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Energy transfer of intrinsic electronic excitation to impurities in the CaSO₄-Mn system

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Energy transfer of intrinsic electronic excitation to impurities in the $CaSO_4 - Mn$ crystal

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The nature of the impurity emission center and the energy transfer mechanisms from intrinsic electronic excitations to the Mn^{2+} impurity centers in the $CaSO_4 - Mn$ crystal have been investigated. The methods of vacuum ultraviolet, atomic absorption and luminescence spectroscopy are used in a wide temperature range from 5 K to 300 K. The energy transfer of intrinsic electronic excitations to impurity emission centers in $CaSO_4 - Mn$ has been detected.

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

Introduction

In commercial dosimeters $CaSO_4 - Dy, Mn$ irradiated with X-rays, γ -rays, electron beams and other high-energy particles, impurity Mn^{2+} ions play the role of a transformer of the energy of intrinsic electronic excitations to the emitter. Pure $CaSO_4$ crystals exhibit intrinsic emissions associated with the recombination of electrons with nonequivalently localized holes of the type SO_4^- - at 3.8 eV, 4.1-4.3 eV and about 5.0 eV [1]. In a number of ionic crystals activated by Mn^{2+} ions, intracenter radiation was studied [2-8]. In $CaSO_4$ crystals activated by

rare-earth ions, where Mn^{2+} impurities act as co-activators, radiation-stimulated recombination emission has been investigated [8-14]. It is shown that Mn^{2+} impurities increase the yield of recombination emission in the $CaSO_4 - Dy^{3+}$, Mn^{2+} crystal, which has practical application as dosimeters. In $CaSO_4 - Dy^{3+}$, Mn^{2+} , when using the Mn^{2+} impurity as a co-activator, the dosimetric TSL peak at 220-230°C increases 1.8-2.0 times [14]. In works [15-18], the energy transfer of intrinsic electronic excitations to impurities Dy^{3+} , Eu^{3+} , Ce^{3+} , Cd^{3+} and Mn^{2+} were investigated. The authors of [19] investigated thermoelectric properties. In [20-21], the dependence of the Mn^{2+} peaks on irradiation with γ -rays and the effect of the impurity concentration on Eg were investigated. In this work, the nature of intracenter luminescence and the mechanism of energy transfer by intrinsic electronic excitations to impurities in $CaSO_4 - Mn$ is investigated.

Objects and methods of research

$CaSO_4 - Mn$ powders were prepared by mechanical placement followed by annealing. $CaSO_4$ powders with a purity of 99% (CAS: 7778-18-9 Sigma-Aldrich) and 4 $MnSO_4 \times H_2O$ with a purity of $\geq 99\%$ (CAS: 10034-96-5 Sigma-Aldrich) were carefully placed in a 2:1 ratio mechanically into mortar for 3 hours. After, it was placed in a muffle furnace and slowly warmed up to 700°C. At a temperature of 700°C, the samples were annealed for 2 hours, followed by sharp cooling on a metal plate. The cooled $CaSO_4 - Mn$ powder was pressed into copper molds under a pressure of 1 MPa. Thus, samples were obtained in tablet form. For excitation in the ultraviolet region, a source of VUV radiation was used - discharge hydrogen-flow lamp with a photon energy of $6.2 \div 11.5$ eV. A Solar CM 2203 spectrofluorometer 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 $4 \div 11.5$ eV spectral range was carried out by vacuum monochromator assembled according to the Seya-Namioka scheme in a wide temperature range of 15–400 K. The crystal emission was recorded by MDR-23U monochromator using a 1P28 Photomultiplier tube (Hamamatsu, Japan). The excitation spectrum is corrected for the spectral distribution of the excitation radiation intensity.

XRD

Figure 1 shows X-ray diffraction of $CaSO_4 : Mn$ powder at room temperature. The diffraction peaks are indexed by comparing them with the diffraction peaks of standard data in the literature and corresponds to the card 00-037-0184 and 00-035-075. They confirm the formed connections.

The results of the experiment and their discussion

Figure 2 shows the emission spectra of the $CaSO_4 - Mn^{2+}$ phosphor upon excitation by photons with an energy of 3.76 eV at 80 K (curve 1) and 300 K (curve 2). It is shown that emissions of 2.34 eV and 2.25 eV appear, corresponding to the

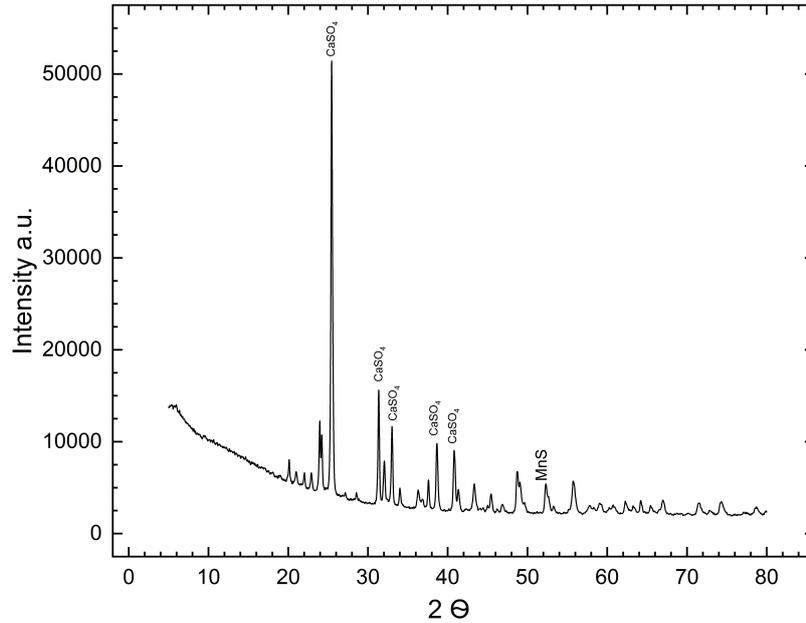


Figure 1. XRD spectra of $\text{CaSO}_4 : \text{Mn}$ at room temperature.

intracenter emission of the Mn^{2+} impurity. The positions of the emission peaks depend on the synthesis conditions.

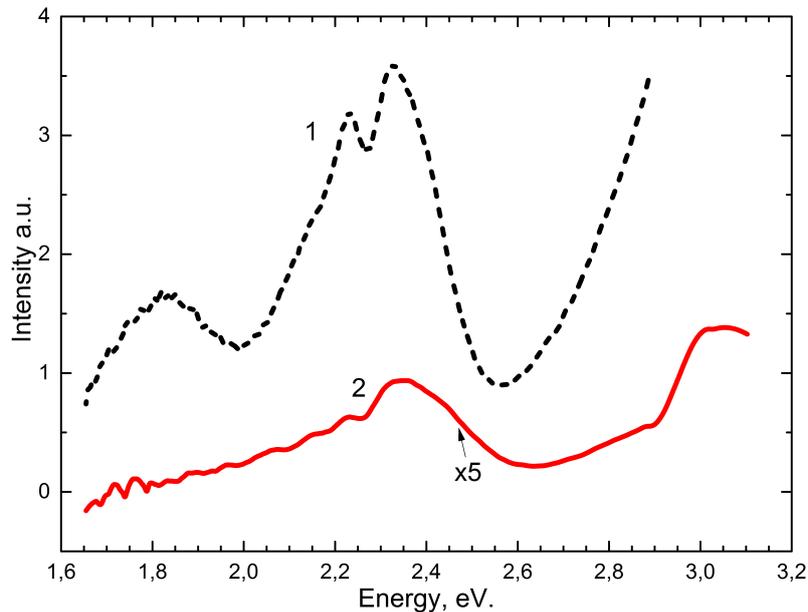


Figure 2. Luminescence of $\text{CaSO}_4 - \text{Mn}^{2+}$ upon excitation by photons with an energy of 3.76 eV at 80 K (curve 1) and 300 K (curve 2).

Figure 3 shows the emission spectrum of the $\text{CaSO}_4 - \text{Mn}$ phosphor upon excitation by photons with an energy of 5.9 eV at 80 K (curve 1) and at 300 K (curve 2). It is shown intracenter emissions of Mn^{2+} impurity - 2.34 and 2.25 eV appear, as well as a band of recombination emission of the matrix CaSO_4 at 3.1 eV, corresponding to the generation of intrinsic electron-hole trapping centers. It should be noted that the intracenter emission band of the Mn^{2+} impurity appears upon excitation in the fundamental region of the matrix.

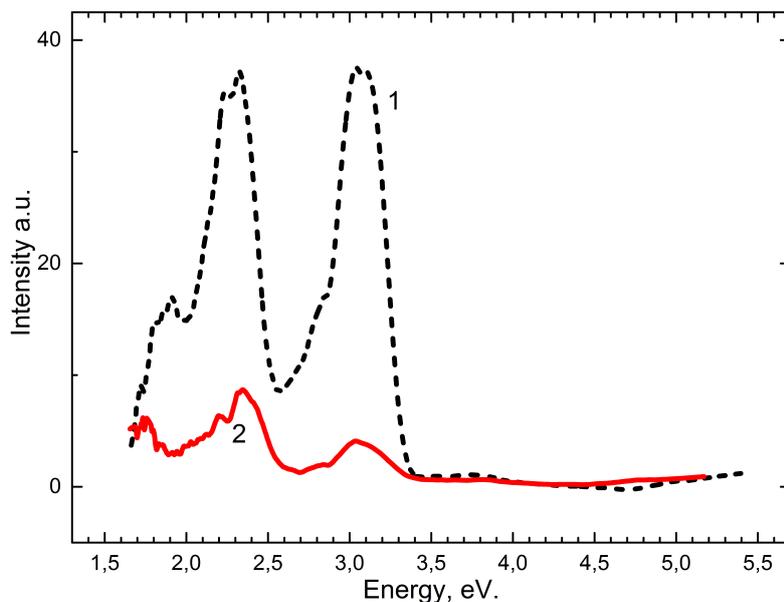


Figure 3. Luminescence of $\text{CaSO}_4 - \text{Mn}$ upon excitation by photons with an energy of 5.9 eV at 80 K (curve 1) and at 300 K (curve 2).

Figure 4 shows the emission spectrum of the $\text{CaSO}_4 - \text{Mn}$ phosphor upon excitation by photons with energies of 6.2 eV, 5.9 eV, 5.64 eV (curve 1,2,3) and 3.7 eV, 3.54 eV (curve 7,8). The intracenter emission of the Mn^{2+} impurity at 2.48 eV, 2.34 eV and 2.25 eV is excited more efficiently in the fundamental region at 5.64-5.9 eV, where free electron-hole pairs are created. Mn^{2+} impurities are also excited at an intracenter electronic transition of 3.7-3.54 eV.

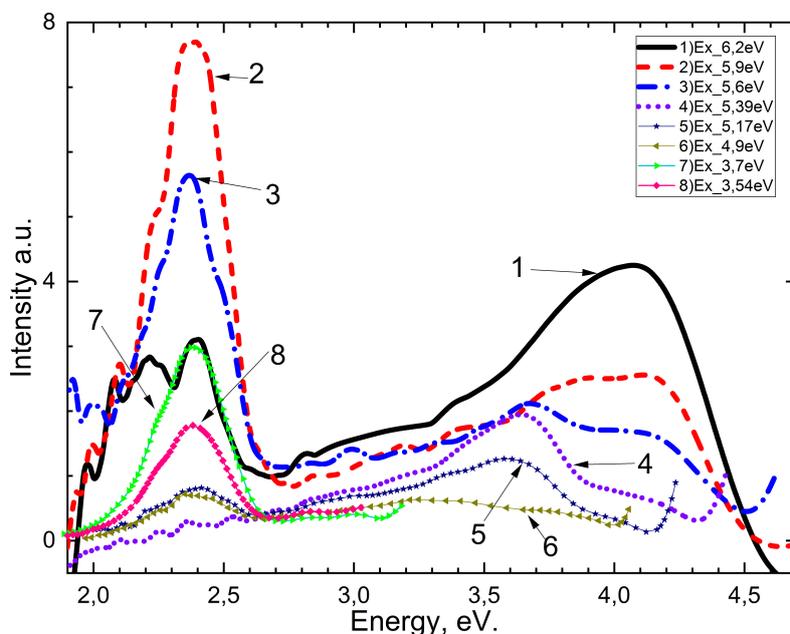


Figure 4. Luminescence of $\text{CaSO}_4 - \text{Mn}$ excitation by a photon with energies of 6.2, 5.9-5.64 eV and 3.7-3.54 eV (curve 7,8).

In Figure 5 the excitation spectrum of intracenter emission at 2.34 eV and 2.25 eV are reported. It is shown that the intracenter emission of the Mn^{2+} impurity is excited more efficiently in the fundamental region of the spectrum at photon

energies of 5.64-5.9 eV and less efficiently in the region of intracenter electronic transitions at 3.54-3.7 eV in $CaSO_4 : Mn$.

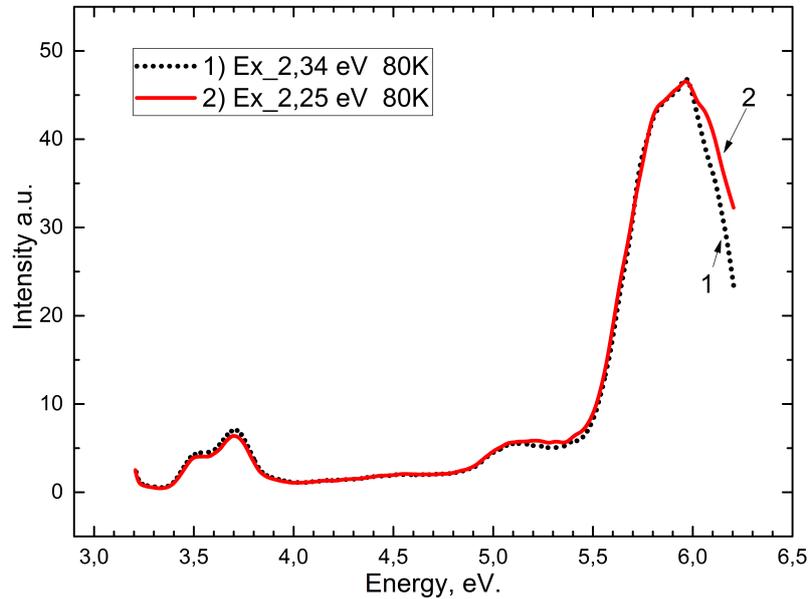


Figure 5. Excitation spectrum of $CaSO_4 - Mn^{2+}$ emission at 1) 2.34 eV and 2) 2.25 eV.

In work [22], the excitation spectrum of intracenter emission was measured at 2.5 eV of a $CaSO_4 - Mn$ crystal in the vacuum-ultraviolet region at 80 K. Figure 6 shows that intracenter emission at 2.5 eV is more efficiently excited at photon energies of 8.5 eV, less efficiently at photon energies of 5.9-6.2 eV and 10-11 eV.

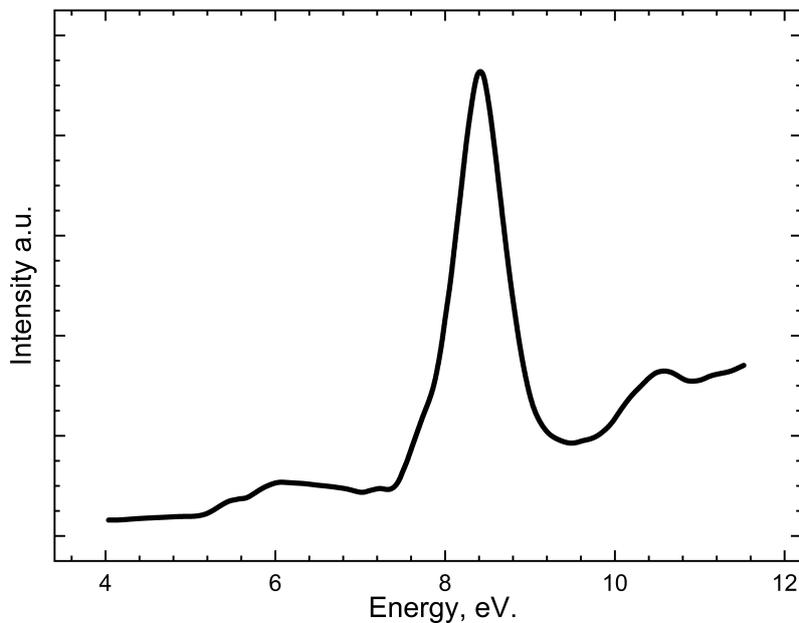


Figure 6. Excitation spectrum of $CaSO_4 - Mn^{2+}$ emission at 2.5 eV at 80 K [22].

Figure 7 shows the emission spectrum upon excitation by electron at temperatures of 5 K and 380 K. It is shown that the cathodoluminescence peaks appear at 2.5 eV, 2.0 eV, 2.9-3.0 eV (curve 1). After termination off the excitation,

phosphorescence of $\text{CaSO}_4 - \text{Mn}^{2+}$ appears at 5 K (curve 2) and at 80 K (curve 3).

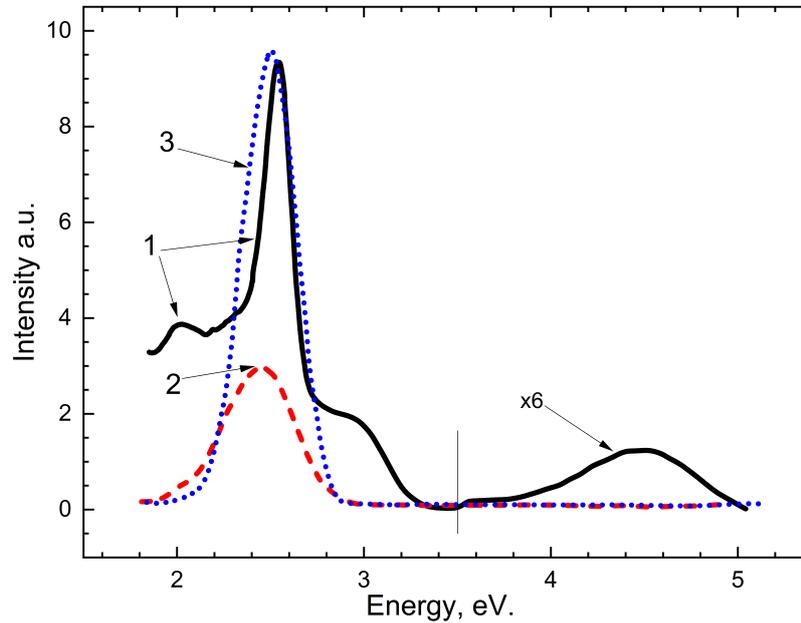


Figure 7. 1) Cathodoluminescence spectrum (curve 1) at 5 K and phosphorescence (curve 2) at 5 K, (curve 3) at 80 K. [22].

Thus, upon excitation in the absorption region of the Mn^{2+} impurity in the CaSO_4 matrix, intracenter emissions appear at 2.34 eV, 2.25 eV, 2.48 eV at 80 K. When excited in the fundamental region of the $\text{CaSO}_4 - \text{Mn}^{2+}$ at photon energies of 5.64-6.2 eV, intrinsic emissions appear at 4.1-4.3 eV, 3.7-3.8 eV, recombination emissions at 3.0-3.1 eV and intracenter emissions at 2.34, 2.25 eV, 2.48 eV at 80 K. Intracenter emissions at 2.48-2.5 eV, 2.34-2.25 eV upon excitation by photons with energies of 5.6-6.2 eV and 8.4 eV was detected by us for the first time in the $\text{CaSO}_4 - \text{Mn}^{2+}$. In work [19], showed that the bands of intrinsic recombination emission at 3.7-3.8 eV, 4.1-4.3 eV, and 5 eV arise during transitions of electrons from the first, second, and third subbands of the valence the band formed from the $2p$ states of oxygen in the anionic complex SO_4^{2-} to the conduction band. These intrinsic emissions are excited at photon energies of 5.9-6.2 eV, 7-8 eV, and 9-11 eV in irradiated CaSO_4 at 15 K. It is assumed that the excitation by photons with energies of 5.64-5.9 eV and 8.4 eV of impurity emission 2.5-2.48 eV, 2.34 eV and 2.25 eV in the $\text{CaSO}_4 - \text{Mn}$ in the fundamental region is associated with energy transfer of electron-hole pairs of the CaSO_4 matrix to Mn^{2+} impurities. The coincidence of the spectral position of the 2.48 eV impurity emission with the phosphorescence of 2.5 eV Fig. 6 (curve 1, 2) is associated with the superposition of 2.48 eV impurity emission with recombination emission at impurity trapping centers in the irradiated $\text{CaSO}_4 - \text{Mn}$.

Conclusion

In the synthesized phosphor $\text{CaSO}_4 - \text{Mn}^{2+}$, impurity emissions of 2.45 eV, 2.34 and 2.25 eV were detected upon excitation by photons of 3.54 eV and 3.7 eV.

Based on the measurement of the excitation spectrum of impurity emission at 5.64 - 5.9 eV and 8.4 eV, the transfer of energy of intrinsic electronic excitation to Mn²⁺ impurities in the $\text{CaSO}_4 - \text{Mn}$ phosphor has been detected for the first time. The observed phosphorescence upon electron excitation at 5 K and 380 K $\text{CaSO}_4 - \text{Mn}$ is associated with the formation of impurity electron-hole trapping centers.

Acknowledgments

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