

## Electron-hole trapping centers in uv-irradiated Na<sub>2</sub>SO<sub>4</sub>-Mn and K<sub>2</sub>SO<sub>4</sub>-Mn

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**Abstract.** The nature of electron-hole trapping centers in Na<sub>2</sub>SO<sub>4</sub>-Mn and K<sub>2</sub>SO<sub>4</sub>-Mn ferroelectric crystals was studied by spectroscopic methods. It is shown that several types of impurity electron-hole trapping centers are created in such crystals under electrons and holes are localized at broken lattice sites near the Mn<sup>2+</sup> impurity.

**Keywords:** luminescence, emission, alkali metals, impurity, TSL, recombination emission, ferroelectric.

### 1. Introduction

Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> crystals activated by Mn<sup>2+</sup> impurities have anisotropic optical properties and are ferroelectrics with several phase transitions. Phase transitions consist in various variants of the ordered orientation of the most rigid structural elements – the SO<sub>4</sub><sup>2-</sup> tetrahedral groups in the Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> compounds. The studies of the authors of [1] showed that in an irradiated K<sub>2</sub>SO<sub>4</sub>-Mn crystal, upon excitation in the fundamental spectral region  $E_g > 5.5$  eV, emission bands appear at 3.65–3.75 eV related with the recombination of electrons with localized holes SO<sub>4</sub><sup>-</sup>. The introduction of Mn<sup>2+</sup> impurities, which are electron acceptors in sulfates, enhances the intrinsic luminescence intensity. The light sum under the low-temperature TSL peak at 120–190 K in irradiated K<sub>2</sub>SO<sub>4</sub>-Mn is several times greater than the light sum under the TSL peak at 190–200 K in pure K<sub>2</sub>SO<sub>4</sub> under the same conditions. The experimental result proves that the emission at 3.65–3.75 eV is due to the recombination of electrons with a localized hole.

In sulfates of alkali and alkaline earth metals activated with Mn<sup>2+</sup> ions, thermoluminescence of optically stimulated luminescence and phosphorescence, which means the formation of impurity electron-hole trapping centers in irradiated with X-ray, gamma, and ultraviolet rays, were studied [2]. The authors of [3] found thermally stimulated luminescence peaks at 485 K, 504 K, 526 K in irradiated CaSO<sub>4</sub>-Mn, which exceeded the TSL light sum in commercial TLD dosimeters LiFMg, Cu; P. In irradiated BaSO<sub>4</sub>-Mn, TSL peaks at 420 K, 498 K, and 608 K were found. In CaSO<sub>4</sub>-Mn irradiated with  $\gamma$ -beams with induced defects, a TSL peak at 383 K was detected by photostimulation [4]. It was shown in [5] for a CaSO<sub>4</sub>-Mn crystal that the emission of the Mn<sup>2+</sup> impurity at 2.25 eV is excited in the fundamental region 10 times more efficiently than with intracenter excitation of the Mn<sup>2+</sup> impurity at 3.5 eV and 3.65 eV.

In a ZnS-Mn piezoelectric crystal synthesized in a field of self-propagating high-temperature electromagnetic emission, the authors of [6] detected recombination emission arising at impurity trapping centers upon excitation by an LGI-23 nitrogen laser (337 nm). The authors suggest that the appearance of groups of recombination emission is related with the formation of vacancy and interstitial trapping centers near Mn<sup>2+</sup> impurities. In irradiated alkali metal sulfates activated with Mn<sup>2+</sup>, recombination emission appear in similar spectral regions at the generated trapping centers near Mn<sup>2+</sup>.

The main objective of this work is to study the nature of trapping centers arising in the irradiated ferroelectric crystal Na<sub>2</sub>SO<sub>4</sub>-Mn and K<sub>2</sub>SO<sub>4</sub>-Mn.

### 2. Objects and methods of research

The Na<sub>2</sub>SO<sub>4</sub>-Mn and K<sub>2</sub>SO<sub>4</sub>-Mn crystals were grown from a saturated aqueous solution by slow evaporation at a temperature of 50 °C. The plates 3–5 mm thick and 10–15 mm in diameter

were cut from the crystal. We have studied  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal and powder samples with a purity of 99.99%. The excitation spectrum is corrected for the spectral distribution of the intensity of the exciting emission.

The Solar CM 2203 spectrofluorimeter was used to measure the emission spectra in the spectral range of 1.5–6.2 eV. This setup makes it possible to carry out experimental studies on the measurement of photoluminescence spectra, excitation spectra and absorption spectra, solid-state samples and solutions at 80–300 K temperature. The spectral range in the spectrometer mode is from 200 to 820 nm, and in the spectrophotometer mode 200–1100 nm.

### 3. The results of the experiment and their discussion

Fig.1 shows the emission spectrum of the  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal upon excitation by photons with an energy of 6.2 eV at 80 K. Fig.1 (curve 1) shows that emission bands appear at 1.82 eV, 3.1 eV, 2.93 eV, 2.4 eV and 2.25 eV and a weak emission band at 3.4–3.6 eV. Similar emissions arise upon excitation of a photon with an energy of 4.96 eV (curve 2) and 5.39 eV (curve 3) at 80 K.

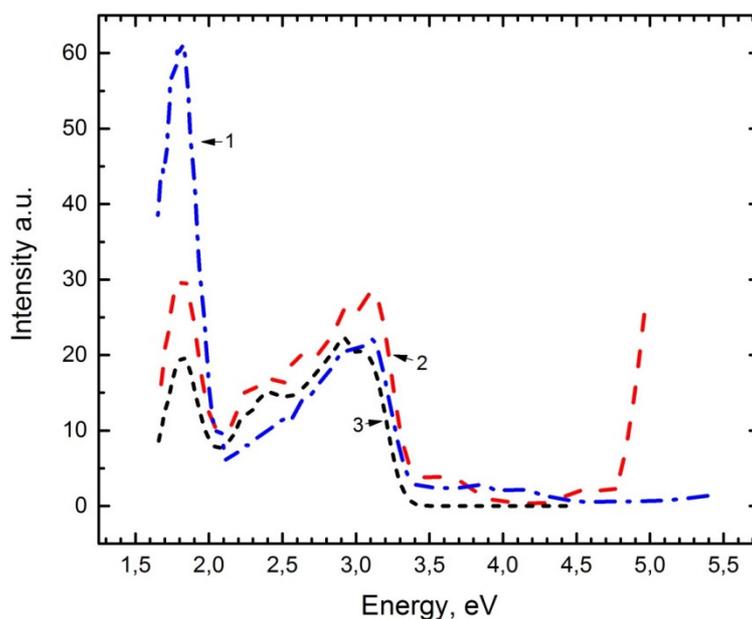


Fig.1. Emission spectrum of a  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal upon excitation by photons with an energy of 6.2 eV (curve 1), 4.96 eV (curve 2), and 5.39 eV (curve 3) at 80 K.

Fig.2 shows the excitation spectrum of the main emission band at 1.82 eV associated with  $\text{Mn}^{2+}$  impurities. The figure shows that the 1.82 eV emission band is excited at photon energies of 2.4 eV, 2.93 eV, 3.1 eV, 3.4–3.6 eV, 4.96 eV, 5.5 eV and higher 6.0 eV. When crystals are excited in the fundamental region at 4.96 eV and 5.5 eV and above 6 eV, electron-hole pairs are created, which, during relaxation, are trapped by lattice defects and form electron-hole trapping centers. The excitation bands at 3.4–3.6 eV are attributed by the authors of [5] to transition center in the  $\text{Mn}^{2+}$  ion.

The other three excitation bands at 2.4 eV, 2.93 eV, and 3.1 eV are related to impurity and intrinsic electron-hole trapping centers localized near the impurity  $\text{Mn}^+$ . In our previous works [7] in the  $\text{Na}_2\text{SO}_4\text{-Cu}$  crystal, recombination emission bands corresponding to the intrinsic  $\text{SO}_4^{3-}\text{-SO}_4^-$  at 3.0–3.1 eV and impurity  $\text{Cu}^0\text{-SO}_4$  trapping centers at 3.17 eV.

It can be assumed that similar recombination emissions at  $\text{Mn}^+\text{-SO}_4$  impurity trapping centers are formed in the  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal. It is possible that recombination emission at 2.93 eV corresponds to the decay of an impurity trapping center, and the band at 3.1 eV corresponds to the

decay of an intrinsic trapping center  $\text{SO}_4^{2-}\text{-SO}_4$ . The excitation band at 2.4 eV, as in the ZnS-Mn crystal, corresponds to  $\text{Mn}^+\text{-SO}_4$  trapping centers in disturbed areas of the anisotropic  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal.

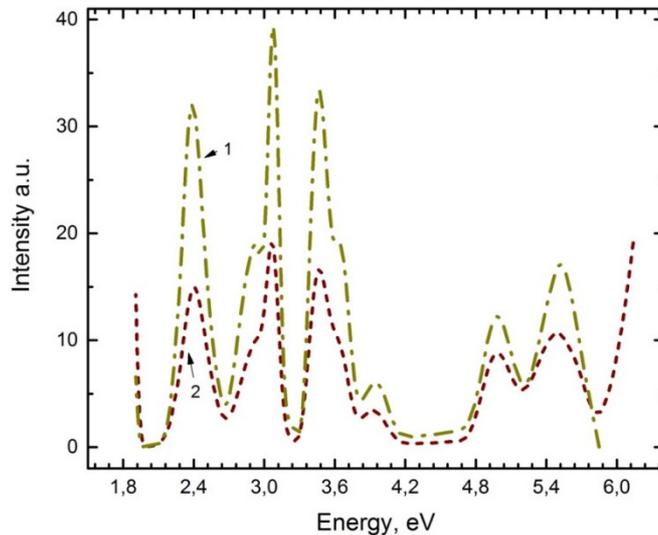


Fig.2. Excitation spectrum for the 1.82 eV emission band of the  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal at 80 K (curve 1) and 300 K (curve 2).

Fig.3 shows the emission spectrum of a  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal with induced electron-hole trapping centers upon excitation in the decay band of impurity trapping centers at 2.4 eV, 2.93 eV, 3.1 eV. The appearance of 1.82 eV emission upon excitation by photons with an energy of 3.4–3.6 eV should be related to the excitation center of the  $\text{Mn}^{2+}$  ion.

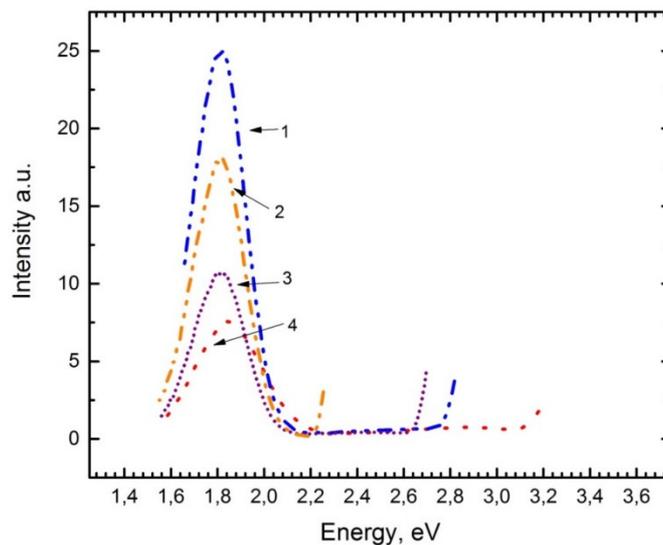


Fig.3. Emission spectrum of a  $\text{Na}_2\text{SO}_4\text{-Mn}$  crystal with induced electron-hole centers and capture centers upon excitation by photons with an energy of 3.1 eV (curve 1), 2.4 eV (curve 2), 2.93 eV (curve 3) and 1.82 eV (curve 4).

Thus, in the recombination decay of the 2.4 eV, 2.93 eV, and 3.1 eV emission bands, energy is transferred to  $\text{Mn}^{2+}$  impurities and we observe  $\text{Mn}^{2+}$  emission near lattice defects. Different energy distances in impurity electron-hole trapping centers should be related to different crystallographic

directions of hole groups  $\text{SO}_4^-$  anisotropic crystal  $\text{Na}_2\text{SO}_4$ . Similar data were obtained for the  $\text{K}_2\text{SO}_4$ -Mn crystal.

#### 4. Conclusion

In anisotropic crystals of sulfate of alkali and alkaline earth metals, in which there is a twinning of the crystal lattice, electron and hole trapping centers can be created in different crystallographic directions. Therefore, the energy distances between impurity capture centers and recombination emission can be different.

#### 5. References

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