Electron-hole trapping centers in alkali metal sulfates with Dy^{3+} impurities

T.N. Nurakhmetov[1], T.T. Alibay[*,1], R.Z. Bakhtizin[2],
S. Pazylbek[3], A.Zh. Kainarbay[1], A.M. Zhunusbekov[1],
B.M. Sadykova[1], D.A. Tolekov[1], R.K. Shamieva[1],
A.S. Nurpeissov[1]

[1]L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

[2]Ufa University of Science and Technology, Ufa, Russia,

[3]Tashenov University, Shymkent, Kazakhstan

E-mail: temirulanalibay@gmail.com

The $Na_2SO_4 - Dy$ samples were obtained by slow evaporation method. The spectroscopic methods were used to study the mechanisms of formation of electron and hole trapping centers. Intrinsic recombination emission of 2.9–3.1 eV and impurity emission of 2.55 eV and 2.15 eV are excited at 4.0–4.5 eV. Intrinsic $SO_4^{3-} - SO_4^-$ and impurity $Dy^{2+} - SO_4^-$ trapping centers were revealed. The local levels corresponding between the electron and hole trapping center are 4.0–4.5 eV.

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

Introduction

Sodium sulfate (thenardite) Na_2SO_4 is a chemically very simple compound that has found many applications. Based on sodium sulfate with various impurities, phosphors and dosimetric materials with different characteristics, cathode-ray tubes, TV screens, etc. are being developed. The luminescence characteristics of

materials based on Na_2SO_4 are affected by the phase state of the matrix. It is known that Na_2SO_4 has five different polymorphs modifications depending on temperature [1]. The hexagonal modification Na_2SO_4-I (space group P63/mmc) is stable in the temperature range from $240°C$ to the melting point, which is $885°C$ [2]. After cooling from the melting point, the crystal changes from the I$\rightarrow$ II $\rightarrow$ III structure. Phase II can exist only in a narrow temperature range from $230°C$ to $229°C$, at which the third phase occurs. At room temperature, the III phase is metastable, while the V phase is stable. Upon reheating, a direct transition from phase III to phase I occurs. The stable phase V passes into phase I at $240°C$. Phase IV is poorly investigated [3]. According to Rasmussen et al. [4], phase II exists only in the temperature range of $8°C$ from 230 to $240°C$; at the same time, the I-II transition is reversible, while the II-III transition is irreversible; the structure of this phase is considered as pseudoorthohexagonal. The luminescence characteristics of Na_2SO_4

Materials for radiation dosimeters based on sulfates doped with rare earth elements have been widely studied due to their high luminescence sensitivity [5]. $Na_2SO_4 - Dy$ is a potential thermoluminescent material. In [2, 3, 6–13] works the luminescent characteristics of sodium sulfate doped with rare-earth ions were studied. In [14–15], the mechanisms of formation of electron-hole trapping centers in mixed and impurity sulfates of alkali metals were studied. And in works [16–20], intrinsic and impurity radiations in alkali sulfates were studied.

In sulfates of alkali and alkaline earth metals, long-wavelength recombination emission bands appear at 3.0–3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV [21–22]. These emission bands appear at photon energies from 6 eV to 12.4 eV, where free electron-hole pairs are created. The generated electron-hole pairs are trapped by impurities and create electron and hole trapping centers. Thus, the accumulated radiation defects are proportional to the absorbed dose by the crystals.

An unsolved issue is the study of the sensitizing effects of accumulated intrinsic and impurity electron and hole trapping centers during energy transfer to Dy^{3+} impurities during their recombination decay.

Materials and methods

$Na_2SO_4 - Dy$ microcrystals were obtained by slow evaporation method. Na_2SO_4 powder (purity 99 % Sigma Aldrich, CAS 7757-82-6) is dissolved in a stoichiometric volume in distilled and deionized water. Dysprosium oxide (Dy_2O_3) dissolved in highly concentrated sulfuric acid is added to the prepared solution. The resulting solution is stirred in a magnetic stirrer for 1 hour and dried in a muffle furnace at a temperature of $80°C$ for 8 hours in an air atmosphere. The resulting powder is annealed at a temperature of $400°C$ for 4 hours [7, 23]. The obtained samples are pressed in a copper substrate in the form of a tablet.

Spectrometric methods were used to study the emission and excitation spectra of $Na_2SO_4 - Dy$. The obtained results were measured on a Solar CM 2203 spectrofluorimeter. 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. Absorption

spectra were obtained on a Jasco V-770 spectrophotometer.

Results and discussion

The diffusion absorption spectrum for the $Na_2SO_4 - Dy^{3+}$ sample is shown in figure 1. The absorption spectrum coincides with the absorption spectra of sulfates of alkaline earth metals. Absorption peaks were found at 3.2 eV and 3.54 eV corresponding to the excitation of Dy^{3+}.

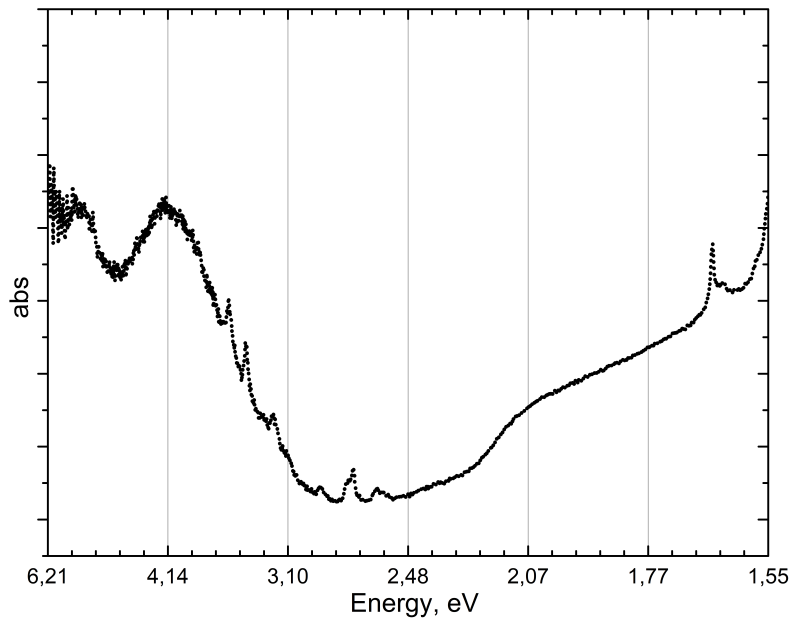Figure 1. Diffusion absorption spectrum of $Na_2SO_4 - Dy3+$ at 300 K.

Studies of nature of the creation of electron and hole trapping centers in pure sulfates of alkaline earth metals are described in detail in [15]. The influence of the Dy^{3+} impurity on electron-hole trapping centers is studied in this work. The emission spectra of the pressed tablets of $Na_2SO_4 - Dy^{3+}$ powder is shown in figure 2. When excited by photons of 6.2 eV, emissions of 2.2–2.4 eV and 2.9–3.1 eV appear. At room temperature (curve 2), characteristic emission bands corresponding to Dy^{3+} at 2.15 eV (575 nm) and 2.55 eV (485 nm) stand out noticeably.

The energies of local states of electron and hole trapping centers were studied on the excitation spectra (Figure 3). It can be seen that the recombination emission corresponding to the band at 3.1 eV is excited in the spectral region and 5.5–6.2 eV. The 5.5–6.2 eV region refers to the fundamental region of the matrix, where electron-hole pairs are created. In turn, the excitation bands ~ 4.0 eV, ~ 4.5 eV are associated with the trapping of electrons by the anionic complex SO_4^{2-}, and holes are localized in the form of the radical SO_4^-. These processes proceed according to the following reaction: $SO_4^{2-} + e^- \rightarrow SO_4^{3-}$. Accordingly, upon excitation of SO_4^{3-} and SO_4^-, tunneling recombination emission (2.9–3.1 eV) appears.

In the next stage, to study the emission bands of the impurity, the sample was excited by 3.5 eV and 3.2 eV (Figure 4). The energies 3.5 eV and 3.2 eV are
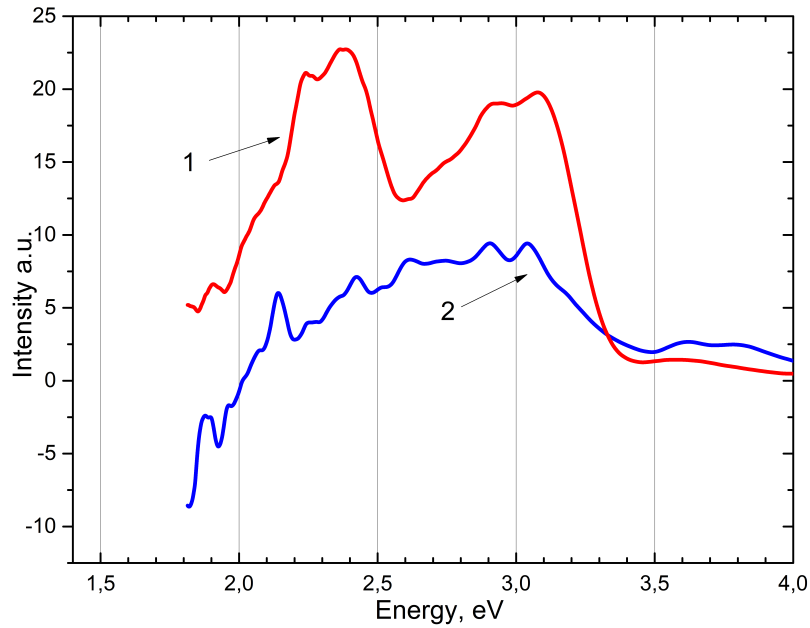
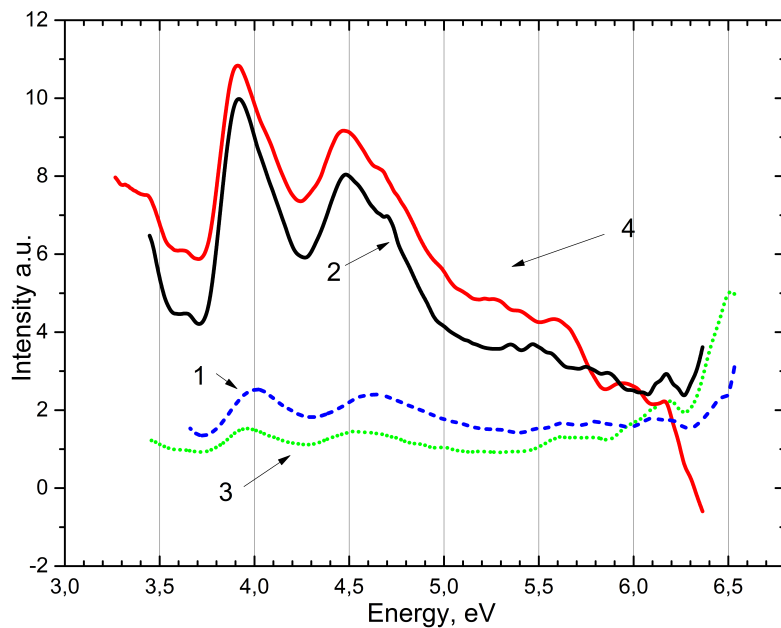Figure 2. Emission spectrum of $Na_2SO_4 - Dy^{3+}$: 1) upon excitation 6.2 eV at 80 K; 2) upon excitation 6.2 eV at 300 K.

Figure 3. Excitation spectrum of the $Na_2SO_4 - Dy^{3+}$ emission bands: 1) for 3.1 eV at 300 K; 2) for for 3.1 eV at 80 K; 3) for 2.9 eV at 300 K; 4) for 2.9 eV at 80 K.

excitation energy of Dy^{3+} emission centers. It was shown that impurity emission bands at 2.15 eV (575 nm) and 2.55 eV (485 nm), as well as intrinsic recombination emission bands (2.9–3.1 eV) are intensely revealed (curves 1 and 2).

The intense emission bands at 2.15 eV and 2.55 eV are associated with the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions, respectively. The less intense emission peak at 1.85 eV is explained by the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition. The intensity ratio of the emission band peaks may depend on the I-V polymorphs modifications of Na_2SO_4.

In the irradiated $Na_2SO_4 - Dy$ crystal, in addition to the emission center of the matrix at 3.1 eV, emission bands appear corresponding to impurity electron
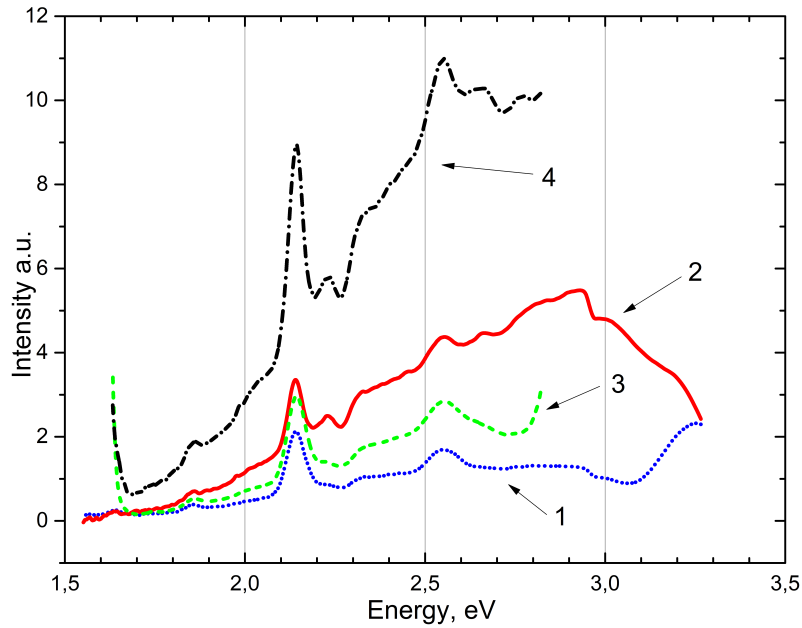
Figure 4. Emission spectrum of $Na_2SO_4 - Dy^{3+}$: 1) at 3.5 eV excitation at 300 K; 2) upon excitation 3.5 eV at 80 K; 3) upon excitation 3.2 eV at 80 K; 4) upon excitation 3.2 eV at 80 K.

and hole centers $Dy^{3+} - SO_4^-$, which, when electrons are captured by Dy^{3+} are formed into the 2.9 eV band.

To reveal the nature of impurity electron-hole centers, the emission spectra of impurity emission bands were studied (Figure 5). It can be seen that the impurity emission corresponding to the bands at 2.15 eV (575 nm) and 2.55 eV (485 nm) is excited in the spectral region 2.7–3.5 eV, 4.0–4.5 eV and 5, 8–6.2 eV.

Thus, the recombination emission of the matrix and the emission cneter of the impurity are excited in the same spectral energy intervals at 4.0–4.5 eV.
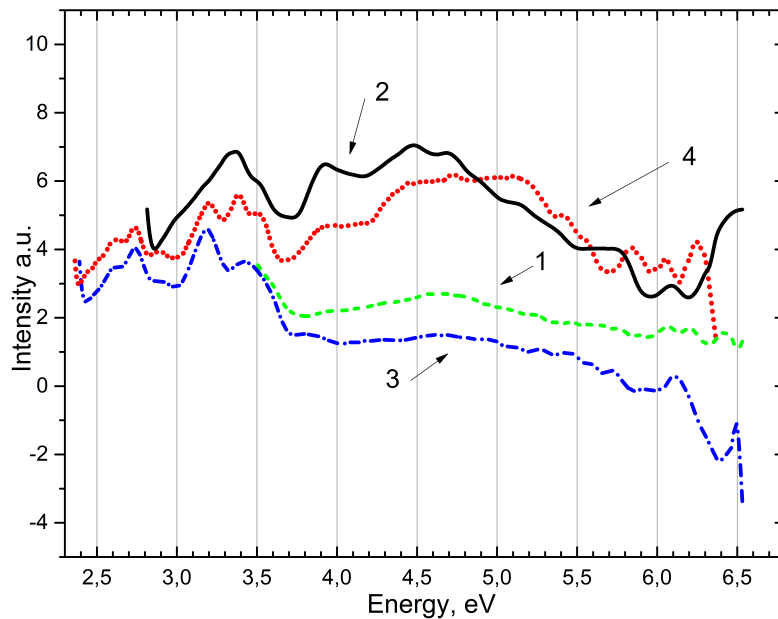

Figure 5. Excitation spectrum of the $Na_2SO_4 - Dy^{3+}$ emission bands: 1) for 2.55 eV at 300 K; 2) for for 2.55 eV at 80 K; 3) for 2.15 eV at 300 K; 4) for 2.15 eV at 80 K.

The proof of the difference between intrinsic (2.9–3.1 eV) and impurity 2.15

eV, 2.55 eV centers is the temperature dependence of the emission spectra when excited by 6.2 eV, which is shown in Figure 6.
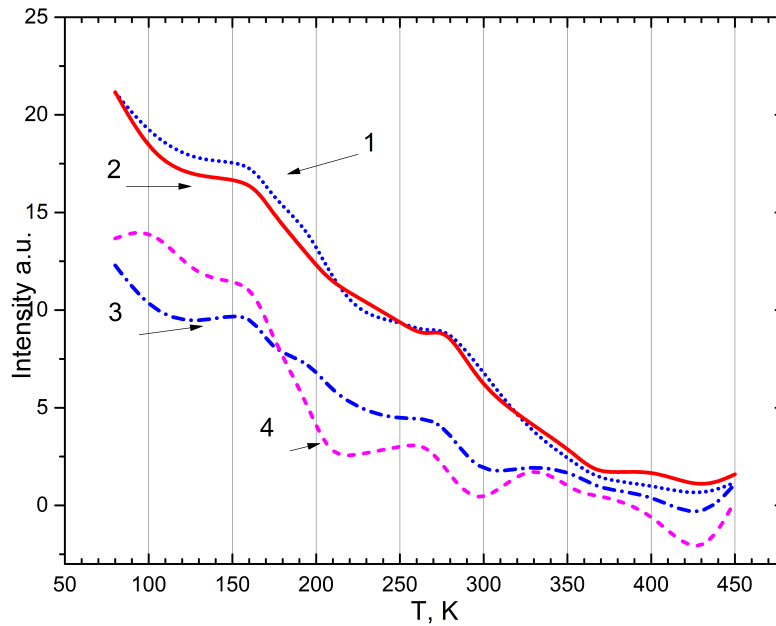

Figure 6. Temperature dependence of emission spectra upon excitation by 6.2 eV: 1) for 3.1 eV; 2) for 2.9 eV; 3) for 2.55 eV; 4) for 2.15 eV.

a) according to the spectra of the temperature dependence of the intrinsic emission bands 2.9–3.1 eV, one can see that it is stable up to a temperature of about 250 K (curve 1, 2) in $Na_2SO_4 - Dy^{3+}$. As the temperature increases, the electron delocalizes from the trapping center, and the intensity of the recombination emission band decreases to a minimum value.

b) the change in the emission intensity of the impurity (curves 3,4) is associated with the trapping center $Dy^{2+} - SO_4^-$ and occurs according to the reaction: $Dy^{2+} \rightarrow e^- \rightarrow Dy^{3+}$ - is restored impurity Dy^{3+}. The intensity of the emission band ~ 2.3 eV corresponding to the emission of Dy^{3+} increases.

In pure crystals, the appearance of recombination emission is associated with intrinsic electron-hole trapping centers $SO_4^{3-} - SO_4^-$. In doping crystals, along with intrinsic electron-hole trapping centers $SO_4^{3-} - SO_4^-$, impurity electron-hole trapping centers $Dy^{2+} - SO_4^-$ appear.

An impurity trapping center appears during the impurity's capture of created electrons. The experimentally determined energy between the local states of the capture centers $Dy^{2+} - SO_4^-$ is 4.0–4.5 eV. The same energy corresponds to intrinsic electron-hole trapping centers $SO_4^{3-} - SO_4^-$.

Conclusion

Intrinsic recombination emission of 2.9–3.1 eV and impurity emission of 2.55 eV and 2.15 eV are excited at 4.0–4.5 eV. Intrinsic $SO_4^{3-} - SO_4^-$ and impurities $Dy^{2+} - SO_4^-$ electron and hole trapping centers are excited in a close energy interval of 4.0–4.5 eV.

At low temperatures it predominantly emits Dy^{2+}, at room temperature it emits Dy^{3+}.

The experimental results suggests that in dosimetric crystals and phosphors with various impurities, intrinsic electron and hole trapping centers are formed near the impurity, upon recombination of which the impurity radiates.

Acknowledgments

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