

## Article

# Specific Features of Formation of Electron and Hole Trapping Centers in Irradiated CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn

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**Abstract:** Spectroscopic and thermoactivation methods were used to study the processes of accumulation of electron and hole trapping centers and energy transfer of electronic excitations to impurities in CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn. It is shown that electronic trapping centers are created during the excitation of an anionic complex as a result of charge transfer from O<sup>2-</sup> → SO<sub>4</sub><sup>2-</sup> to closely spaced anionic complexes SO<sub>4</sub><sup>2-</sup> in CaSO<sub>4</sub> and BaSO<sub>4</sub>. In CaSO<sub>4</sub> and BaSO<sub>4</sub>, energy transfer from the host to impurities occurs at the moment of charge transfer from the excited anionic complex to the combined radiative electronic state at 2.95–3.1 eV. This combined state is formed from electronic trapping centers Mn<sup>+</sup>-SO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>3-</sup>-SO<sub>4</sub><sup>-</sup>. It was found that the emerging combined radiative states at 2.95–3.1 eV of sulfates, which are formed as a result of charge transfer from the excited anionic complexes to the excited state of impurities, Tl<sup>+</sup>, Cu<sup>+</sup>, and Mn<sup>2+</sup>, occupy the same energy levels as the intrinsic electronic trapping center SO<sub>4</sub><sup>3-</sup> of the host at 2.95–3.17 eV. Experimental results show that during UV photon irradiation, anionic complexes are excited mainly near impurities in sulfates.

**Keywords:** intrinsic emission; recombination; electron-hole trapping centers; sulfate; phosphor



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## 1. Introduction

The practical use of these materials as phosphors, dosimeters, detectors, etc. is connected to the research of the mechanism of the formation of electron and hole trapping centers in irradiated sulfates of alkaline earth metals [1–3]. In irradiated sulfates of alkaline earth metals, the electronic excitations produced at trapping sites [4–6] relax as intrinsic and recombination emissions.

The creation of electron and hole trapping centers is related to the practical use of these crystals as dosimeters and detectors. The concentration of accumulated electron and hole trapping centers in TL (Thermo-luminescent) dosimeters is used to quantify the absorbed dosage in crystals [7–10]. Stability is a key issue for dosimeters. Stability may be enhanced by implementation difference impurities. Stability of ionic compounds [11,12] and perovskites [13] doped with impurities studied in term of continuous illumination with UV light. Local levels below the conduction band and above the top of the valence band correspond to intrinsic trapping centers in the host transparency region. Special impurities are added to concentrate accumulated defects and radiate the energy of recombination processes [14–16].

Experimental evidence has demonstrated that accumulated defects in practically all sulfates are associated with long-wavelength recombination emission bands at 3.0–3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV. At photon energies between 6 and 12.4 eV, free electron-hole pairs are formed, which results in the formation of these recombination emissions. It has been experimentally shown that, upon excitation in the recombination emission bands at 3.0–3.1 eV and 2.6–2.7 eV, excitations appear corresponding to 3.9–4.0 eV and 4.45–4.5 eV [17–20]

in the transparency region of the host. These excitation energies must correspond to the local levels of electron  $\text{SO}_4^{3-}$  and hole  $\text{SO}_4^-$  trapping centers.

When impurities capture electrons in irradiated  $\text{K}_2\text{SO}_4\text{-Tl}^+$  and  $\text{Na}_2\text{SO}_4\text{-Cu}^+$  crystals, it leads to the formation of electron trapping centers such as  $\text{Tl}^0$  [21] and  $\text{Cu}^0$  [18]. These centers are associated with  $\text{SO}_4^-$  and as a result create a hole trapping centers located under the conduction band. Within the 2.9–3.0 eV spectral range, the recombination emission bands that correspond to the impurity trapping centers are located below the conduction band. They are closely situated to the recombination emission of the host which is observed at 3.0–3.17 eV. In contrast to the emission band of the electronic impurity trapping centers, the emission centers of these impurities in sulfates,  $\text{Tl}^+$  (4.2 eV), and  $\text{Cu}^+$  (2.6–2.7 eV), are in distinct spectral ranges.

The formation of electron trapping centers complementary to hole trapping centers has been investigated in other similar ionic–molecular compounds. In these works, possible mechanisms for the creation of electronic trapping centers during the excitation of anionic complexes are discussed. For example, in the work [22] in the compounds  $\text{KSrPO}_4\text{-Eu}^{3+}$ , the formation of electronic trapping centers  $\text{Eu}^{2+}$  is assumed because of charge transfer from the anionic complex  $\text{-Eu}^{3+}$  impurities  $\text{Eu}^{3+}$ . As a result, electronic trapping centers  $\text{Eu}^{2+}$  are formed. It is possible that a similar mechanism for the formation of impurity electron trapping centers is realized in activated sulfates of alkali and alkaline earth metals.

The main objective of this work is to study the mechanisms of creation of electronic  $\text{Mn}^+$  and hole  $\text{SO}_4^-$  trapping centers, as well as their sensitizing role in energy transfer to emitters. According to the intensity of TSL (thermostimulated luminescence), the dose absorptions are estimated.

## 2. Materials and Methods

Natural calcium sulfate crystals and extra pure barium sulfate 99.99% (Sigma Aldrich, St. Louis, MO, USA) were used as investigated samples.  $\text{CaSO}_4\text{-Mn}$  and  $\text{BaSO}_4\text{-Mn}$  samples were prepared by mechanical friction method. Powder samples were pressed in a form of tablet to convenience of measurements. As raw reagents  $\text{CaSO}_4$ ,  $\text{BaSO}_4$ , and  $\text{MnSO}_4$  powders with 99.99% (Sigma Aldrich) purity were used.

Thermo activation and vacuum ultraviolet spectroscopic techniques were used. An irradiation was performed by X-ray source based on BSV-23 X-ray tube with a copper anode. During the experiments the tube's current was 10 mA, voltage was 40 kV, and its photon energy was 10–15 keV. Photoluminescence measurements were performed on XBO 150 W xenon lamp (OSRAM, Munich, Germany) with a photon energy of 1.5–6.2 eV. Measurements in VUV area were performed by vacuum monochromator with a photon energy of 6.2–12 eV based on hydrogen lamp. Vacuum monochromator is assembled according to the Seya–Namioka scheme. The Solar M 266 with photomultiplier Hamamatsu H 11, 890–110 was used as a recorded monochromator. All measurements were carried out in a wide temperature range from 15 to 300 K. The excitation spectrum in VUV area was corrected for the spectral distribution of the excitation emission intensity. XRD analysis is performed on X-ray Diffraction (XRD) System—SmartLab (Rigaku, Akishima, Tokyo, Japan).

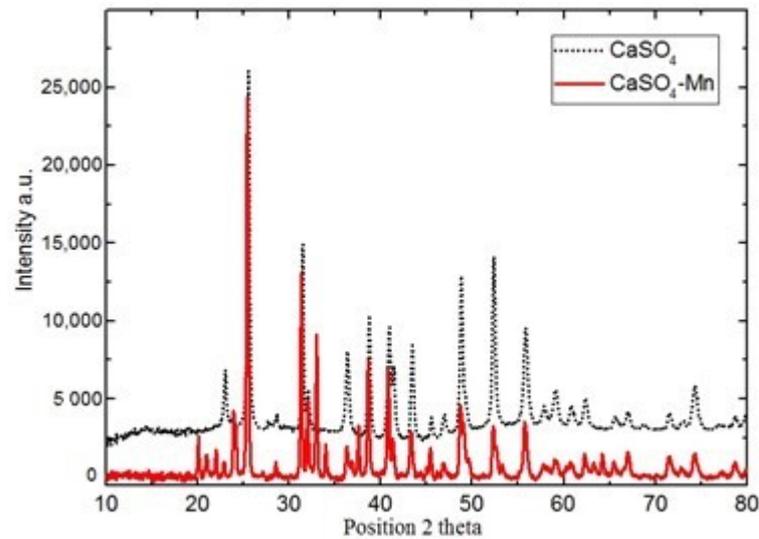
In this work the mechanism of generation of electron and hole trapping centers as well as the creation of electron and hole trapping centers in  $\text{CaSO}_4\text{-Mn}$  and  $\text{BaSO}_4\text{-Mn}$  are investigated.

## 3. Results

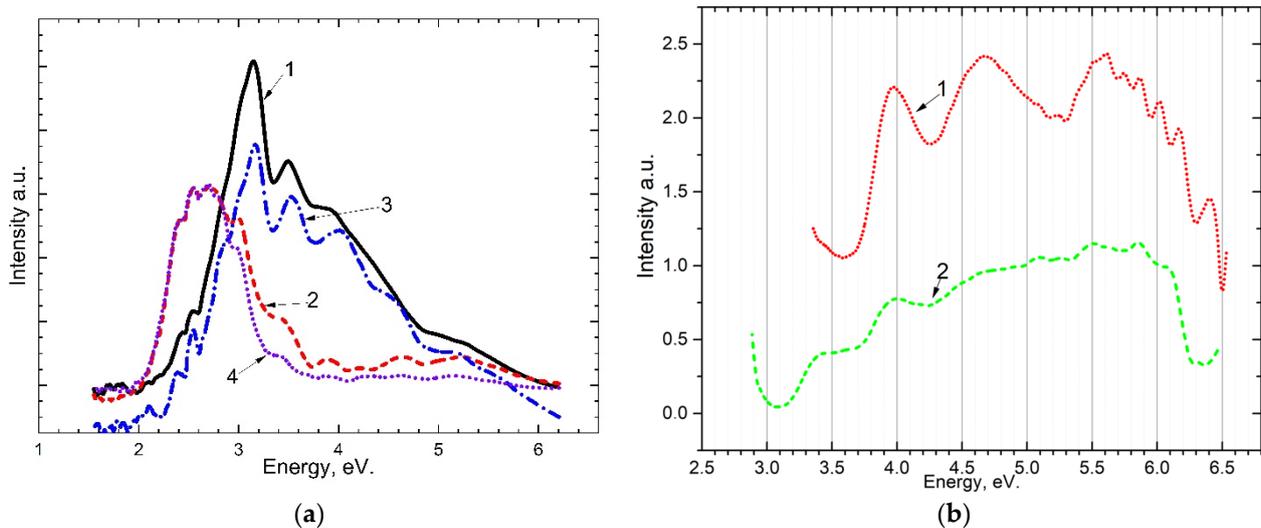
The sample's XRD pattern is illustrated in Figure 1. The spectrum data shows that the sample of  $\text{CaSO}_4\text{-Mn}$  has orthorhombic structure and corresponds to JCPDS card no. 06-0226. Obtained results confirm the purity and existence of Mn in investigated samples. Similar results were also obtained for  $\text{BaSO}_4\text{-Mn}$  sample.

The emission Figure 2a and excitation Figure 2b spectra for the  $\text{CaSO}_4$  crystal are shown in Figure 2. When excited by photons with energies from 5.4 eV to 7.75 eV, long-wavelength emission bands at 2.3–2.4 eV, 2.6–2.7 eV, 3.0–3.1 eV, and short-wavelength at

3.45–3.8 eV, 4.5–5.0 eV appear. As a result of measuring the excitation spectrum of long-wavelength emission bands of 3.0–3.1 eV and 2.6–2.7 eV, it was shown that these bands of recombination emission are excited at photon energies of ~4.0 eV and ~4.5 eV in the region of transparency  $\text{CaSO}_4$ .



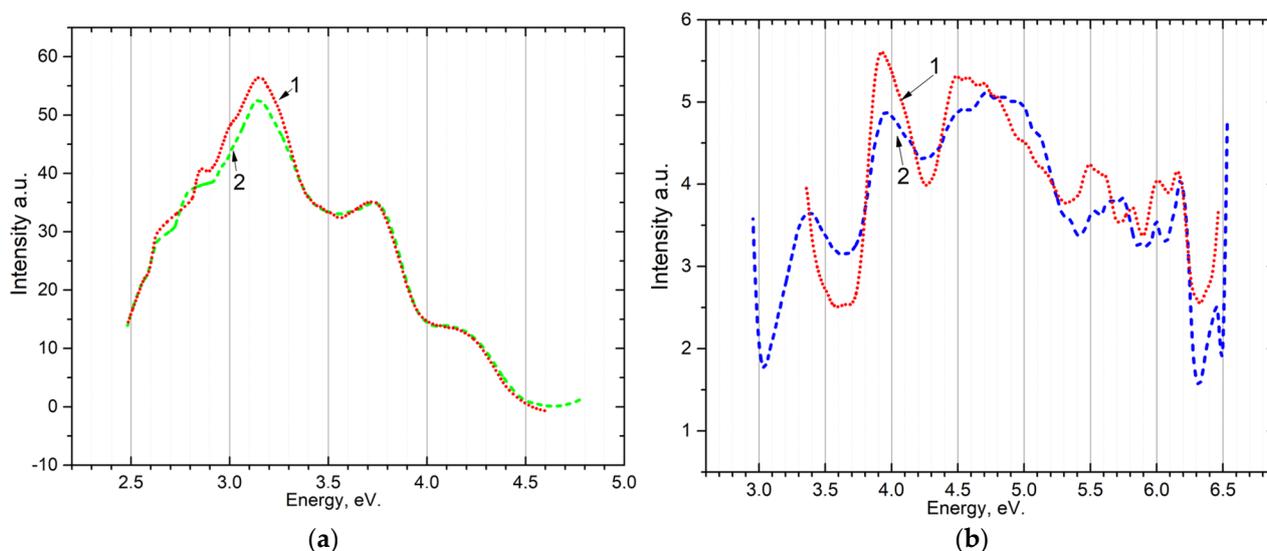
**Figure 1.** XRD spectra of  $\text{CaSO}_4$  and  $\text{CaSO}_4\text{-Mn}$  at room temperature.



**Figure 2.** (a) emission spectra of the  $\text{CaSO}_4$  crystal upon excitation by: 1—7.75 eV at 15 K; 2—7.75 eV at 300 K; 3—7.3 eV at 15 K; 4—7.3 eV at 300 K; (b) excitation spectrum of the  $\text{CaSO}_4$  crystal at 80 K after irradiation of 6.2 eV for 10 min: for the band ~3.1 (curve 1) and the band 2.7 (curve 2).

The emission Figure 3a and excitation Figure 3b spectra for the  $\text{BaSO}_4$  powder sample are shown in Figure 3. When excited by photons with energies from 5.4 eV to 7.75 eV, long-wavelength emission bands appear at 2.3–2.4 eV, 2.6–2.7 eV, 3.0–3.1 eV, and short-wavelength at 3.45–3.8 eV, 4.0–4.5 eV. The excitation spectrum of recombination emission 2.6–2.7 eV and 3.0–3.1 eV was measured. It can be seen that the bands of recombination emission are excited at photon energies of 4.0 eV and 4.5 eV in the  $\text{BaSO}_4$  transparency region.

In order to clarify the correspondence between the values of the excitation spectra at 4.0 eV and 4.5 eV for recombination emissions of 3.0–3.1 eV and 2.6–2.7 eV, the samples were excited by photons with an energy of 4.0 eV and 4.5 eV.



**Figure 3.** (a) emission spectrum of BaSO<sub>4</sub> powder at 80 K upon excitation by: 1—5.64 eV; 2—5.4 eV; (b) the excitation spectrum of the BaSO<sub>4</sub> powder after irradiation with 6.2 eV for 10 min: for the band ~3.1 (curve 1—80 K) and the band 2.7 (curve 2—300 K).

The emission spectrum of an irradiated CaSO<sub>4</sub> crystal and BaSO<sub>4</sub> powder is shown in Figure 4. Under excitation by photons with the energies of 4.0 eV and 4.5 eV the recombination emissions reappear at 3.0–3.1 eV and 2.6–2.7 eV in the CaSO<sub>4</sub> crystal (curves 1, 2) and BaSO<sub>4</sub> (curves 3, 4). The experimental fact proves that recombination emission at 3.0–3.1 eV and 2.6–2.7 eV in CaSO<sub>4</sub> and BaSO<sub>4</sub> is associated with tunneling electronic transitions between local electronic levels at trapping centers.

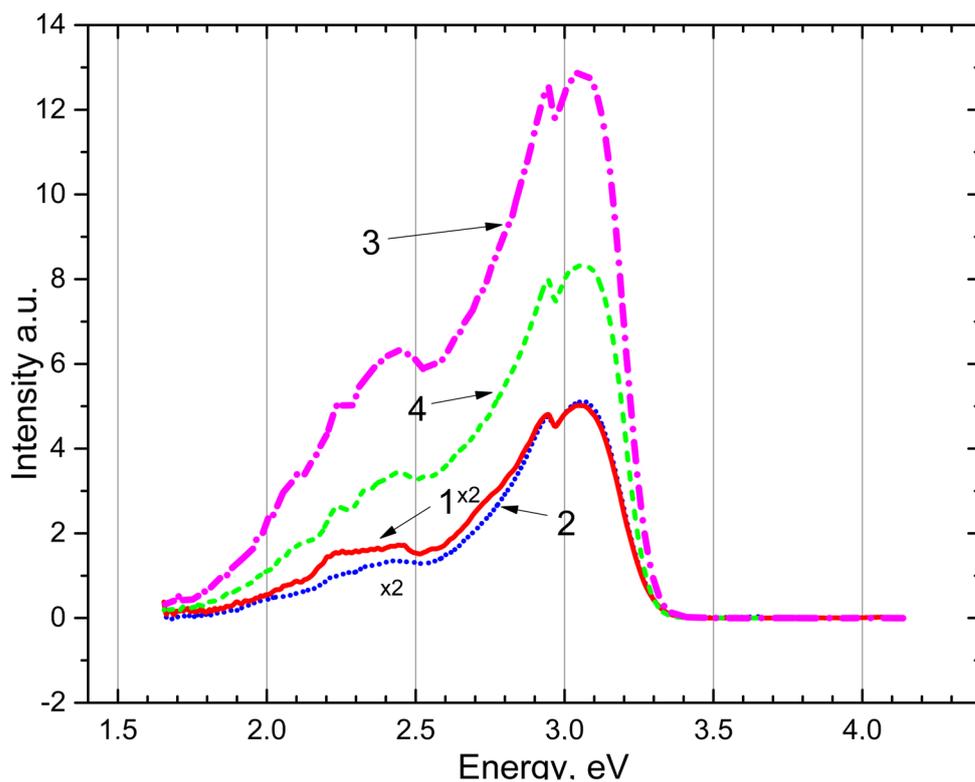
Thus, according to emission and excitation spectra the mechanisms of accumulation of electron-hole trapping centers in pure CaSO<sub>4</sub> and BaSO<sub>4</sub> are studied. It is shown that in irradiated crystals, electrons are trapped by the anionic complex SO<sub>4</sub><sup>2-</sup>, and holes are localized in the form of the radical SO<sub>4</sub><sup>-</sup>. Electronic trapping centers are created by the reaction: SO<sub>4</sub><sup>2-</sup> + e<sup>-</sup> → SO<sub>4</sub><sup>3-</sup>. When electron-hole trapping centers SO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>-</sup> in irradiated crystals are excited with an energy of 5.5–6.2 eV, tunneling recombination emission ~3.1 eV and ~2.6–2.7 eV occurs. These bands are excited in the transparency region of the host ~4.0 eV and ~4.5 eV. These bands are bands of the absorption and excitation spectra of electron and hole trapping centers.

At the next stage, the mechanisms of accumulation of trapping centers and their recombination decay in CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn were studied.

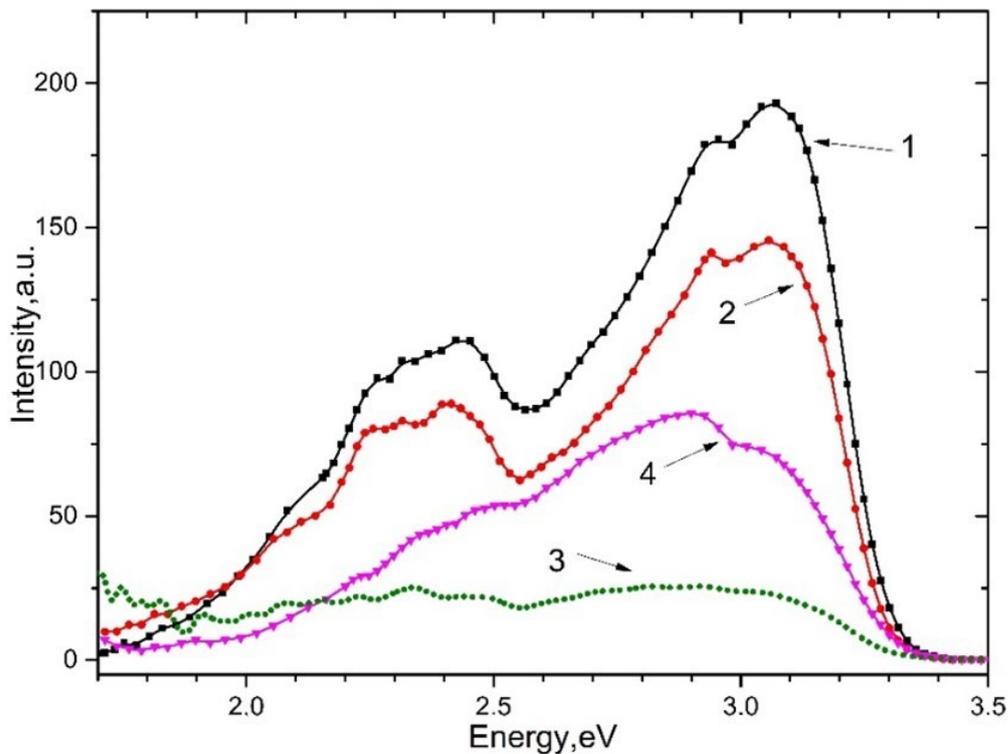
The photoluminescence of CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn irradiated (curves 1 and 4) and unirradiated (curves 2 and 3) with x-rays upon excitation by 5.6 eV photons at a temperature of 80 K is shown in Figure 5. It can be seen that emission associated with with an impurity of Mn<sup>2+</sup> at ~2.3–2.4 eV and emission bands at ~2.95 eV and ~3.1 eV are arisen. The emission bands at 2.95 eV and 3.1 eV refer to intrinsic and impurity electron-hole trapping centers.

Following this, an analysis on the excitation spectra (as shown in Figure 6) of the emission center of Mn<sup>2+</sup> impurity for the 2.3–2.4 eV band at 80 K, for CaSO<sub>4</sub>-Mn (curve 2) and BaSO<sub>4</sub>-Mn (curve 1) was conducted. As can be observed, excitation occurs in three spectral ranges: near 3.35 eV, 4.0 eV, 4.5 eV and the spectral interval 5.0–6.2 eV. The fundamental spectral area of the host is defined as 5.0–6.2 eV. New electron-hole trapping centers are formed in this region.

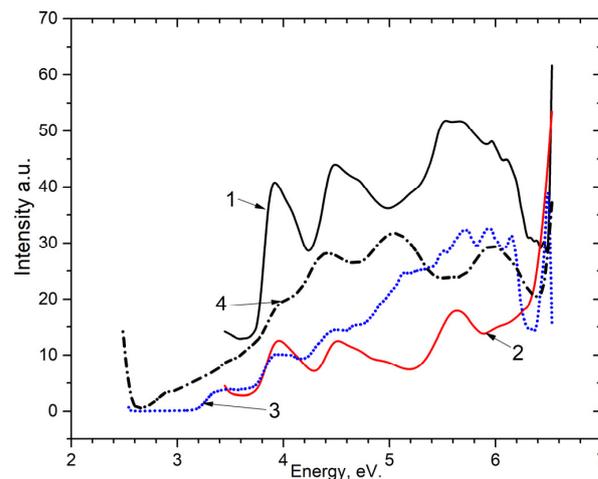
Figure 6 also displays the BaSO<sub>4</sub>-Mn powder's recombination emission excitation spectra at 3.1 eV (curve 3) and 2.7 eV (curve 4). The excitation bands observed in the ~4.0 eV and ~4.5 eV was found to be analogous to pure BaSO<sub>4</sub> samples (as shown in Figures 2 and 3).



**Figure 4.** The emission spectrum after irradiation by photons of 7.3–7.75 eV for 20 min at 80 K: CaSO<sub>4</sub> crystal (curves 1, 2) and BaSO<sub>4</sub> powder (curves 3, 4) excited photons 4.5 eV and 4.0 eV, respectively.



**Figure 5.** The emission spectrum of crystals upon excitation of 5.6 eV, 80 K. For BaSO<sub>4</sub>-Mn (curve 2) and CaSO<sub>4</sub>-Mn (curve 3) and pre-irradiated with X-rays for 10 min (curve 1 and 4, respectively).



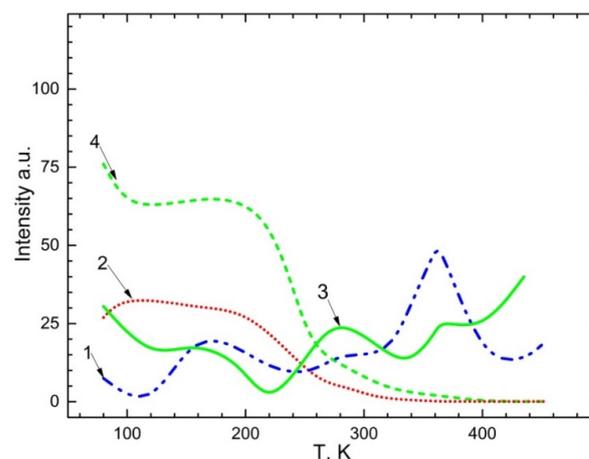
**Figure 6.** Excitation spectra in 1—for the emission band of 2.3–2.4 eV at 80 K in BaSO<sub>4</sub>-Mn; 2—for the emission band of 2.3–2.4 eV at 80 K in CaSO<sub>4</sub>-Mn; 3—for the emission band 3.1 eV at 80 K in BaSO<sub>4</sub>-Mn; 4—for the emission band 2.7 eV at 80 K in BaSO<sub>4</sub>-Mn.

It was experimentally shown that the excitation spectra of 4.0 eV and 4.5 of the recombination emission of an electron-hole trapping center in CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn coincide with the excitation energies of the Mn<sup>2+</sup> impurity in these hosts.

The temperature dependency of the emission spectra of 2.3–2.4 eV Mn<sup>2+</sup> impurities as well as 2.95 eV and 3.1 eV recombination emissions are illustrated in Figure 7. The exciting energy of bands was 4.5 eV and 5.6–5.9 eV for CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn. From Figure 7, one could observe that:

(a) In CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn crystals, emission ~2.95 eV and 3.1 eV are steady up to 200–220 K (curve 4, 2). The band's intensity starts to decline at a temperature of 200–220 K. It is presumable that after the electron delocalizes from the Mn<sup>+</sup> trapping centers at this temperature. The intensity of the recombination emission band gradually diminishes until it reaches a minimum value.

(b) the impurity is ionized from the Mn<sup>+</sup>-SO<sub>4</sub><sup>-</sup> trapping centers in accordance with the following reaction: Mn<sup>+</sup> → e<sup>-</sup> → Mn<sup>2+</sup>, i.e., the Mn<sup>2+</sup> impurity is restored (curves 1, 3); the intensity of the emission band ~2.3–2.4 eV corresponding to the emission of Mn<sup>2+</sup> increases. The delocalization of SO<sub>4</sub><sup>-</sup> holes from Mn<sup>3+</sup>-centers, which occurs in the temperature range of 350–360 K, is linked to an increase in the Mn<sup>2+</sup> impurity's emission intensity.



**Figure 7.** Temperature dependence for emission bands: 1—2.3–2.4 eV upon excitation of 5.9 eV CaSO<sub>4</sub>-Mn; 2—2.95–3.1 eV upon excitation of 4.5 eV in CaSO<sub>4</sub>-Mn; 3—2.95–3.1 eV upon excitation of 5.9 eV BaSO<sub>4</sub>-Mn; 4—2.3–2.4 eV upon excitation of 4.5 eV BaSO<sub>4</sub>-Mn.

#### 4. Discussion

The excitation spectrum of recombination emission at 2.95–3.1 eV and 2.6–2.7 eV was measured. It is shown that emission is excited at photon energies of 4.5 eV and 4.0 eV. Under reverse excitation of CaSO<sub>4</sub> and BaSO<sub>4</sub> samples with induced trapping centers, with photon energy of 4.5 eV and 4.0 eV recombination emission 2.95–3.1 eV and 2.6–2.7 eV are detected. Based on the obtained results, a mechanism of the formation of trapping centers is proposed. We propose a band scheme for the arrangement of local states of trapping centers. Electron trapping centers are produced in accordance with the reaction  $\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{3-}$  when electrons are trapped by anionic complexes or during charge transfer  $\text{O}_2\text{-SO}_4^{2-}$  during excitation of the anionic complex  $\text{SO}_4^{2-}$ . The hole excitation component is localized in the form of the radical  $\text{SO}_4^-$ . The formation of the radical  $\text{SO}_4^{3-}$  in irradiation sulfates was established by the authors of [23] using the EPR technique. This is how electron and hole trapping centers are formed in the form  $-\text{SO}_4^-$ . The trapping centers correspond to recombination emission.

Based on theoretical calculations by the authors of [24], it was predicted that holes exist in various local states from the top of the valence band. These calculations revealed that the ground state of the unpaired electron in the  $\text{SO}_4^-$  radical will differ in each of the three crystallographic directions. Additionally, experimental evidence shows that the thermal decollation of a  $\text{SO}_4^-$  hole of two types in CaSO<sub>4</sub> occurs at various temperatures [25]. All these data indicate the existence of three local states from the top of the valence band, corresponding to localized holes  $\text{SO}_4^-$ —differ—crystallographic directions in the transparency region of the crystal. As a result, the produced holes are localized at distinct distances of 3.35 eV, 4.0 eV, and 4.5 eV from the local level of electronic trapping centers.

The authors of [18–20] studied the mechanisms of energy transfer to impurities in alkali metal sulfates, in activated CaSO<sub>4</sub>-Mn and Na<sub>2</sub>SO<sub>4</sub>-Cu crystals. The excitation spectra of impurities and intrinsic recombination emissions of the host were measured. In these and our previous works, the relation between the excitation spectra of the recombination emission of the host and impurities was not specified.

It is assumed that in the irradiated crystals and powders of CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn in the spectral region of 2.95–3.1 eV, corresponding to the recombination emission of the host, a combined band appears, including the emission of its intrinsic recombination emission and the emission arising on impurity electron-hole trapping centers. The combined emission band 2.95–3.1 eV is excited in the same way at photon energies of 3.9–4.0 eV and 4.5–4.6 eV as shown on Figure 6. It is assumed that in the CaSO<sub>4</sub>-Mn and BaSO<sub>4</sub>-Mn powders irradiated with UV photons, upon excitation of the  $\text{SO}_4^{2-}$  anionic complex, a combined radiative state of 2.95–3.1 eV is created by two mechanisms:

- during charge transfer from oxygen to impurities ( $\text{O}^{2-}\text{-Mn}^{2+}$ );
- when electron-hole pairs are trapped by  $\text{Mn}^{2+}$  impurities.

In both cases, an impurity electron-hole state  $\text{Mn}^-\text{-SO}_4^-$  is created.

Parallel in the host:

- when charge is transferred from oxygen ( $\text{O}^{2-}\text{-SO}_4^{2-}$ ) to the next to anionic complex  $\text{SO}_4^{2-}$ , intrinsic electron-hole trapping centers  $\text{SO}_4^{3-}\text{-SO}_4^-$  are created near the impurity;
- when an electron is captured by an anionic complex  $\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{3-}$  and a hole is localized in the form of  $\text{SO}_4^-$ , similar capture centers  $\text{SO}_4^{3-}\text{-SO}_4^-$  can be created.

Recombination decays of emerging trapping centers occur:

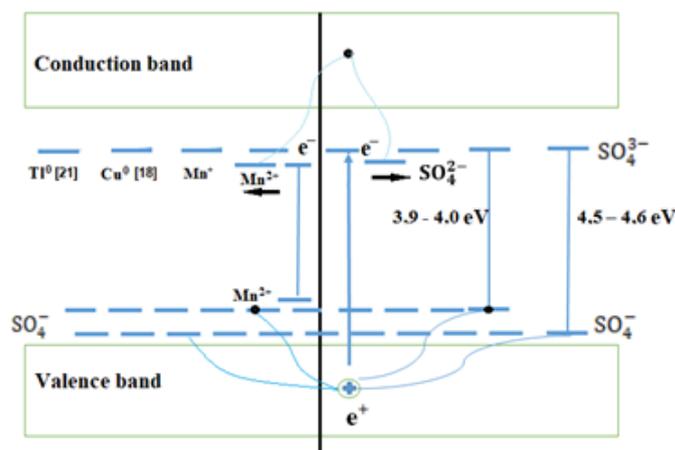
during the decay of  $\text{SO}_4^{3-}\text{-SO}_4^-$ , emission of 2.95–3.1 eV occurs;

during the decay of  $\text{Mn}^+\text{-SO}_4^-$ , an electron recombines with a hole located near the impurity  $\text{Mn}^{2+}$  and the energy of the recombination process excite impurities, emission of impurities is observed at 2.3–2.4 eV.

The formation of combined states 2.95–3.1 eV appear during the measurement of the temperature dependence of the recombination emission band and the intracenter emission of  $\text{Mn}^{2+}$ . At a temperature of 220–250 K, where electron delocalization from  $\text{Mn}^+$  centers

occurs, an increase in the intensity of the intra-center emission band corresponding to  $Mn^{2+}$  ions ( $Mn^{+} - e^{-} \rightarrow Mn^{2+}$ ) is observed.

The exhibition of combined states is also characteristic of other alkali metal sulfates activated by  $Cu^{+}$  and  $Tl^{+}$  impurities. We have shown the formation of such states in the band diagram in Figure 8.



**Figure 8.** Band scheme of impurity ( $Mn^{+}-SO_4^{-}$ ) and intrinsic ( $SO_4^{3-}-SO_4^{2-}$ ) electron and hole trapping centers.

We have experimentally shown that impurity emission at 2.3–2.4 eV and recombination emission of 2.95–3.1 eV are excited at the same energies 4.0 eV and 4.5 eV. The pattern of formation of electron and hole trapping centers with different energy states in the transparency region of the host should be a characteristic feature of sulfates of alkali and alkaline earth metals. A distinctive characteristic of these hosts is the creation of  $Tl^0$ ,  $Cu^0$ ,  $SO_4^{3-}$ , and  $Mn^{+}$  electronic trapping centers in both pure and doped sulfates, which possess local radiative energy states of approximately 2.95–3.17 eV.

## 5. Conclusions

1. The charge transfer by anionic complexes occurs during the excitation of  $SO_4^{2-}$ . Trap centers  $SO_4^{3-}$  are created as a result of charge transfer from  $O^{2-}-SO_4^{2-}$ . The alternative mechanism of formation  $SO_4^{3-}$  occurs as trapping free electrons on  $SO_4^{2-}$ .
2. Energy transfer to impurities occurs at the time of charge transfer  $O^{2-}-Mn^{2+}$ . A common combined electronic state of 2.95–3.1 eV is created. The combined radiative state 2.95–3.1 eV consists of the radiative levels of  $SO_4^{3-}$  and  $Mn^{+}$  trapping centers.
3. In sulfates with  $Tl^{+}$ ,  $Cu^{+}$ , and  $Mn^{2+}$  impurities, the combined radiative state 2.95–3.17 eV is formed during charge transfer  $-M^{x+}$  (M-metal).
4. In sulfates, anionic complexes  $SO_4^{2-}$  are excited mainly near impurities.

**Author Contributions:** Conceptualization, T.N.N. and A.M.Z.; methodology, A.Z.K.; software, T.T.A.; validation, D.H.D., A.Z.K. and B.M.S.; formal analysis, D.A.T.; investigation, R.K.S.; resources, K.B.Z.; data curation, D.H.D.; writing—original draft preparation, T.T.A.; writing—review and editing, T.T.A.; visualization, B.M.S.; supervision, T.T.A.; project administration, A.M.Z.; funding acquisition, D.H.D. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data that support the findings of this study are available upon reasonable request from the authors.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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