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Energy Transfer in the $CaSO_4-Dy$ Thermoluminescent Dosimeter from the Excited State of the SO_4^{2-} Anionic Complex to the Impurities

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Abstract: The creation of a combined radiative state at 2.95–3.1 eV in the phosphor $CaSO_4-Dy^{3+}$ has been investigated using vacuum ultraviolet and thermoactivation spectroscopy methods. It is shown that the combined radiative electronic state is formed from the radiative electronic states of the impurity electronic trapping centers $Dy^{2+}-SO_4^-$ and the intrinsic electronic radiative states $SO_4^{3-}-SO_4^-$ during the excitation of the anion complex SO_4^{2-}, as a result of charge transfer from the excited anion complex $O^{2-}-Dy^{3+}$ to the impurities and the neighboring anion complex $O^{2-}-SO_4^{2-}$. In the $CaSO_4-Dy$ phosphor, the combined radiative electronic state and impurity emission of Dy^{3+}, 2.16 eV and 2.56 eV are excited by photons with energies of 3.95–4.0 eV and 4.5–4.6 eV. Energy transfer from the matrix to the Dy^{3+} impurities is revealed upon thermal exposure as a result of the ionization of the electronic capture centers of Dy^{2+} and SO_4^{3-}.

Keywords: electron; hole; recombination emission; spectroscopy; electronic state; dosimeter

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1. Introduction

The $CaSO_4-Dy$ compound is a personal dosimeter that is widely used in nuclear power plants, synchrotrons, particle accelerators, etc. It is known that the absorbed dose in TL dosimeters is always (except for ultra-high doses) proportional [1] to the concentration of induced electron–hole trap centers. The concentration of induced defects created via radiation is estimated from absorption at the trapping centers or from the light sum under the TSL band, which arise during the recombination of induced defects. Then, the concentration of newly formed induced defects is measured depending on the duration of X-ray or γ irradiation. In the theoretical works of other authors [2–4], it has been shown that the band gap is 5.5–5.9 eV. Experimentally, based on measurements of the spectrum of the creation of intrinsic emission arising from the recombination of electrons with holes in the works of the authors [5–7], the band gap was estimated as 5.4–6.2 eV. By measuring the excitation spectra of the rare earth ions Dy^{3+}, Tb^{3+}, and Gd^{3+} in $CaSO_4$, the authors of [8] showed that these ions are excited at a photon energy of 8.0–8.4 eV, where an electron–hole pair is created. The criterion for the formation of electron–hole trapping centers is the appearance of tunnel emission, phosphorescence, and thermally stimulated luminescence (TSL) arising during the recombination decay of electron–hole trapping centers.

The introduction of the Dy^{3+} impurity ion significantly increases the sensitivity of the TL dosimeter $CaSO_4-Dy$. The authors of [9–12] suggest that in γ- irradiated $CaSO_4-Dy$ crystals and powders, as a result of the radiolysis of the SO_4^{2-} anionic complex, SO_4^-, SO_3^-, SO_2^-, O_3^- radicals appear, which have absorption bands from 220 nm to 360 nm. During annealing up to 400 °C, these induced centers are annealed. These centers are responsible for the appearance of dosimetric TSL peaks in the temperature range of 220–250 °C.

Barkyoumb J. H. et al. [13], in irradiated $CaSO_4 - Dy$, detected a low-temperature TSL peak at 150–200 K, with spectral compositions of 490 nm and 580 nm corresponding to the Dy^{3+} ion in the form of tunnel luminescence.

In the recent work of Cano N. F. et al. [14], four types of radicals, SO_4^-, SO_3^-, and O^- were identified via EPR in γ-irradiated undoped $CaSO_4$ crystals, which during annealing, correlated with the dosimetric TSL peaks at 200 °C and 268 °C.

Okada G. et al. [15] assumed that during irradiation, small parts of Dy^{3+} are converted into Dy^{2+}, and during thermal annealing, the Dy^{3+} emissions are restored. No emission corresponding to the Dy^{2+} impurity ion was detected.

From a brief review of the literature, we can conclude the following: Numerous experimental data have shown that the delocalization of SO_4^-, SO_3^-, SO_2^-, O_3^-, and O^- radicals is responsible for the appearance of dosimetric TSL peaks from 200 °C to 400 °C, with subsequent recombination with the electronic centers. Experimental evidence of the joint annealing of hole and electron trapping centers has not been found. Previous works are mainly devoted to technological methods of increasing the sensitivity of TL dosimeters by introducing various impurities and annealing samples.

In phosphates [16,17], it has been shown that electronic trapping centers of Eu^{2+} and Bi^{2+} and Mn^{+} are created during the excitation of anionic complexes PO_4 and $P_4\,O_{12}$ as a result of the charge transfer from oxygen O^{2-}—Eu^{3+}, Bi^{3+}, and Mn^{3+} to the impurities. It is assumed that similar processes can occur in sulfates of alkaline earth metals ($CaSO_4 - Dy$); upon excitation of a similar SO_4^{2-} complex, the charge can be transferred to an impurity or a neighboring anion. $O^{2-} - Dy^{3+}$ or $O^{2-} - SO_4^{2-}$ creates electron centers $Dy^{3+} - SO_4^{2-}$ and $SO_4^{3-} - SO_4^-$, trapping centers that are complementary to the holes in SO_4^-.

In sulfates, there is no experimental work on the creation of electron–hole pairs and the transfer of energy to impurities via similar mechanisms. It is possible that the appearance of recombination emission, absorption, reflection, and changes in such basic parameters as refractive indices and dielectric constants at much lower energy levels than the energy of the band gap is associated with similar mechanisms for the creation of defects and energy transfer from the matrix to the impurities [18–20].

In this work, the mechanisms of energy transfer from the matrix to the impurities and the formation of electron–hole trapping centers in the dosimetry compound $CaSO_4 - Dy$ (so-called TLD-900) were studied.

2. Experiment

The study samples were synthesized using the method described in [21] via acid distillation. Highly pure 99.99% (Sigma-Aldrich, St. Louis, MO, USA) Dy_2O_3 powders were dissolved in highly concentrated acid H_2SO_4. To prepare the sample, 0.5 g of $CaSO_4{\cdot}2H_2O$ powder and 0.3mol% (0.41 g) of Dy_2O_3 were used as starting substances, calculated using the formula:

$$m_1 = m_2 \frac{M_1 n}{M_2(100-n)}$$

where m_1 is the mass of the activator, m_2 is the mass of the main substance, M_1 and M_2 are the molar masses of the activator and the main substance, respectively, and n is the needed molar percentage of the activator. The solution was slowly heated, and $CaSO_4{\cdot}2H_2O$ powder (Sigma-Aldrich) was added and dissolved via stirring. The resulting solution was evaporated at 250 °C. Next, the samples were rinsed with distilled water 2 times and dried at 70 °C. The resulting powders were annealed in a muffle furnace at 900 °C. The finished powders were pressed into tablets that were 8–9 mm in size and 1–2 mm thick. The optimal concentration of Dy impurity in the $CaSO_4$ matrix was found to be 0.3 mol%. Increasing the concentration above 0.3 mol% increased the intensity of the intratester Dy^{3+} emission. The resulting 0.3 mol% Dy impurity was the optimal concentration for the spectroscopic properties of the studies. Emission and excitation spectra were obtained using a SM2203 spectrofluorometer (Belarus).

Thermally stimulated luminescence was obtained after irradiation with X-rays using URS-55 X-ray apparatus (Burevestnik, Leningrad, USSR). The study of thermally stimulated luminescence was carried out at a heating rate of 0.1–0.2 K/s. Irradiation occurred at a current of 10 mA for 5 min. To record the TSL spectra, a Hamamatsu 1p28 photomultiplier (Hamamatsu Corporation, Hamamatsu, Japan) was used. To measure the integral thermally stimulated luminescence, the sample was irradiated with X-rays at 80 K cryostat. After the end of irradiation, the sample was rotated towards the photomultiplier (without a monochromator), and data were recorded during constant heating.

The measurement results in the vacuum ultraviolet region were obtained using a VMR-2 installation. The source of radiation in the vacuum ultraviolet region is flowing hydrogen produced using a hydrogen generator. The results obtained were recorded on an M266 monochromator (Belarus) (Solar laser systems, Minsk, Belarus). The excitation spectra of the vacuum ultraviolet study were corrected using the spectra of sodium salicylate.

3. Results

In all the alkaline [22] sulfates, after irradiation with UV rays or X-rays, long wavelength recombination emissions appeared at 3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV. These emissions are associated with the formation of electron–hole trap centers. These electron–hole trap centers have not been studied in alkaline earth metal sulfates.

To solve this problem, we investigated $CaSO_4 - Dy$ for the formation of these recombination emissions. The main results are related to the study of the $CaSO_4 - Dy$ formation of recombination emissions at 3.1 and 2.6–2.7 eV.

The phosphor $CaSO_4 - Dy$ was irradiated at 300 K with photons with an energy of 6.2 eV (Figure 1, curve 1). From Figure 1, it is clear that intracenter emissions from the Dy^{3+} impurity are observed at 2.16 eV and 2.56 eV, corresponding to the 4f-4f electronic transitions of rare earth Dy^{3+} ions in $CaSO_4 - Dy$. In the next stage, the $CaSO_4 - Dy$ phosphor was irradiated with photons with an energy of 6.2 eV at 80 K (curve 2). After irradiation, the intensity of intracenter emission decreased significantly, and new emission bands appeared at 2.95 eV, 3.1 eV, 2.6–2.7 eV, 2.40 eV, and 3.7–3.8 eV (curve 2). The nature of the short-wavelength emission band 3.7–3.8 eV has previously been investigated. The band appears when an electron recombines with a localized hole SO_4^-.

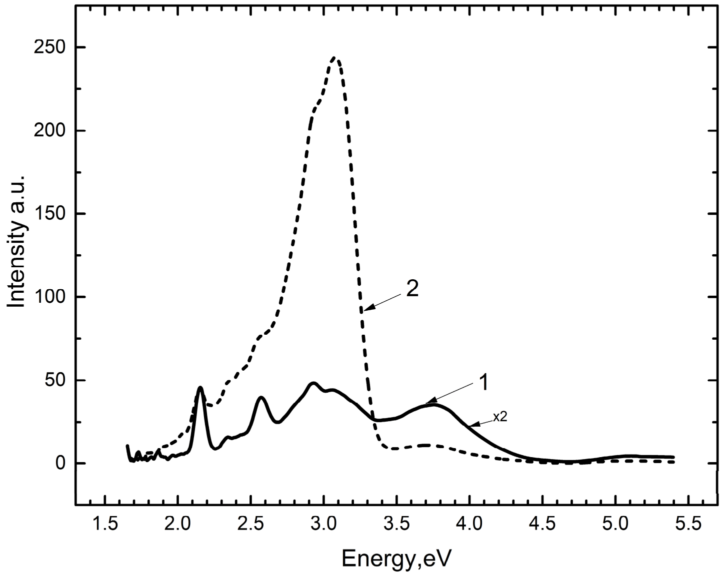

Figure 1. Emission spectrum of the phosphor $CaSO_4 - Dy$ when excited by photons with an energy of 6.2 eV at 300 K (curve 1) and 80 K (curve 2). ×2 means that intensity multiplied 2 times.

By measuring the excitation spectra (Figure 2) for the 3.1 eV (curves 1 and 2) and 2.95 eV (curves 3 and 4) bands, we showed that these bands are excited in the transparency region of the $CaSO_4 - Dy$ phosphor at 3.9–4.0 eV and 4.5–4.6 eV at 80 K (curves 1 and 3, Figure 2). At 300 K, these bands are not stable. In addition, at 80 K, these bands are created at photon energies equal to 5.5–6.2 eV, where intrinsic electronic excitations of the $CaSO_4$ matrix arise.

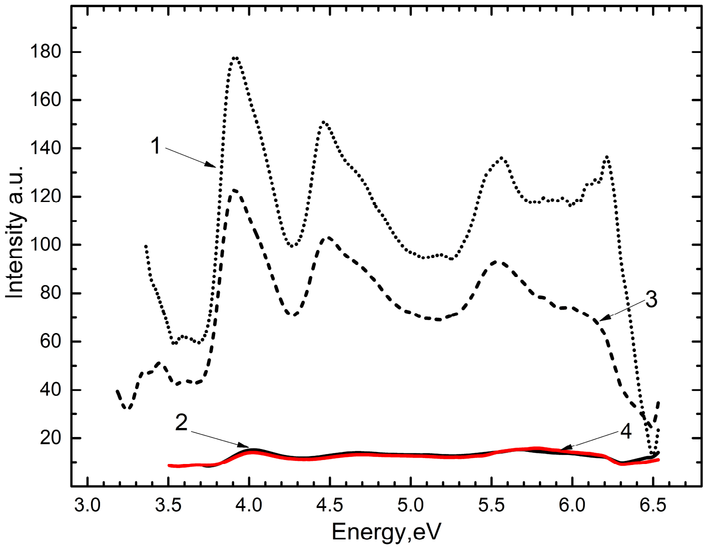

Figure 2. Excitation spectrum of $CaSO_4 - Dy$ for the emission bands of 2.95 eV and 3.1 eV: for band of 3.1 eV at 80 K (curve 1) and 300 K (curve 2); for band of 2.95 eV at 80 K (curve 3) and 300 K (curve 4).

In order to verify that the excitation bands at 3.9–4.0 eV and 4.5–4.6 eV (curves 1 and 3, Figure 2) are the excitation bands of recombination emission at 2.95 eV and 3.1 eV, we conducted a verification experiment.

By irradiation with photons with an energy of 6.2 eV for 10–20 min, electron–hole trapping centers were created in the $CaSO_4 - Dy$ crystal at 80 K (Figure 3), which create recombination emissions of 2.95 eV and 3.1 eV. Then, the (Figure 3) crystal with induced defects was selectively excited by the photons with energies of 3.9–4.0 eV (curves 1 and 3) and 4.5–4.6 eV (curves 2 and 4) at 80 K and 300 K, respectively. The emission spectrum was measured in the spectral range from 1.5 eV to 3.8 eV. Figure 3 shows the emission spectrum of the $CaSO_4 - Dy$ phosphor with induced defects or electron–hole trapping centers when excited by photons with an energy of 3.9–4.0 eV (curves 1 and 3) or 4.5–4.6 eV (curves 4 and 2) at 80 and 300 K. The figure shows that at 80 K intense recombination emissions appear at 3.1 eV and 2.95 eV (curves 1 and 2). The experimental results indicate that recombination emission is indeed excited at photon energies of 3.9–4.0 eV and 4.5–4.6 eV. This means that between the ground and excited local state of emissions at 3.1 eV and 2.95 eV, there are corresponding energies of 3.9–4.0 eV and 4.5–4.6 eV. From Figure 3, it is clear that at 300 K, the photon energies of 4.5–4.6 eV and 3.9–4.0 eV and impurity emissions for Dy^{3+} of 2.16 eV and 2.56 eV are excited (curves 1 and 4, Figure 3). This phenomenon is reflected in the following experiment (Figure 4).

To clarify the pattern of excitation by photons with energies of 4.0 eV and 4.5–4.6 eV, recombination emissions of 2.95 eV and 3.1 eV, and impurity emission Dy^{3+} at 2.16 eV and 2.56 eV, we simultaneously conducted the following experiment.

In the pre-irradiated $CaSO_4 - Dy$ with induced electron–hole trapping centers at 80 K and 300 K, we measured (Figure 4) the excitation spectrum of the impurity emission Dy^{3+} at 2.56 eV (curves 1 and 2) and 2.16 eV (curves 3 and 4). The spectral position of the emissions for Dy^{3+}, which is shown above (2.56 eV and 2.16 eV), is described in a review by Lakshmanan, A. R. [23]. It can be seen from the figure that the impurity emission Dy^{3+} at 2.56 eV and 2.16 eV is excited at 3.2 eV and 3.40–3.52 eV, corresponding to the impurity intracenter excitation of the Dy^{3+} ion, as well as at 3.9–4.0 eV and 4.5–4.6 eV, corresponding to the excitation of long-wavelength recombination emission at 3.1 eV and 2.95 eV. These emissions are also excited close to fundamental regions of the matrix, 5.0 eV and 5.5–6.2 eV. The excitation of the Dy^{3+} ion in intracenter absorption in the matrix, as well as close to the fundamental region of the $CaSO_4 - Dy$ crystal, was already known [23].

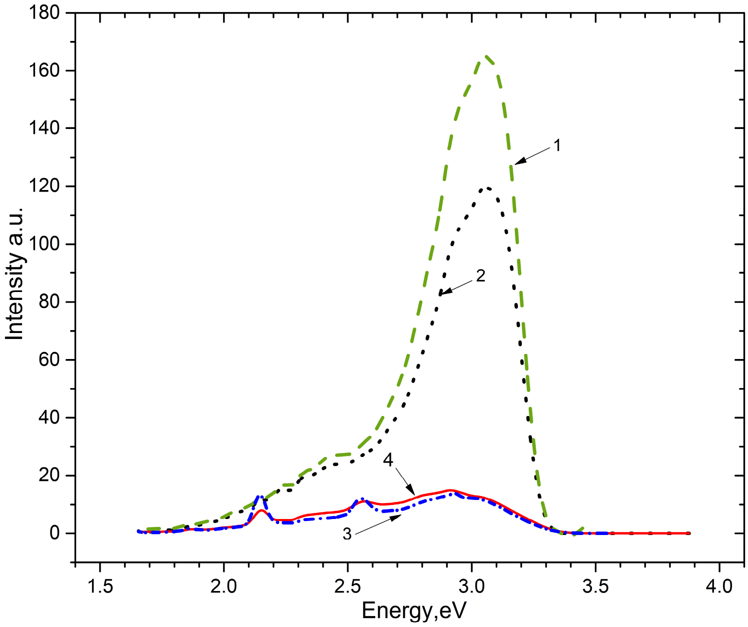

Figure 3. Emission spectrum of the phosphor $CaSO_4 - Dy$ when excited by photons with energies of 3.95 eV at 80 K (curves 1), at 300 K (curves 3), 4.5 eV at 80 K (curves 2), and at 300 K (curves 4).

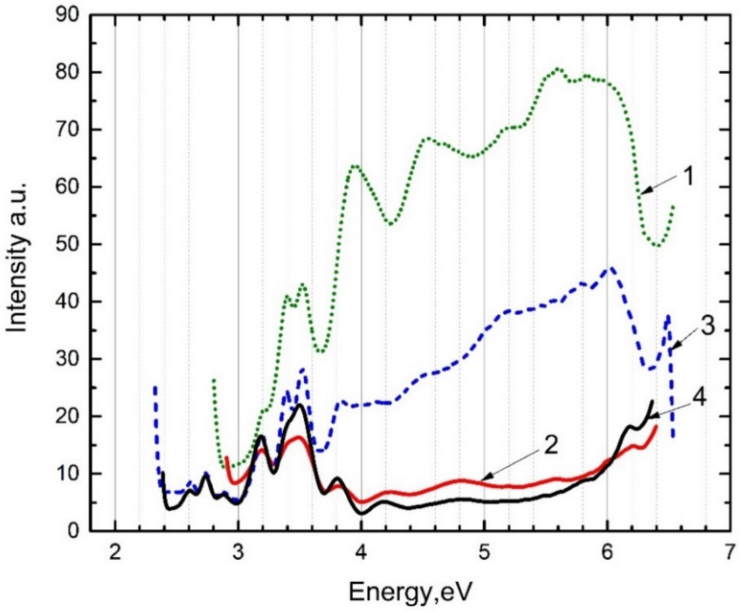

Figure 4. Excitation spectrum of $CaSO_4 - Dy$ for the emission band of 2.56 eV at 80 K (curve 1), at 300 K (curve 2), 2.16 eV at 80 K (curve 3), and 300 K (curve 4).

At the next stage, the excitation spectra of the intracenter emissions of 2.56 eV and 2.16 eV at 15 K of the $CaSO_4 - Dy$ powder in the vacuum ultraviolet region were studied. Previously, Dorenbos P. [24] showed that intracenter emission of 2.65 eV in the Dy^{3+} ion was excited at 5.6 eV and 7.3 eV in the f transition, corresponding to the $4f \rightarrow 4f$ transitions. According to the authors of [24], the detected excitation spectrum at 8.4 eV should correspond to the excitation of the oxyanion complex SO_4^{2-}. It is assumed that the energy value of 8.4 eV corresponds to the band gap in $CaSO_4$. Figure 5 shows the excitation spectrum of the $CaSO_4 - Dy$ phosphor for the 2.56 eV band in the spectral region from 4 eV to 12 eV. From Figure 5, it is clear that excitation bands appear at 5.6 eV and 7.3 eV, as previously detected by other authors [24]. Excitation bands were also detected at 8.0 eV and ~8.3–8.4 eV. Figure 5 shows the excitation spectrum of recombination emission at 3.1 eV. From Figure 5 (curve 3), it is clear that recombination emission of 3.1 eV is excited in the energy range from 6 eV to 8.4 eV with an increasing intensity.

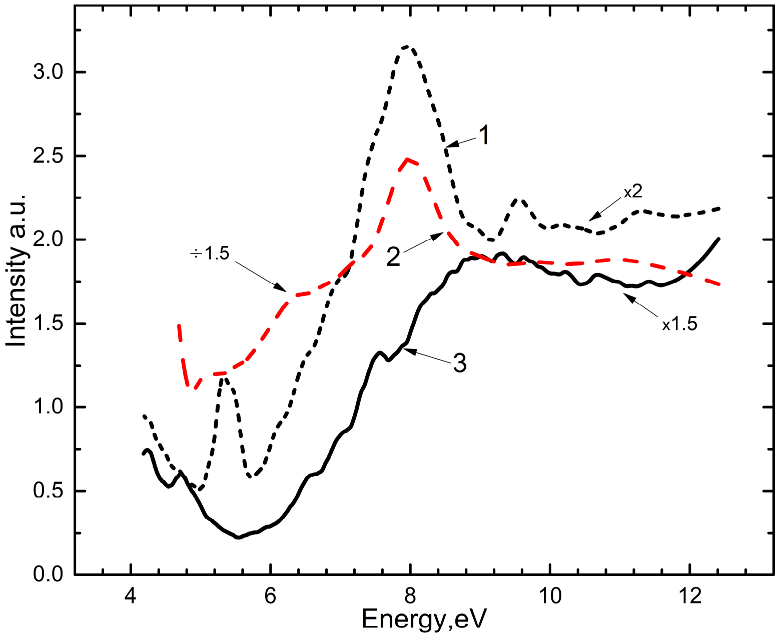

Figure 5. Excitation spectrum of $CaSO_4 - Dy$ in the vacuum ultraviolet region. Emissions of 2.56 eV at 15 K (curve 1), 2.16 eV at 15 K (curve 2), and 3.1 eV at 15 K (curve 3). ×1.5 means that intensity is multiplied 1.5 times; ÷1.5 means that intensity is divided 1.5 times.

Figure 6 shows the temperature dependence of the intensity of recombination emissions (excited by 6.2 eV) of 2.95 eV and 3.1 eV and intracenter impurity emission Dy^{3+} of 2.16 eV from 15 K to 380 K. From Figure 6, the intensities of the emissions at 2.95 eV (curve 2) and 3.1 eV (curve 1) decrease in the temperature range of 150–200 K. Then, a slight increase is observed at 220–250 K and 300–370 K, and a decrease to a minimum value was observed. The intensity of Dy^{3+} impurity emission at 2.16 eV (curve 3) has a similar pattern of intensity decreasing to 190 K. After 210 K, there is a temperature-dependent release of energy from 220–280 K and above 330 K. The release of energies above 330 K is presumably associated with a similar Dy^{3+} band as in TSL (Figure 7), where there are similar temperature peaks in the region of 330–400 K.

Figure 7 shows the curves of integral thermally stimulated luminescence (TSL) of the $CaSO_4 - Dy$ phosphor irradiated with X-ray radiation at 80 K. From the figure, it can be seen that that TSL peaks appear at 220–270 K, 330–400 K, and 420–450 K and higher. In the same figure, due to limitations with the experimental equipment, the 420–450 K bands are not clearly visible. The bands for TSL at these temperatures are known from the work of the authors [23] on the study of the thermo- and photoluminescence of $CaSO_4$.

The temperatures at which TSL curves appear in $CaSO_4 - Dy$ irradiated with X-ray emissions correspond to the temperature dependence of the emission of the Dy^{3+} impurity at 2.56 eV, which arise during the recombination of an electron with a hole trapped by the Dy^{3+} mpurity. The emission intensity of the impurity 2.56 eV reflects the intensity of the appearance of the TSL peak.

The spectral composition of the TSL peak was not measured. Comparing the dependence of the Dy^{3+} impurity emission band with the intensity of the TSL peaks measured in the temperature range from 100 K to 450 K, one can see that the spectral composition of the TSL peak corresponds to the emission of the Dy^{3+} impurity.

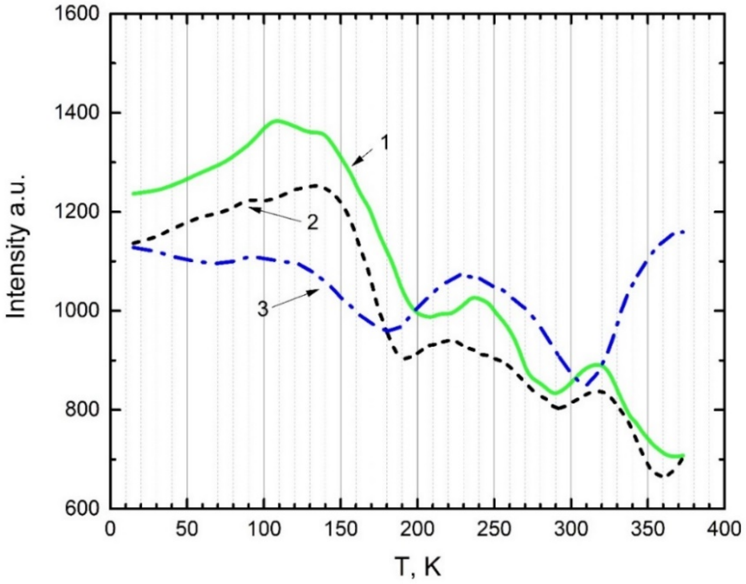

Figure 6. Temperature dependence (15 K–380 K) of luminescence (excited by 6.2 eV) of the main bands of $CaSO_4 - Dy$ at 3.1 eV (curve 1), 2.95 eV (curve 2), and 2.16 eV (curve 3).

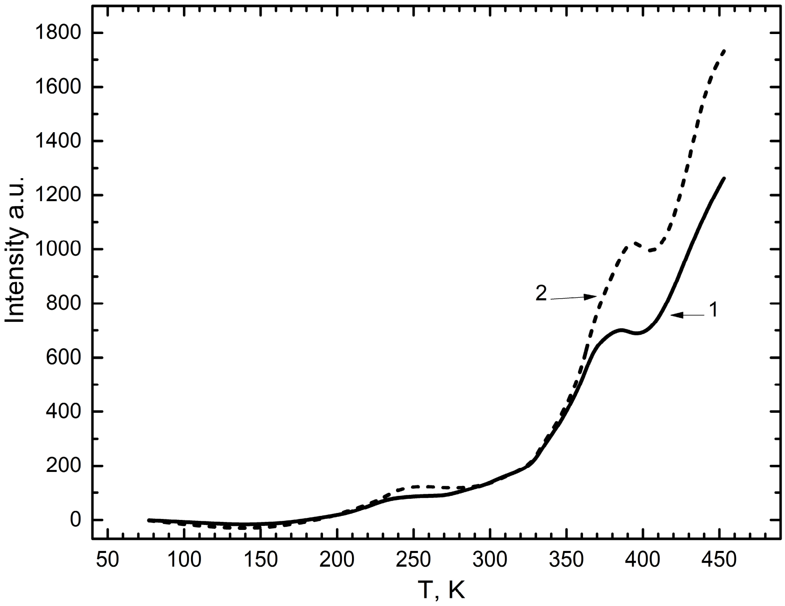

Figure 7. Thermally stimulated luminescence of $CaSO_4 - Dy$ after irradiation 5 min (curve 1) and 10 min with X-rays at a temperature of 80 K (curve 2).

4. Discussion

In irradiated $CaSO_4 - Dy$ sulfates, new combined radiative states at 2.95 and 3.1 eV are created with the participation of impurity and intrinsic radiative states. Previously, we showed that in the irradiated Na_2SO_4 at 80 K, a new emissive state is created at 3.0–3.1 eV [22]. The radiative state is excited at photon energies of 4.0 eV and 4.5 eV. It was assumed that these values correspond to the absorption and excitation of a recombination emission of 3.0–3.1 eV.

In the $CaSO_4 - Dy$ phosphor, new radiative states of 2.95 eV and 3.1 eV are created as a result of the transformation of impurity and intrinsic radiative states. The new radiative states at 2.95 and 3.1 eV and the impurity emissions of Dy^{3+} at 2.56 eV and 2.16 eV are excited by the photons with energies of 3.9–4.0 and 4.5–4.6 eV. At a liquid nitrogen temperature of 80 K, the intensity ratio of radiative states predominates in the direction of newly formed radiative states. The measurements of the temperature dependence show that at a certain temperature, the intensity ratio of the radiative states changes towards the impurity emission Dy^{3+}. It is assumed that at low temperatures, due to a change in the valence of the impurity $Dy^{3+} + e^{-} \rightarrow Dy^{2+}$, its intensity is suppressed.

In phosphates with double cations [16], it was shown that a change in valence occurs as a result of the charge transfer from the excited anionic complex to $O^{2-} - Dy^{3+}$ impurities. In our case, from the excited anionic complex SO_4^{2-}, as a result of the charge transfer to $O^{2-} - Dy^{3+}$ impurities, electronic trap centers of Dy^{2+} are formed, correlated with the localized holes $Dy^{2+} - SO_4^{-}$. By analogy, $O^{2-} - SO_4^{2-}$ are created in the intrinsic matrix as a result of the charge transfer from the excited anion to the neighboring anion complex. As a result, electronic trapping centers SO_4^{-3} are created, which correlate with a hole in the form of the radical SO_4^{-}.

At a low temperature, combined electronic states of 2.95 eV and 3.1 eV are formed. In the temperature range 150–200 K, the intensity of the combined radiative state decreases significantly. The intensity of the impurity emission Dy^{3+} of 2.16 eV at temperatures from 220 K to 250 K and 330–370 K increases. It is assumed that in the temperature range of 220–370 K, the electronic trapping centers are ionized according to the reaction $Dy^{2+} \rightarrow\ e^{-} \rightarrow Dy^{3+}$. The electron center of Dy^{2+} is ionized, and a free electron and Dy^{3+} are formed.

As a result of the recombination of an electron with a hole trapped by the ground state of the Dy^{3+} impurity, the fraction of the radiative state Dy^{2+}–SO_4^{-} in the combined radiative state decreases. The energy released during recombination process is transferred to the Dy^{3+} impurities. The process of energy transfer to the Dy^{3+} impurities occurs in this way. It seems to us that the emission arising as TSL, from which the absorbed dose is estimated, is associated with the annealing of accumulated holes localized near the impurities. We discussed one of the possible channels for the emergence of combined electronic radiative states. There is also another channel for the formation of a combined radiative electronic state. When they are irradiated with high-energy photons with an energy exceeding the band gap, free electron–hole pairs appear. When free electrons are trapped by impurities and anion complexes, impurity and intrinsic electron trapping centers arise, correlated with localized holes near the Dy^{3+} impurities. Both the processes of the formation of a combined radiative electronic state occur contemporaneously. At low photon energies, starting from 4–5 eV, combined radiative states are formed during the excitation of anionic complexes as a result of the charge transfer $O^{2-} - Dy^{3+}$ to the impurities and anionic radicals $O^{2-} - SO_4^{2-}$. This can be seen from Figure 5 (curve 3). The formation of a combined radiative electronic state at 2.95–3.1 eV occurs with an increasing intensity in the energy range from 6 eV to 8.4–9 eV (Figure 5).

First, combined radiative electronic states are formed via the first mechanism, and then by the second mechanism during the trapping of electrons and holes by the Dy^{3+} impurities or the anionic complex SO_4^{2-}.

The combined electronic radiative state is formed from the radiative electronic state of the impurity trapping centers of $Dy^{2+} - SO_4^{-}$ and intrinsic trapping centers $SO_4^{3-} - SO_4^{-}$. Intrinsic and impurity radiative states can be formed via the first mechanism as a result of the charge transfer from oxygen $O^{-2} - SO_4^{2-}$ and $O^{-2} - Dy^{3+}$ to the impurities.

These same radiative states can be created via the second mechanism. If the $CaSO_4 - Dy$ phosphor is excited at photon energies exceeding the band gap, then free electron–hole pairs are created in the matrix. The electrons can be trapped by the impurities Dy^{3+} and the anionic complex SO_4^{2-} via the reaction $Dy^{3+} + e^{-} \rightarrow Dy^{2+}$ and $SO_4^{2-} + e^{-} \rightarrow\ SO_4^{3-}$. Thus, the trapping centers $Dy^{2+} - SO_4^{-}$ and $SO_4^{3-} - SO_4^{-}$ are formed via the second mechanism during the trapping of electrons and holes.

5. Conclusions

In the irradiated phosphor $CaSO_4 - Dy$, as a result of the charge transfer from the excited state of the anion complex to the neighboring anion or Dy^{3+} impurities, combined emissive states are created at 2.95–3.1 eV.

Combined radiative states are formed from the electronic radiative states of the intrinsic trapping centers $SO_4^{3-} - SO_4^{-}$ and impurity trapping centers $Dy^{2+} - SO_4^{-}$ during the excitation of phosphors using ultraviolet rays.

Combined radiative states can be formed when the electrons and holes are trapped by the anionic complex and Dy^{3+} impurities when excited by photon energies exceeding the band gap.

By measuring the excitation spectra of the combined radiative state of 2.95 eV and 3.1 eV and impurity emissions of Dy^{3+} of 2.56 eV and 2.16 eV, it was shown that they are excited at photon energies of 3.9–4.0 eV and 4.5–4.6 eV.

Thermal excitation leads to the decay of a new combined state $Dy^{2+} - SO_4^{-}$ and $SO_4^{3-} - SO_4^{-}$ as a result of the ionization of SO_4^{3-} and Dy^{2+} centers. During the recombination of an electron with a hole trapped by the ground state of Dy^{3+}, energy is transferred to the Dy^{3+} impurities.

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