Eurasian Journal of Physics and Functional Materials

2021, 5(3), 235-241

Mechanisms for the creation of intrinsic electron-hole trapping centers in a $CaSO_4$ crystall

T.N. Nurakhmetov, K.B. Zhangylyssov*, A.M. Zhunusbekov, D.H. Daurenbekov, T.T. Alibay, B.M. Sadykova, B.N. Yussupbekova, D.A. Tolekov

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

E-mail: keleshek92@yandex.ru

DOI: **10.32523/ejpfm.2021050308**
Received: 10.09.2021 - after revision

The mechanism of creation of electron-hole trapping centers in $CaSO_4$ at 15-300 K was investigated by the methods of vacuum-ultraviolet and thermoactivation spectroscopy. It is shown that electron-hole trapping centers are formed upon trap of electrons in the anionic complexes SO_4^{2-} and localization of holes in the form of SO_4^- radical. Based on the measurement of the spectrum of excitation of long-wavelength recombination emission at 3.0-3.1 eV and 2.7 eV, the energy distance of the formed electron-hole trapping centers was estimated (4.43 eV and 3.87 eV).

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

Introduction

In irradiated $CaSO_4$ crystals with UV photons and X-rays, two types of intrinsic emission arise: a group of short-wavelength emission at 3.7-3.8 eV, 4.1-4.3 eV, 4.5 eV and about 5 eV formed upon excitation by UV photons 6.2-12.3 eV.

The second group of long-wavelength (low energy) emission occurs together with short-wavelength (high energy) emission at 3.0-3.1 eV, 2.6-2.7 eV, and 2.3-2.4 eV in almost all irradiated sulfates of alkali and alkaline earth metals. In our previous works [1], based on the experimental results obtained in $CaSO_4$

and K_2SO_4, it was assumed that these bands arise when electrons from three subbands of the valence band of the SO_4^{2-} complex formed from the 2p state of oxygen into the conduction band. Short-wavelength emissions arise from the recombination of electrons from the conduction band with nonequivalently located holes localized above the valence band. The formation of electron-hole trapping centers is the basis for the operation of thermoluminescent dosimeters, phosphors and various detectors [1-3]. It was assumed that defects in sulfates of alkaline earth metals are created during the decay of the excited annionic complex SO_4^{2-} [3-6]. Specially introduced impurities increase defect formation in many sulfates of alkali and alkaline earth metals by tens of times [6-11]. The mechanisms of the creation of defects have been studied in sulfates activated by rare-earth ions. It was believed that electron-hole pairs created by irradiation are trapped by impurities and impurity electron-hole trapping centers are created [12-14]. The structures and mechanisms of the creation of defects in pure sulfates have hardly been studied. In the last works of the authors [11], based on the Na_2SO_4 crystal, it was shown that defects are created during the trapping of electrons by the anionic complexes SO_4^{2-} and the localization of holes in the form of SO_4^{-} radicals. Low energy recombination emission in sulfates at 3.0-3.1 eV and 2.6-2.7 eV results from tunneling luminescence at such created trapping centers [11]. In this work, we investigate the mechanisms of the formation of electron-hole trapping centers in a $CaSO_4$ dosimetric crystal. Knowledge of the mechanisms of electron-hole trapping centers opens up new energy transfers under induced irradiation with X-rays and UV rays, which are needed for use in dosimeters.

Objects and methods of research

Crystals $CaSO_4$ were 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 studied samples of powders of chemical purity 99.99% $CaSO_4$ SigmaAldrich CAS: 7778-18-9. Crystals and powders of $CaSO_4$ were studied by photoluminescence, X-ray luminescence, and vacuum-ultraviolet spectroscopy. For excitation in the ultraviolet region of the spectrum, a D200VUV deuterium lamp (Heraeus Noblelight, Germany) with a photon energy of 6.2-11.5 eV and an XBO 150W xenon lamp (OSRAM, Germany) with a photon energy of 1.5-6.2 eV were used. A Solar CM2203 spectrofluorimeter was used to measure the emission and excitation spectra in the spectral range of 1.5-6.2 eV. The measurement of the excitation and emission spectra in the 4-11.5 eV spectral region was carried out on a vacuum monochromator assembled according to the Seya-Namioka scheme in a wide temperature range 15-400 K. The crystal radiation was recorded through an MDR-41 monochromator using a 1P28 Photomultipliertube (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral distribution of the intensity of excitation radiation.

The results of the experiment and their discussion

It was assumed that the nature of the long-wavelength recombination emission bands is associated with the formation of electron-hole trapping centers [11]. $CaSO_4$ crystals were irradiated with high-energy photons in the fundamental region of the crystal, where free electron-hole pairs are created.

The emission spectrum of a $CaSO_4$ crystal excited by photons with an energy of 7.75 eV (curve 1) at 15 K and at 300 K (curve 2) and 7.3 eV (curve 3) at 15 K and at 300 K (curve 4) is shown in Figure 1. It can be seen that, in irradiated $CaSO_4$, two groups of emission bands appear, as in other sulfates:

- high energy emission bands: : 4.5 eV; 4.0-4.2 eV; 3.7-3.8 eV and 3.5-3.6 eV are effectively created at 15 K.

- low energy emission bands at 3.0-3.1 eV 2.6-2.7 eV and 2.3-2.4 eV are more efficiently created at 80 K and 300 K.

We purposefully investigated the nature of the low energy emission of the $CaSO_4$ crystal upon excitation by photons with an energy of 6.26 eV at 80 K.

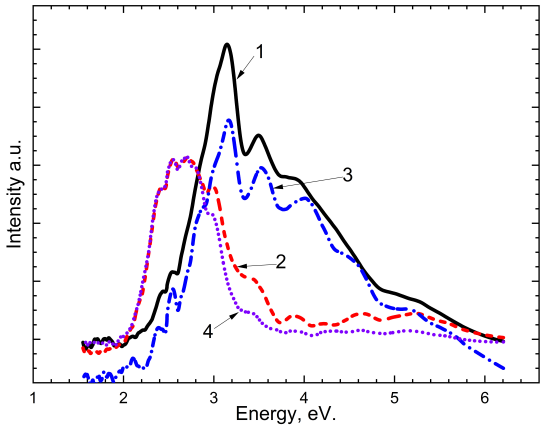

Figure 1. Luminescence of a $CaSO_4$ crystal excited by photons with an energy of 7.75 eV (curve 1) at 15 K, at 300 K (curve 2) and 7.3 eV (curve 3) at 15 K, at 300 K (curve 4).

The excitation spectrum for the recombination emission at 3.0-3.1 eV at 80 K (curve 1) and 300 K (curve 2) are shown in Figure 2. It can be seen that (curve 1) recombination emission of 3.0-3.1 eV is excited in the spectral range of 3.35 eV, 3.95 eV, and 4.51 eV in the transparency region of the $CaSO_4$ crystal. The same figure 2 (curve 2) shows the excitation spectrum of the same emission band of 3.0-3.1 eV at 300 K. At 300 K. The excitation spectrum of this recombination emission changes insignificantly.

The excitation spectrum of low energy recombination emission for 2.7 eV at 80 K is shown in Figure 3 (curve 1). It can be seen that (curve 1) in the excitation spectrum for the 2.7 eV band, the same bands appear at 3.35 eV, 3.87 eV and 4.43-4.45 eV. To increase the number of trapping centers of the crystal in $CaSO_4$ at 80 K, it was irradiated with X-rays. In this case, new electron-hole trapping centers are created. After X-ray irradiation at 80 K, the intensity of the excitation spectrum for the 2.7 eV recombination emission increased 3-4 times (curve 2).

In the next step, assuming that a certain concentration of electron-hole trapping centers had accumulated in the pre-irradiated crystal at 80 K, the crystal

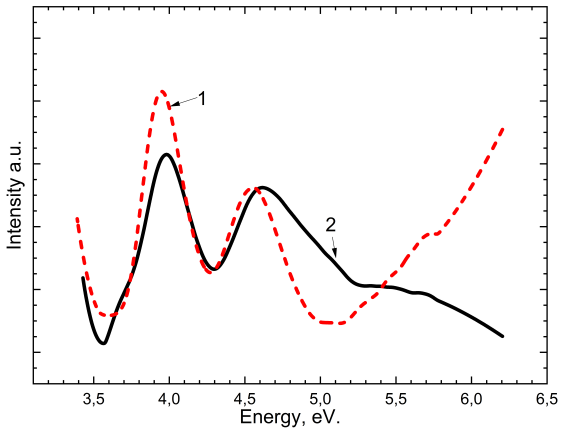

Figure 2. Excitation spectrum of $CaSO_4$ crystal for 3.0-3.1 eV at 80 K (curve 1) and at 300 K (curve 2).

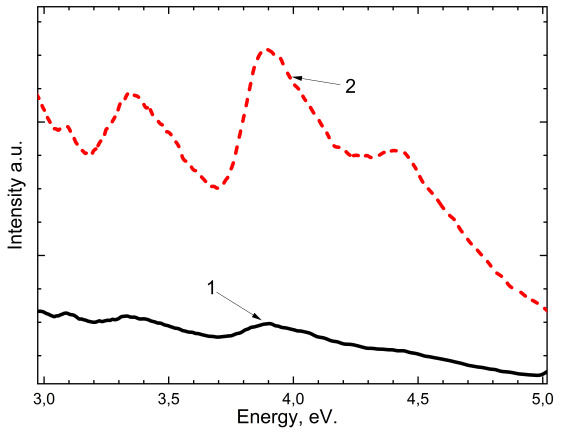

Figure 3. Excitation spectrum for 2.7 eV emission at 80 K (curve 1) and after preliminary irradiation for 5 minutes with X-rays (curve 2) of the $CaSO_4$ crystal.

was excited by photons with an energy of 4.43 eV (see Figure 4 (curve 1)). It is seen that (curve 1), after excitation, low energy recombination emission appears at 3.2 eV. To be convincing that real low energy emissions arise upon excitation of accumulated electron-hole trapping centers, we created a certain number of electron-hole trapping centers by additional irradiation with X-rays. In Figure 4 (curve 2, 3, 4) it is shown that with an increase in the time of exposure to X-rays (3, 5, 10 minutes), the intensity of recombination recombination emission of 3.2 eV increases approximately 3 times.

A similar experiment is shown in Figure 5. In this case, a $CaSO_4$ crystal with created electron-hole trapping centers was excited with a photon energy of 3.87 eV. In this case, recombination emission appeared at 3.2 eV (curve 1). X-ray irradiation increased the number of electron-hole trapping centers (3, 5, 10 minutes of irradiation) and, accordingly, the intensity of the low energy emission spectra at 3.2 eV increased 3-4 times (curve 2-4).

Experimental facts convincingly prove that the long-wavelength emission arising during irradiation in the fundamental region of the $CaSO_4$ crystal is associated with the accumulation of electron-hole trapping centers, which manifest themselves in the form of tunneling recombination emission.

The temperature dependence of the recombination tunneling emission at 3.0-3.1 eV and 2.7 eV, at the trapping centers created by ultraviolet radiation

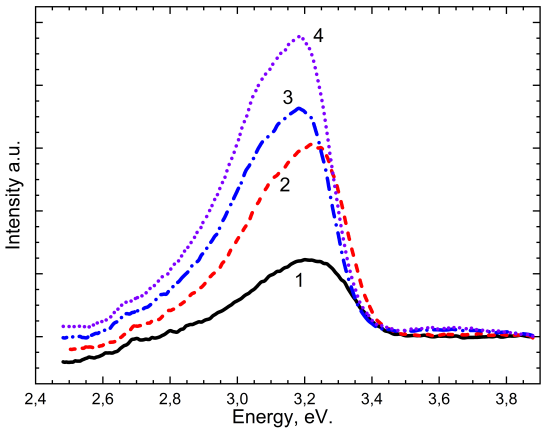

Figure 4. Emission upon excitation by photons with an energy of 4.43 eV after excitation by UV photons of 6.2 eV (curve 1): after 3 min of exposure to X-rays (curve 2); after 5 min of X-ray irradiation (curve 3); after 10 min of X-ray irradiation (curve 4) at 80 K.

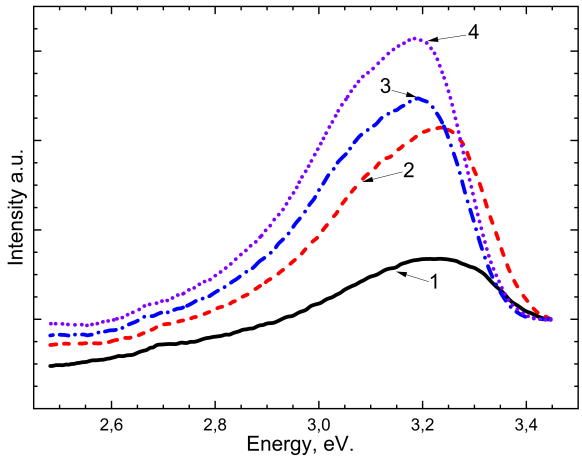

Figure 5. Emission upon excitation by photons with an energy of 3.87 eV at 80 K: after excitation by UV photons with an energy of 6.2 eV (curve 1); after 3 min of X-ray irradiation (curve 2); after 5 min of X-ray irradiation (curve 3); after 10 min of X-ray irradiation (curve 4).

4.84 eV at 80 K are shown in Figure 6. It can be seen that, depending on the temperature, the intensity of the recombination emission at 3, 1 eV (curve 1) and 2.7 eV (curve 2) gradually decreases and in the temperature range 250-300 K. First, the emission band flares up and then gradually decreases. It is assumed in this temperature range that electrons from the electron trapping center are ionized and recombine in hole centers of SO_4^- radicals. Thus, the first stage of annealing with recombination emission of 3.0-3.1 eV and 2.7 eV is carried out. In the temperature range 350-450 K, where the hole components SO_4^- trapping centers are delocalized and the electron-hole trapping centers are completely annealed.

Crystals $CaSO_4 - Dy^{3+}$ are a commercial TLD dosimeter for recording ionizing radiation. Although crystals have long been used as a thermoluminescent dosimeter, the nature of the main dosimetric peak of TSL (230-240° C) has not been clarified. In any case, the TSL peak appears as a result of the recombination of intrinsic electron - hole trapping centers. The introduction of various impurities that are emitters or stabilizers of primary defects should increase the thermal stability and light sum under the TSL dosimetric peak.

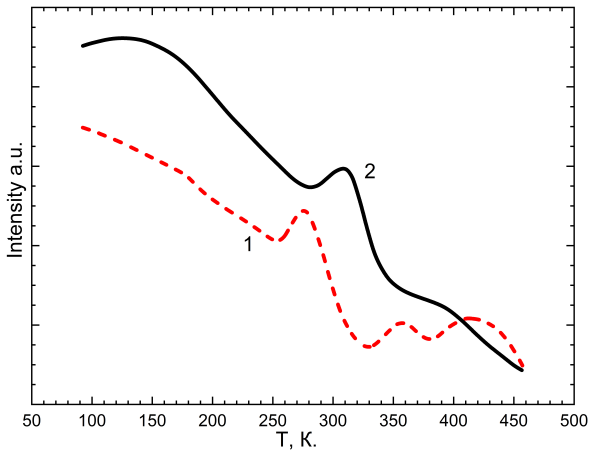

Figure 6. Temperature dependence of emission at 3.0-3.1 eV and 2.7 eV at the trapping centers created by ultraviolet radiation 4.84 eV at 80 K.

According to our assumptions, long-wavelength recombination emissions at 3.0-3.1 eV, 2.6-2.7 eV, and 2.3-2.4 eV in all sulfates arise as a result of the recombination of electron-hole trapping centers. As a result of measuring the excitation spectrum of these low energy recombination emissions, it was shown that they are excited in the transparency region of the crystal at photon energies of 4.43 eV, 3.87 eV, and 3.33 eV. Upon excitation of alkaline earth metal sulfate crystals with induced trapping centers by photons with energies of 4.43 eV, 3.87 eV, and 3.35 eV, we received back long-wavelength emission at 3.0-3.1 eV and 2.6-2.7 eV. Measurements of the temperature dependences of these recombination emissions at 3.1 eV and 2.6 eV showed that the intrinsic electron trapping centers are stable up to 300 K. Above this temperature, the efficiency of creating electron-hole trapping centers sharply decreases in all sulfates, including $CaSO_4$. The introduction of various impurities increases the concentration and thermal stability of electron-hole trapping centers.

Conclusion

Based on the results obtained, it is logical to make the following conclusions: In the $CaSO_4$ crystal, electron-hole trapping centers are created during the trapping of electrons by the anionic complexes SO_4^{2-} and the hole is localized in the form of radicals SO_4^{-}. Long-wavelength emission arising during irradiation of $CaSO_4$ with UV photons is associated with tunneling decay of electron-hole trapping centers. In irradiated $CaSO_4$, electron-hole trapping centers are created at an energy distance of 3.35 eV, 3.87 eV, and 4.43 eV at 80 K in the transparency region of the crystal.

Acknowledgments

This work was supported by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan, grants IRN AP09259303.

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