recombination decay of two electron-hole trapping centers, the energy is transferred to the emitters, i.e. impurities Cu^+ in $\text{Na}_2\text{SO}_4 - \text{Cu}$. In the $\text{Na}_2\text{SO}_4 - \text{Cu}$ crystal lattice, the detected trapping centers are formed close

to each other.

Acknowledgments

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