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Electron-hole trapping centers in Na_2SO_4 with a transition metal impurity Mn

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The Na_2SO_4 samples were obtained by slow evaporation method. The mechanisms of the formation of electron and hole trapping centers are investigated by spectroscopic methods. Intrinsic recombination emission of 2.9–3.1 eV and impurity emission of 1.85 eV are excited at 4.0–4.5 eV. Intrinsic $\text{SO}_4^{3-} - \text{SO}_4^-$ and impurity $\text{Mn}^+ - \text{SO}_4^-$ trapping centers were revealed. The local levels corresponding between the electron and hole trapping center are 4.0–4.5 eV. The decay of intrinsic and impurity trapping centers was recorded at temperatures of 130–150 K and 280–350 K.

Keywords: electron; hole; recombination emission; intrinsic emission; sulfate; excitation

Introduction

It is known that pure alkali and alkaline earth metal sulfates are not effective thermoluminescent materials. A higher efficiency of TL is achieved by doping such systems with appropriate impurities that act as activators of the starting materials [1]. In paper [2], MgSO_4 doped with Dy and codoped with Mn was studied for its TL efficiency. In $\text{MgSO}_4 - \text{Dy,Mn}$, the dosimetric peak at 383°C showed high TL sensitivity, and a linear response to gamma radiation. The

authors of [3] report that the intensity of the emission peaks of two bands near 480 nm and 580 nm in Dy and Mn sharply decreases compared to MgSO_4 doped only with Dy, except for temperatures above 300°C . The authors suggest that the structure of the trapping centers of the $\text{MgSO}_4 - \text{Dy}$ phosphor changes significantly under the action of the Mn codopant, while no changes are observed in the wavelengths of the emission spectra.

The EPR data show that Mn^{2+} ions replace K^+ in the K_2SO_4 single crystal [4]. It is reported that doping with Mn^{2+} impurity reduces the phase transition temperature in K_2SO_4 , which can affect the luminescence characteristics of the single crystal. Eu^{2+} -, Mn^{2+} activated $\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{F}_2$ (CMPF) phosphors with variable radiative properties from blue to yellow were synthesized by the method of high-temperature solid-phase reaction. Energy transfer from Eu^{2+} ions to Mn^{2+} ions in CMPF samples doped with Eu^{2+} , Mn^{2+} , is possible due to the overlap of the emission spectra of Eu^{2+} and the excitation spectra of Mn^{2+} , and a decrease in the fluorescence decay time of the Eu^{2+} ion with an increase in the Mn^{2+} concentration indicates energy transfer, which provides a tunable color emission from blue to yellow by adjusting the concentration of Mn^{2+} . The mechanism of energy transfer between Eu^{2+} and Mn^{2+} ions is confirmed by the electric dipole-quadrupole interaction. In paper [5], the effects of preradiative defects on recombination luminescence in sulfate K_2SO_4 activated Mn^{2+} and Ni^{2+} were studied. It is reported that manganese and nickel impurity ions increase the rate of light sum accumulation under the TSL peak and act as an electron trapping center. Impurity ions Mn^{2+} and Ni^{2+} occupy cation sites in the crystal host lattice with higher coordination by oxygen atoms.

In $\text{K}_2\text{SO}_4 - \text{Ti}^+$, $\text{K}_2\text{SO}_4 - \text{Cu}^+$, $\text{Na}_2\text{SO}_4 - \text{Mn}^{2+}$, $\text{Na}_2\text{SO}_4 - \text{Dy}^{3+}$ crystals, upon irradiation, e^- are trapped by impurities and electronic trapping centers of the type Ti^0 [6], Cu^0 [7], Mn^+ [8] and Dy^{2+} [9] are formed. The recombination emission bands of these impurity trapping centers are located under the conduction band next to the recombination emission of a pure matrix of 3.0–3.1 eV in the spectral range of 2.9–3.0 eV. In this case, the impurity emission centers are located in different spectral intervals than the impurity trapping centers.

The objective of this work is to study the mechanisms of the formation of electron and hole trapping centers $\text{Mn}^+ - \text{SO}_4^-$ and their sensitizing role in the transfer of energy of electron-hole pairs to emitters. The magnitude of the absorbed dose is determined by the intensity of the emission of the impurity.

The mechanisms of the formation and decay of electron-hole pairs in undoped sulfates of alkali and alkaline earth metals are described in detail in [10–15]. In this work, the mechanisms of formation of electron-hole pairs in Na_2SO_4 doped with the transition metal Mn are investigated.

Materials and methods

$\text{Na}_2\text{SO}_4 - \text{Mn}^{2+}$ polycrystals were obtained by slow evaporation method. As a raw materials were used: Na_2SO_4 and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ powders. Na_2SO_4 powder (purity 99 % Sigma Aldrich, CAS 7757-82-6) is dissolved in a stoichiometric

volume in distilled and deionized water. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ dissolved in distilled and deionized water is added to the prepared solution. The optimal impurity concentration was 1 mol%. After a couple of days, small crystal particles form from the solution. Fine crystal particles are crushed in a mortar and pressed in a form of tablets on copper substrate.

Spectrometric methods were used to study the emission and excitation spectra of $\text{Na}_2\text{SO}_4 - \text{Mn}^{2+}$. The obtained results were measured on a Solar CM 2203 spectrofluorometer. The emission spectra were measured in the spectral range 1.5–6.2 eV. Cooling to 80 K was carried out using a cryostat in vacuum.

Results and discussion

Figure 1 shows the emission spectrum of $\text{Na}_2\text{SO}_4 - \text{Mn}$ upon excitation by UV photons with an energy of 6.2 eV. It can be seen that long-wavelength bands of recombination emission appear at 2.9–3.1 eV and impurity emission band at 1.8 eV. At low temperatures, the intensity of the emission bands almost doubles (Curve 2). This is due to an increase in the number of electron-hole recombination at trapping centers. During irradiation, the SO_4^{2-} anionic complex captures an electron, and the hole is localized as the SO_4^- radical. As a result, electronic trapping centers are created by the reaction $\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{3-}$. The emission peak at 2.9 eV is attributed to intrinsic electronic trapping centers $\text{SO}_4^{3-} - \text{SO}_4^-$.

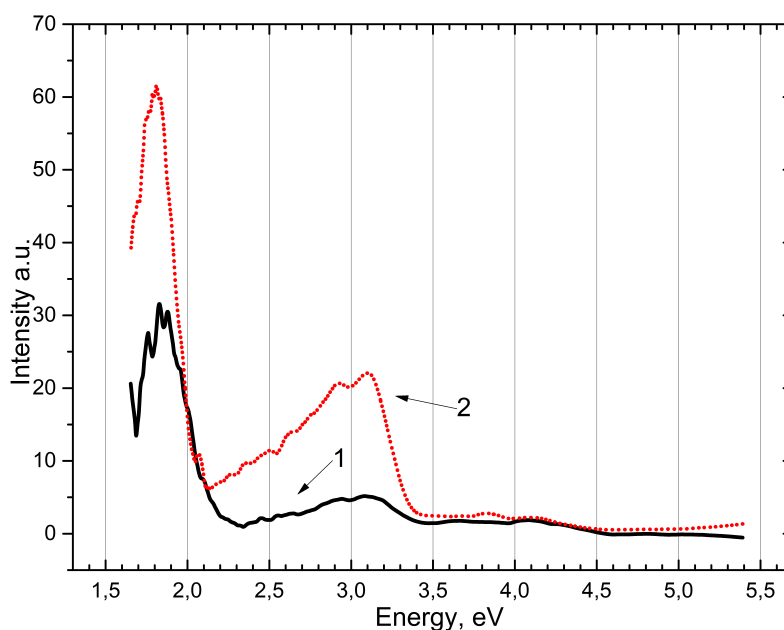


Figure 1. Emission spectrum of $\text{Na}_2\text{SO}_4 - \text{Mn}$ at 6.2 eV excitation: 1) at 300 K; 2) at 80 K.

To clarify the position of the emission spectrum peaks, the excitation spectra were studied (Figure 2). It can be seen that $\text{Na}_2\text{SO}_4 - \text{Mn}$ is excited in the regions of 4.0–4.5 eV and 5.5–6.2 eV.

Figure 3 shows the excitation spectrum for the Mn^{2+} impurity emission band. It can be seen that $\text{Na}_2\text{SO}_4 - \text{Mn}$ is excited in the spectral range from 2.5 eV to

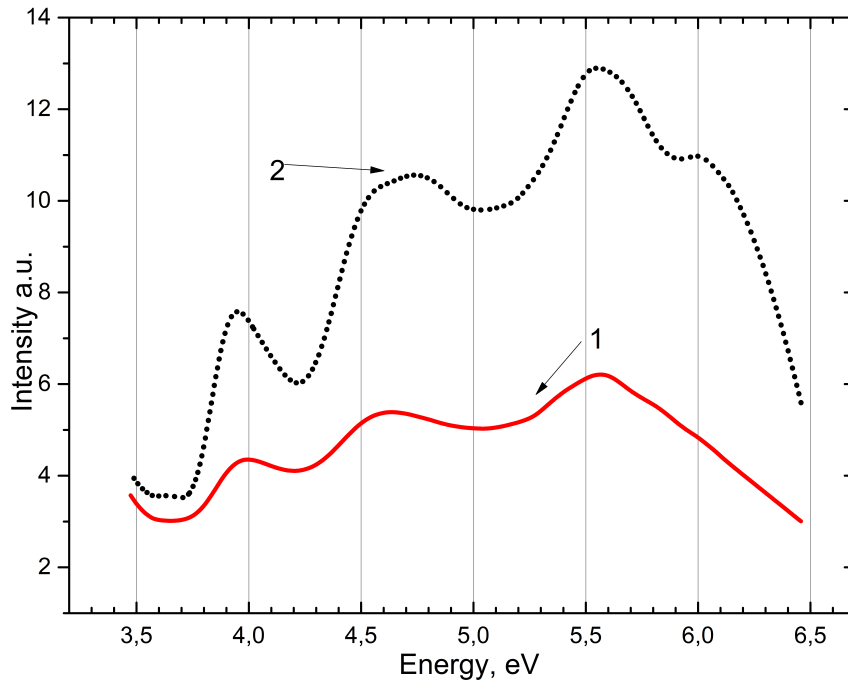


Figure 2. Excitation spectrum of $\text{Na}_2\text{SO}_4 - \text{Mn}$ for the 3.1 eV emission band: 1) at 300 K; 2) at 80 K.

5.5 eV. The spectral interval in which the impurity is excited covers the region of excitation of the main matrix.

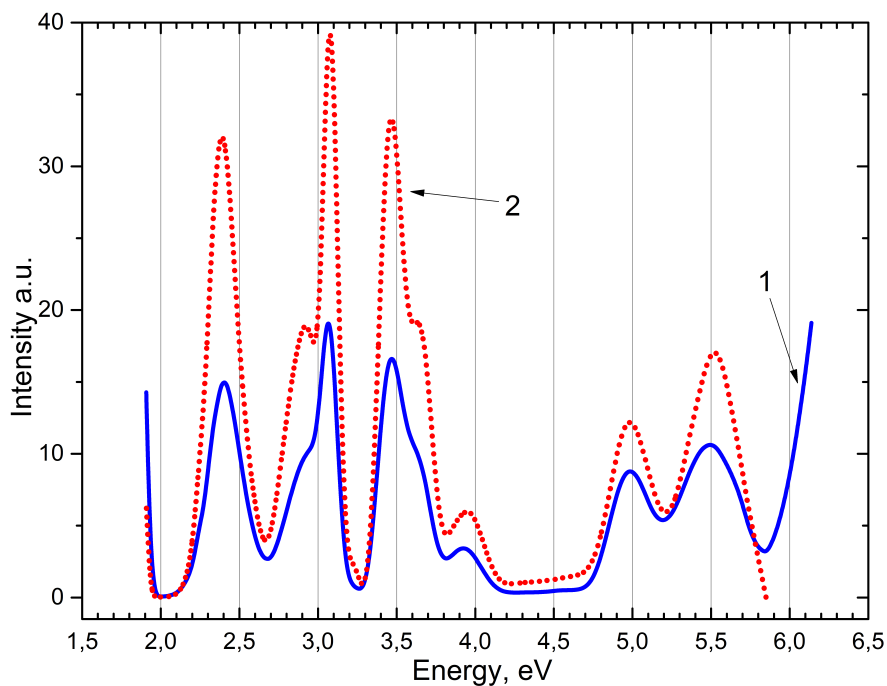


Figure 3. Excitation spectrum of Li_2SO_4 for the 3.1 eV band: 1) crystal; 2) powder with 99.99% purity; 3) for emission $3.7 \div 3.8$ eV at 15 K; 4) for emission $3.7 \div 3.8$ eV at 300 K.

Impurity emission centers are excited when the energy of electron-hole trapping centers is transferred to Mn^{2+} impurities. An electron is trapped by an impurity and an impurity trapping center $\text{Mn}^+ - \text{SO}_4^-$ is formed. An impurity trapping center is formed by the reaction: $\text{Mn}^{2+} + e^- \rightarrow \text{Mn}^+$. In order to study the impurity trapping center, the phosphor was excited with an energy from 3.65

eV to 2.4 eV, corresponding to the main excitation peaks, where free electron-hole pairs are created (Figure 4). Emission at 1.85 eV is well distinguished, which characterizes the emission of impurities.

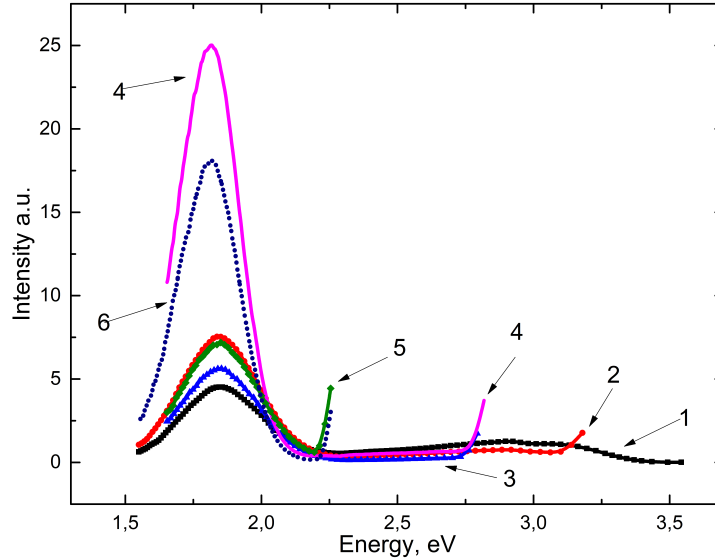


Figure 4. Emission spectrum of $\text{Na}_2\text{SO}_4 - \text{Mn}$ upon excitation: 1) upon excitation 6.65 eV at 300 K; 2) upon excitation 6.65 eV at 80 K; 3) upon excitation 3.1 eV at 300 K; 4) upon excitation 3.1 eV at 80 K; 5) upon excitation 2.43 eV at 300 K; 6) upon excitation 2.43 eV at 80 K.

Figure 5 shows the temperature dependence of the emission spectra upon excitation by UV photons with an energy of 6.2 eV. The temperature dependence of the emission was recorded in the temperature range from 77 to 450 K. The inset shows the temperature dependence of the emission spectrum for an impurity at 1.82 eV. It can be seen that impurity trapping centers decompose in two temperature ranges 130–150 K and 280–350 K. This is because of the fact that the hole is localized at different local distances from the top of the valence zone [16]. Therefore, for the decay of intrinsic and impurity electronic trapping centers located in different crystallographic directions, different thermal impact energies will be required. When the impurity trapping center $\text{Mn}^+ - \text{SO}_4^-$ decays, the Mn^{2+} impurity is restored. A similar process occurs for other emission bands.

Conclusion

Intrinsic recombination emission at 2.9–3.1 eV and impurity emission at 1.85 eV are excited in the same energy intervals. Intrinsic and impurity trapping centers are located close to each other. The decay of intrinsic and impurity trapping centers occurs at temperatures of 130–150 K and 280–350 K. Depending on the energy distance of the hole center from the top of the valence band, different emission bands are observed.

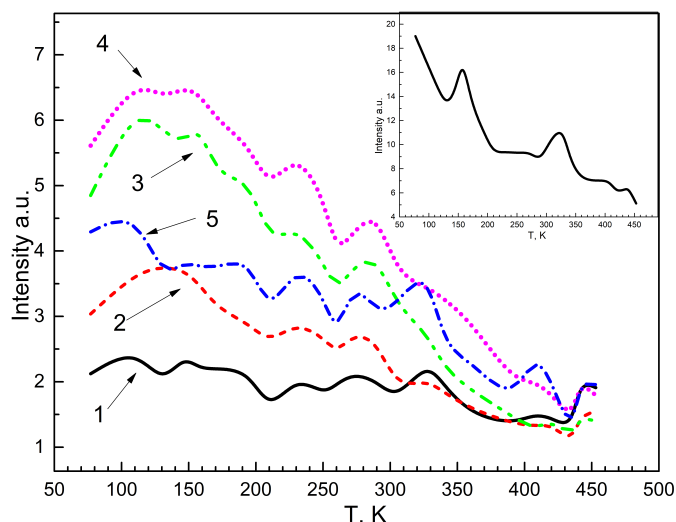


Figure 5. Temperature dependence of the emission bands when excited by 6.2 eV: 1) for the 4.0 eV band; 2) for the 3.65 eV band; 3) for the 3.45 eV band; 4) for the 2.95 eV band; 5) for the 2.43 eV band.

Acknowledgments

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