The nature of intrinsic recombination emission in SrSO$_4$ irradiated with ultraviolet photons

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The synthesized SrSO$_4$ crystalline powders were irradiated at photon energies from 6 ÷ 12 eV, in the temperature range from 15 ÷ 300 K. The investigation was carried out by the methods of atomic absorption, luminescence and vacuum ultraviolet spectroscopy. Intrinsic emissions were found at 3.7-3.8 eV, 4.2-4.6 eV and 4.9-5 eV, and long-wavelength recombination emissions at 2.6-2.7 eV and 2.9-3.0 eV.The synthesized SrSO$_4$ crystalline powders were irradiated at photon energies from 6 ÷ 12 eV, in the temperature range from 15 ÷ 300 K. The investigation was carried out by the methods of atomic absorption, luminescence and vacuum ultraviolet spectroscopy. Intrinsic emissions were found at 3.7-3.8 eV, 4.2-4.6 eV and 4.9-5 eV, and long-wavelength recombination emissions at 2.6-2.7 eV and 2.9-3.0 eV.

Keywords: luminescence, electronic transitions, recombination.

Introduction

Crystals SrSO$_4$, like other sulfates of alkali and alkaline earth metals activated by rare earth ions, are used as phosphors, detectors and dosimeters of ionizing

emission. Typically, the dosimetry characteristics of crystals are evaluated by measuring the intensity of thermostimulated luminescence (TSL) as a function of the absorbed dose temperature, energy and decay time. All these dosimetric characteristics are studied in $SrSO_4$, $BaSO_4$ and $CaSO_4$ crystals activated by impurity ions Dy, Eu, Tb, Sm, etc. [1-7]. It is generally known that TSL arise in irradiated crystals upon recombination of created defects near rare-earth impurities. The energy of the recombination processes is transferred to the impurities. In the spectral composition of TSL, the intracentric emission of impurities is always observed. In the works of the authors of [8], it was experimentally shown that in $SrSO_4$: Mn crystals the intensity of the emerging TSLs is 12 times higher than in pure matrices $SrSO_4$. Thus, impurities of rare earth ions in sulfates stimulate the formation of stable defects. Thereby, the concentration of defects and the area under the TSL peak are increased. The intensity of TSL peaks determines the sensitivity of thermoluminescent dosimeters. In the works of the authors of [9], the nature of defects that recombine during annealing after irradiation of $SrSO_4$ –Sm crystals were determined by the EPR method. In recent years, the dosimetric properties of nanocrystalline $SrSO_4$ powders have been intensively studied. The authors of [10] show that all dosimetric characteristics of $SrSO_4$ –Sm nanopowders are the same as monocrystalline and polycrystalline powders. In this work, we investigate the nature of intrinsic radiation arising in a polycrystalline powder $SrSO_4$ upon excitation by ultraviolet photons at low temperatures of $15 \div 300$ K.

Objects and methods of research

Crystalline $SrSO_4$ powder was prepared as described in [7]. Strontium nitrate was dissolved in 100 ml in double distilled and deionized water. The solution was placed in a beaker and dispensed until uniform. In the placed state at room temperature, 10 ml drop by drop was added. H_2SO_4 to precipitation of $SrSO_4$ powder. After that, the precipitate was centrifuged and washed several times in distilled water to remove excess salt. The precipitates were dried in a muffle furnace at 60° C for 2 hours. Dry $SrSO_4$ powder was annealed in an muffle furnace at 900° C for an hour to obtain a crystalline powder. For excitation in the ultraviolet region of the spectrum, a source of VUV radiation was used - a flow-through hydrogen lamp with a photon energy of 6-12 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 $15 \div 400$ K.

The results of the experiment and their discussion

We are not aware of the works that investigated the intrinsic emission of crystals and their $SrSO_4$ irradiated with ionizing photons.

Figure 1 shows the emission spectrum of the annealed $SrSO_4$ powder at 300 K, excited by ultraviolet photons with an energy of 6.5 eV. It can be seen from the

Figure 1 that an elementary emission appears at 3.7-3.8 eV and a long-wavelength emission associated with electron-hole trapping centers.
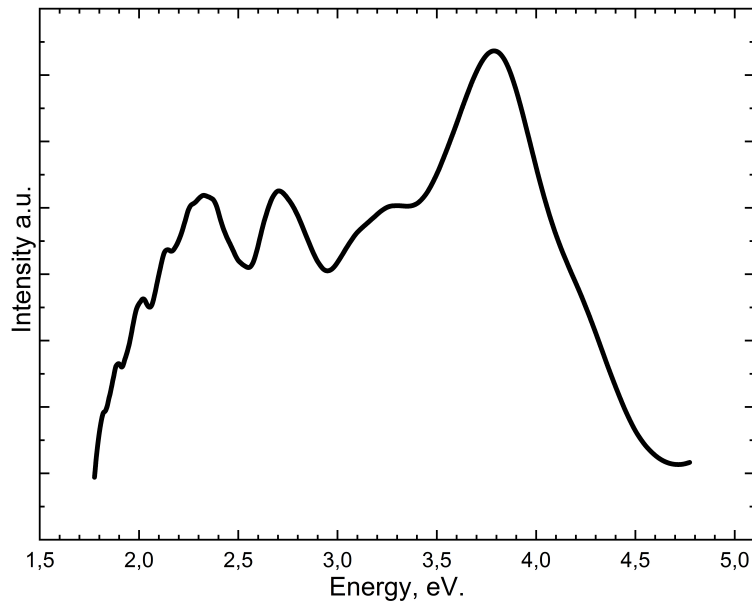

Figure 1. Luminescence of powder $SrSO_4$ upon excitation by photons with an energy of 6.5 eV at 300 K.

Figure 2 shows the emission spectrum of annealed $SrSO_4$ powder at 15 K excited by photons with energies of 8 eV (curve 1) and 10-12 eV (curve 2). From the emission spectrum (curve 1) it can be seen that the main intrinsic recombination emission appears at 3.7-3.8 eV and a long-wavelength emission at 2.9-3.0 eV. Curve 2 shows that a complex emission appears, including short-wavelength emission at 3.7-3.8 eV, 4.2-4.6 eV and about 5 eV, as well as long-wavelength emission at 2.9-3.0 eV and 2.6-2.7 eV.
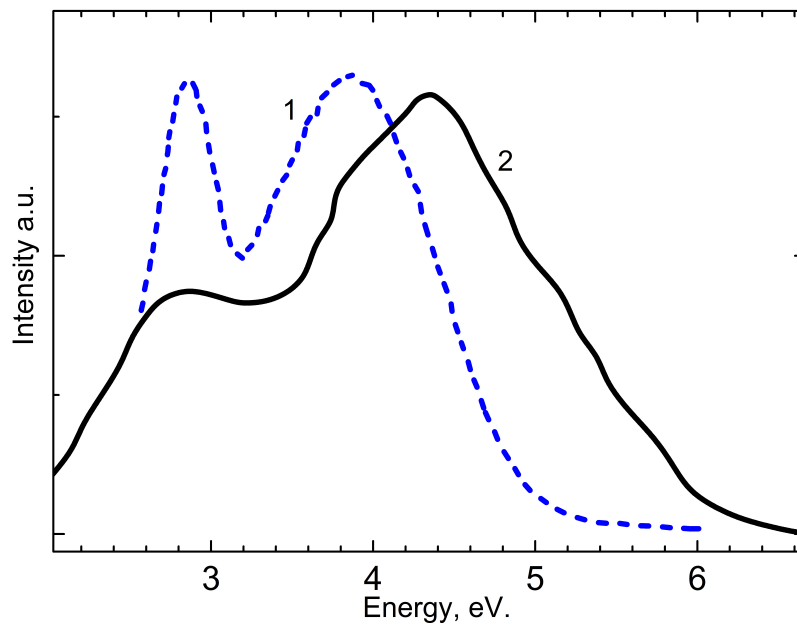

Figure 2. Luminescence of $SrSO_4$ upon excitation by photons with energies: 1) 8 eV; 2) 10-12 eV; at 15 K.

Figure 3 shows the excitation spectrum of long-wavelength emission at 2.7

eV at 15 K (curve 1) and 300 K (curve 2). It can be seen that 2.7 eV emission is excited at photon energies from 5.5 to 6.2 eV.
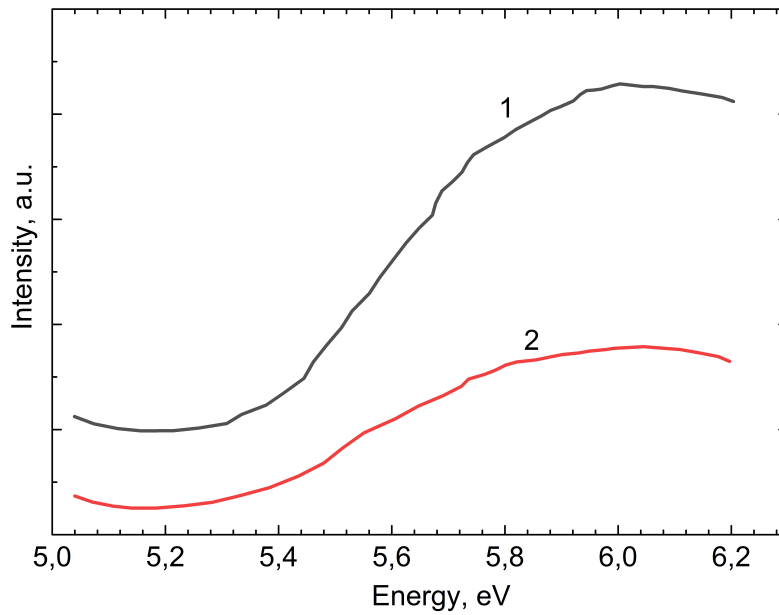

Figure 3. Excitation spectrum of 2.7 eV emission at: 1) 15 K; 2) 300 K.

Figure 4 shows the excitation spectrum for the long-wavelength recombination emission at 2.7 eV at 80 K (curve 1) and 300 K (curve 2). It is shown that emission in a wide spectral range of 2.7 eV is created at photon energies at 5.6-6.4 eV, 7-7.75 eV, 9.2-9.45 eV and 10.4-11 eV, where free electron-hole pairs are effectively formed.
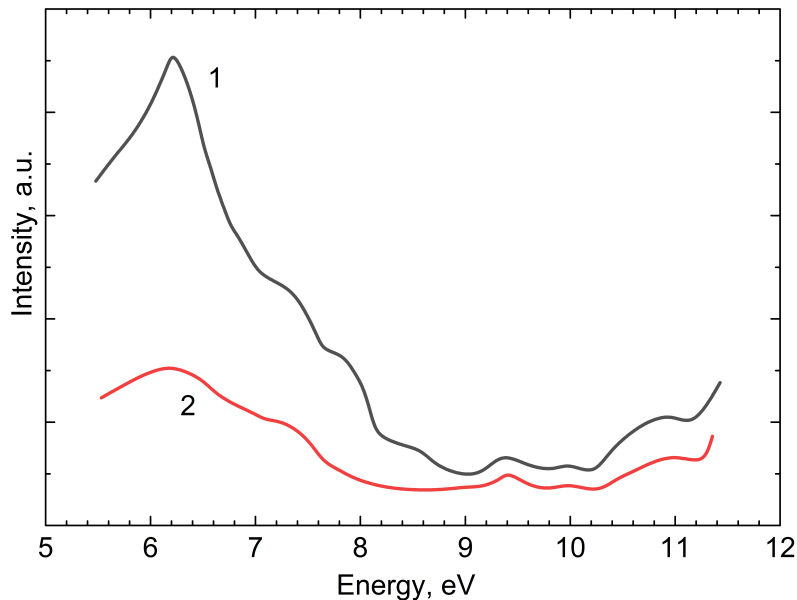

Figure 4. Excitation spectrum for the 2.7 eV emission at: 1) 80 K; 2) 300 K.

Figure 5 shows the excitation spectrum for the main short-wavelength emission at 4.5 eV arising from the recombination of an electron with holes located in the lattice nonequivalently in the form SO_4^-. To measure the excitation spectrum, the

4.5 eV were separated in the first case with the help of UFS-2 filters (curves 1, 2), in the second case - with the help of the combined UFS-2+ $NiSO_4$ filters (curve 3, 4). In the case of the UFS-2 filter, the main short-wavelength emission of 4.5 eV included the long-wavelength emission at 2.9-3.0 eV. These combined emission were efficiently excited in a wide spectral range from $5.6 \div 7.2$ eV, $7.5 \div 8.2$ eV, $9.2 \div 9.5$ eV and $9.8 \div 11$ eV. And in the case of the UFS-2+ $NiSO_4$ filters, the combined emission included only the short-wavelength emission at $4.0 \div 4.5$ eV. These short-wavelength emission were efficiently excited in the spectral region from $7.2 \div 8.2$ eV and above $9.2 \div 11$ eV.
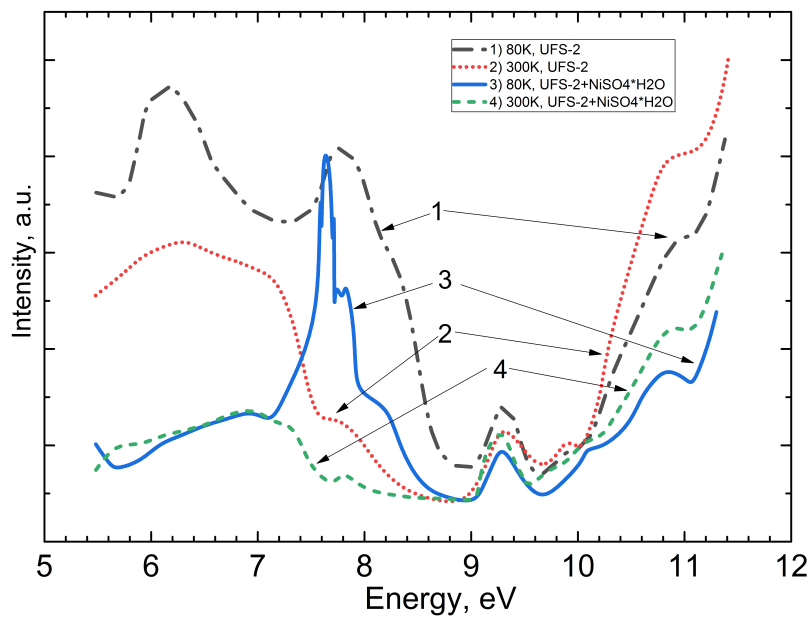

Figure 5. Excitation spectrum of the 4.5 eV emission band with filter UFS-2: 1) 80 K; 2) 300 K; with filter UFS-2+ $NiSO_4$: 3) 80 K; 4) 300 K.

Figure 6 shows the temperature dependence of the intensity of the emission bands of 4.5 eV (curve 1.2) and 2.7 eV (curves 3, 4) upon excitation by photons with energies of 7.8 eV (curves 1, 3) and 6.2 eV (curve 2, 4), respectively. It can be seen that (curve 1) for the 4.5 eV emission created by the 7.8 eV photons exponentially decreases in the temperature range from 80 K to 250 K. This dependence is characteristic of the intrinsic emission of the crystal, which arises during the recombination of an electron with a localized hole. The intensity of the emission of 4.5 eV (curve 2) generated by 6.2 eV photons in the temperature range from 80 K to 480 K changes insignificantly. Temperature dependence of the 2.7 eV long-wavelength emission upon excitation by photons with energies of 7.9 eV (curve 3) and 6.2 eV (curve 4). It can be seen that the intensity of the 2.7 eV emission created by photons with an energy of 7.8 eV from 80 K to 300 K gradually decreases, then changes insignificantly. The intensity of the 2.7 eV emission created with a photon energy of 6.2 eV in the range from 80 K to 480 K decreases gradually by a small amount.

The intrinsic emission spectra of the annealed $SrSO_4$ powders do not differ much from the emission spectra of $CaSO_4$ and $BaSO_4$ crystals [10]. The calculation works of the authors [11-13] showed that for a several of alkali metal
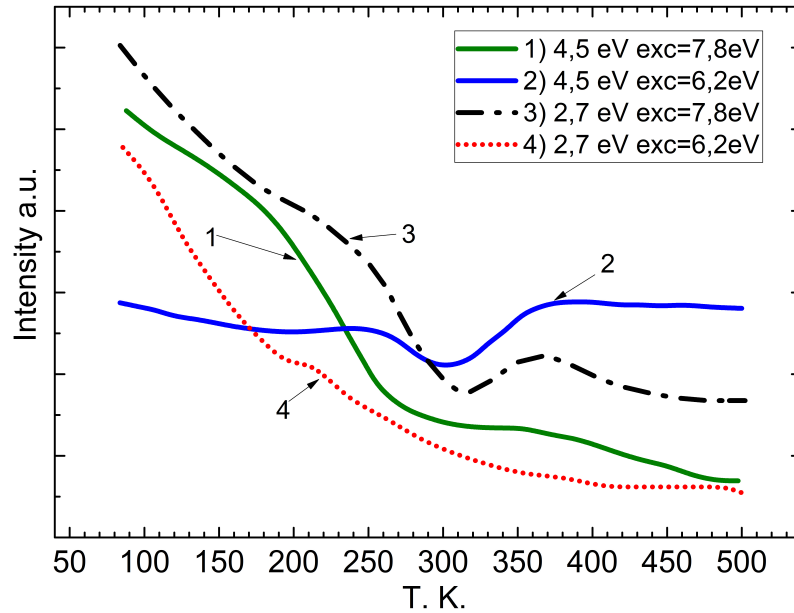
Figure 6. Temperature dependence of luminescence for emission: 4.5 eV upon excitation 1) 7.8 eV, 2) 6.2 eV; 2.7 eV upon excitation 3) 7.8 eV, 6.2 eV.

sulfates the upper part of the valence band is formed from the 2p state of oxygen of the anionic complex SO_4^{2-} and consists of three subbands. The first subband of the valence band is located at a distance of 5.5–6.2 eV from the bottom of the conduction band, the second subband is 7–8 eV, and the third subband is 9–11 eV. Similar experimental results were obtained in works for the $CaSO_4$ crystal [14]. The authors attribute the appearance of several short-wavelength intrinsic recombination emissions to the complex structure of the valence band of the $CaSO_4$ crystal. By analogy with the $CaSO_4$ crystal for the $SrSO_4$ powder, it was shown that the emission band 4.2-4.6 eV and 4.9-5.0 eV is associated with electron transitions from the third subband valence band in the conduction band of the $SrSO_4$ powder. The emission bands of 3.7-3.8 eV should be associated with the transition of an electron from the first and second subbands of the valence band to the conduction band. Thus, the elementary emission bands at 3.7-3.8 eV and short-wavelength emission 4.2-4.6 eV and 4.9-5.0 eV arise upon recombination of an electron from the conduction band with localized holes.

In irradiated $SrSO_4$, along with short-wavelength intrinsic emission, long-wavelength emission of 2.6-2.7 eV, 2.9-3.0 eV appears. As in other sulfates, the long-wavelength emission should be bound by electron-hole trapping centers. Figures 3 and 4 show that these recombination emissions are created at photon energies of 6.2-8 eV and 9-11 eV, where electron-hole pairs are created. As in other sulfates [14], these recombination emission should be associated with tunneling transitions inside electron – hole trapping centers. The course of the temperature dependence of the emission 4.2-4.6 eV shows that the exponential decrease in intrinsic emission, as in other sulfates [14], should be associated with a decrease in hole trapping centers as a result of recombination with electronic trapping centers. In the temperature range 80-300 K, hole trapping centers are destroyed due to tunneling recombination of electron-hole pairs.

Conclusion

Based on the results obtained, it is logical to make the following conclusions:

1. In the annealed $SrSO_4$ powder, intrinsic emissions at $3.7 \div 3.8$ eV, $4.2 \div 4.6$ eV and $4.9 \div 5$ eV were first detected, and these emissions are associated with the recombination of electrons with nonequivalently located localized holes.

2. Detected long-wavelength recombination emissions t 2.6-2.7 eV and 2.9-3.0 eV.

3. Based on the measurement of the excitation spectra for the 4.2-4.6 eV emission band, it is assumed that the emission is associated with an electronic transition from the third subband of the valence band to the conduction band.

Acknowledgements

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