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Recombination Luminescence and Electron–Hole Trapping Centers in $BaSO_4$-Bi Phosphor

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Abstract: This study of the $BaSO_4$-Bi phosphor has revealed that the accumulated energy after external optical excitation exhibits specific characteristics. During irradiation with photon energy exceeding the bandgap, in addition to the intrinsic ultraviolet emission of the Bi^{3+} ion, several recombination emissions and emission from the Bi^{2+} ion are observed. At 80 K, the recombination luminescence states and Bi^{2+} ion emission form combined electronic states. Upon heating of the $BaSO_4$-Bi phosphor, these combined electronic states decay into recombination emissions at 2.34 eV, 2.4 eV, 3.1 eV, and 2.7 eV, as well as Bi^{2+} ion emission at 1.97 eV. It is assumed that the 2.34 eV, 2.4 eV, and 3.1 eV emissions are associated with the recombination of electrons released from ionized SO_4^{3-} electron trapping centers with nonequivalently localized holes in the host lattice. The 2.7 eV emission is attributed to the decay of an exciton formed by electron–hole recombination near a Bi^{3+} ion.

Keywords: luminescence; electron–hole trapping centers; phosphor; phosphates; sulfates; visible emission

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1. Introduction

The interest in phosphors doped with Bi^{3+} and Bi^{2+} ions has significantly increased due to their potential practical applications in various fields, including scintillators, dosimeters, spectral converters for solar cells, and next-generation solid-state light sources such as white light-emitting diodes (WLEDs).

To enhance the practical efficiency of phosphors, it is essential to understand the physical processes occurring within them during the accumulation of electronic excitation energy following external stimulation, and their subsequent relaxation, culminating in energy transfer to emitters. Phosphates, garnets, and other materials activated by Bi^{3+} and Bi^{2+} ions have been studied for their luminescent properties.

In studies [1,2], the phosphor $BaSO_4 - Bi^{2+}$ was synthesized using a three-phase reaction method. It was shown that the emission at 1.97 eV is excited by the ultraviolet (at 4.77 eV), visible (at 2.74 eV), and red (at 2.09 eV) regions of the spectrum, corresponding to the transitions $2P_{1/2} \rightarrow 2S_{1/2}\,/2P_{1/2} \rightarrow 2P_{3/2}\,(1)$, $2P_{1/2} \rightarrow 2P_{3/2}\,(2)$. Similar excitation bands were also observed in the works of the authors of [3].

In study [4], the phosphor $CaSnO_3$-Bi^{2+}, which emits blue light, was synthesized using a high-temperature solid-state reaction method. A broad photoluminescence band (PL) with a maximum at 2.77 eV was observed at 300 K in the range of 3.76–1.82 eV upon excitation with photons of 4.73 eV and 4.02 eV and was associated with the $3P_1 \rightarrow 1S_0$ transition in the Bi^{3+} ion.

In the study [5], the nature of the short-wavelength emission bands at 5.12 eV, which are excited at 5.46 eV at 300 K, was investigated. The band is associated with the A band of the Bi^{3+} ion. Upon excitation with X-rays and photons in the vacuum ultraviolet region of the spectrum, orange-red emissions at 1.85 eV appear, which are attributed to the emission of Bi^{2+}. During excitation with photon energy exceeding the band gap, the generated electrons are trapped by Bi^{3+} ions, forming Bi^{2+} electron trapping centers. The emission at 1.85 eV is associated with electronic transitions $2P_{3/2} - 2P_{1/2}$ in the Bi^{2+} ion.

In the synthesized phosphor $CaAl_4O_7 - Bi$ reported by the authors of study [6], complex emissions associated with both Bi^{3+} and Bi^{2+} ions were observed. Broad emission bands under excitation with photons in the energy range of 4.59–3.35 eV exhibit emission bands at 3.35 eV, 2.55 eV, 2.48 eV, and 2.25 eV, appearing as several distinct emission bands. These emission bands are attributed to the electronic transition $3P_{0/1} \rightarrow 1S_0$ of the Bi^{3+} ion. In the investigated phosphor $CaAl_4O_7 - Bi$, emissions of the Bi^{2+} ion in the deep red and near-infrared regions were observed in the range of 1.72–1.46 eV, which were associated with the electronic transitions $2P_{3/2} \rightarrow 2P_{1/2}$. It was established that these emission bands are observed under radioluminescence.

In the study by the authors [7], the photoluminescent characteristics of $Gd_2O_3 - Bi$ were investigated in the temperature range of 4.2–800 K. It was found that the luminescence of $Bi^{3+}(S_6)$ and $Bi^{3+}(C_2)$ centers with different oxygen environments is due to the electronic transitions of the triplet excited state of the Bi^{3+} ion, corresponding to the transitions of the free Bi^{3+} ion. A narrow band with a maximum at 2.99 eV was observed, which is excited by photons with an energy of 3.32 eV, while a broad band with maxima at 2.26 eV is excited by photons with energies of 3.58 eV and 3.72 eV.

In the excited garnets $Y_3Al_5O_{12}$ and $Lu_3Al_5O_{12}$ doped with Bi^{3+} ions, two emission bands were observed:

- Ultraviolet emission arising from the electronic transitions from the triplet relaxed excited state of the Bi^{3+} ion to its ground state.
- Visible (VIS) emission attributed to an exciton localized around the Bi^{3+} ion.
- In $Y_3Al_5O_{12}$, upon photon excitation, ultraviolet emission with a maximum at 4.01 eV was observed, which is excited at 4.55 eV. This corresponds to the $3P_1 \leftrightarrows 1S_0$ electronic transitions of the free Bi^{3+} ion.
- Visible emission in the $Y_3Al_5O_{12} - Bi$ phosphor, upon excitation in the absorption band of Bi^{3+} ions (A band), appears at 2.64 eV. The position of the visible emission depends on the presence and location of nearby intrinsic and impurity lattice defects into which electrons transition. This emission is characterized as triplet luminescence of exciton-like nature [8–11].

In studies [10,12–14], based on the analysis of temperature dependence, luminescence decay times, and evaluation of the corresponding parameters of the relaxed excited state, the authors concluded that the ultraviolet emission band in $Lu_3Al_5O_{12} - Bi$ arises from the triplet RES of the Bi^{3+} ion and corresponds to the $3P_{1,0} \rightarrow 1S_0$ electronic transitions of the free Bi^{3+} ion at 3.9 eV. In contrast, the visible emission at 2.5 eV is of exciton-like origin and results from the decay of a triplet exciton state localized near the Bi^{3+} ion. According to the authors, the appearance of two different types of emission associated with Bi^{3+} is a characteristic feature of garnets doped with Bi^{3+} ions.

The presence of two bands in the spectral composition of thermally stimulated luminescence (TSL) indicates the existence of trapping centers of the types Bi^{4+} and $[O^{-} - Bi^{3+}]$.

In studies [10,11,15–19], the authors discuss the formation of two types of emission ultraviolet and visible in the phosphors $Y_3Ga_5O_{12} - Bi$ and $Gd_3Ga_5O_{12} - Bi$, exhibiting similar characteristic features.

From the brief literature review, it follows that the nature of the emissions in sulfates, phosphates, and garnets activated with Bi^{3+} ions has not been fully clarified. Ultraviolet, visible, orange-red, and infrared emissions have been observed. The appearance of visible emission remains a controversial and intriguing issue. It is believed to be associated with the decay of certain exciton-like formations near the Bi^{3+} impurity. In the present study, the visible recombination emissions in bismuth-doped phosphors are attributed to the formation and decay of a combined electronic state consisting of intrinsic and impurity electron trapping centers, localized just below the conduction band of the host matrix.

2. Objects and Methods of Research

The $\mathrm{BaSO_4}$ (99.99%, Sigma-Aldrich, Hamburg, Germany) phosphor doped with Bi was synthesized using a wet chemical method. High-purity starting powders of $\mathrm{CaSO_4}$ (99.99%, Sigma-Aldrich, Hamburg, Germany) and $\mathrm{Bi_2O_3}$ (99.99%, Sigma-Aldrich, Hamburg, Germany) were first mixed and dissolved in concentrated $\mathrm{H_2SO_4}$ (99.99%, Sigma-Aldrich, Hamburg, Germany). The resulting solution was evaporated at a high temperature of 250 °C. After the acid evaporation, the powder was washed with distilled water and dried at 70 °C. The final powders were calcined for 3 h at 800 °C and then pressed into tablets with a diameter of 8–9 mm and a thickness of 1–2 mm.

Characteristic

X-ray diffraction (XRD) analysis of the powder was conducted using Ni-filtered Cu-Kα radiation on a D6 PHASER diffractometer from Bruker AXS (Bruker, Madison, WI, USA), operating in the Bragg–Brentano (θ/2θ) geometry. The data were collected in the angle range (2θ) from 20° to 60°, with a step size of 0.02°, and a scanning speed of 1°/min. The diffraction peaks of the sample correspond to the standard reference card Entry #96-100-0038.

For measuring emission and excitation spectra in the spectral range from 1.5 to 6.2 eV, a Solar SM 2203 spectrofluorimeter (Solar LS, Minsk, Belarus) was used. Low-temperature measurements (77 K) were performed using a cryostat with a vacuum of 10^{-4} Pa, with cooling by liquid nitrogen.

3. Results

In the present study, the nature of ultraviolet emission and the formation of a combined electronic state in the $BaSO_4 - Bi$ phosphor are investigated. The decay of this state gives rise to visible recombination emission as well as emission corresponding to the Bi^{2+} ion.

The crystallinity and purity of the synthesized powders were evaluated using X-ray diffraction analysis. The X-ray diffraction pattern of the $BaSO_4 - Bi$ sample after annealing at 800 °C is shown in Figure 1. The diffraction peaks of the $BaSO_4 - Bi$ phosphor confirms the phase purity of the synthesized powder.

Figure 2 presents the emission spectra of the $\mathrm{BaSO_4}$-Bi phosphor irradiated with photons of 5.64 eV energy (curves 1 and 2) at 300 K and 77 K, respectively.

The figure shows the appearance of ultraviolet emission bands at 4.77 eV and 3.76 eV at 300 K, visible emissions at 2.75–2.72 eV and 2.4 eV, and red emissions at 2.34 eV, 1.97 eV, 1.79 eV, and 1.69 eV. Upon excitation at 77 K, the intensity of these emission bands increases by 2–3 times. Additionally, new visible emission bands appear at 3.18–3.1 eV and 2.92 eV, and the emission band at 627 nm becomes particularly prominent, with its intensity increasing several times.

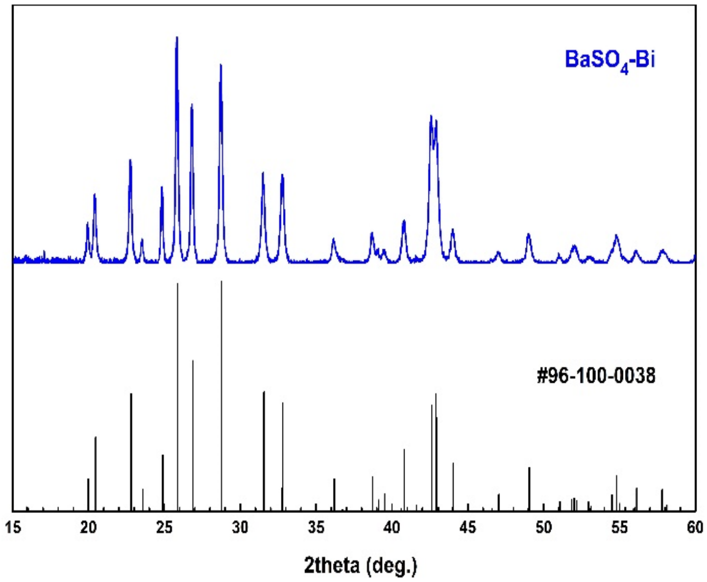


Figure 1. X-ray powder pattern of $BaSO_4 - Bi$.

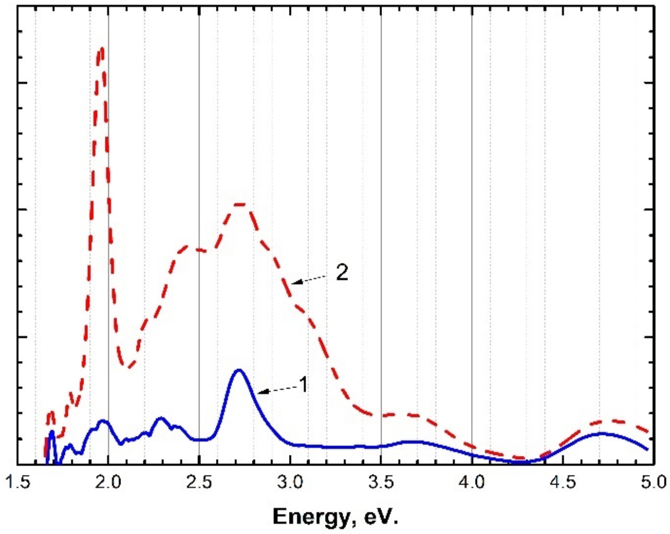


Figure 2. Emission spectra of the BaSO$_4$:Bi phosphor under excitation with photons of 5.64 eV energy (1—at 300 K, 2—at 77 K).

At the next stage, to determine the nature of the emissions in the visible spectral region at 3.18–3.1 eV (curves 1 and 1*), 2.95–2.92 eV (curves 2 and 2*), 2.75–2.72 eV (curves 3 and 3*), 2.4 eV (curves 4 and 4*), and 2.34 eV (curves 5 and 5*), excitation spectra of these recombination emission bands were measured at 300 K (curves 1*, 2*, 3*, 4*, and 5*) and at 77 K (curves 1, 2, 3, 4, and 5). From Figure 3 (curves 1–5), it is evident that the excitation spectra of all recombination bands are more clearly observed primarily at 77 K. All five recombination emission bands are excited by photon energies in the ranges of 3.85–3.9 eV and 4.5–4.53 eV.

The BaSO$_4$-Bi phosphor with induced trapping centers was excited by photons with energies of 3.85–3.9 eV and 4.5–4.53 eV at 77 K. In order to investigate the correlation between the recombination emission groups at 3.18–3.1 eV, 2.95–2.92 eV, 2.72 eV, 2.4 eV, and 2.34 eV and their excitation spectra at 3.85–3.9 eV and 4.5–4.53 eV, we assumed that the appearance of recombination or tunneling emissions must be associated with the formation of electron–hole trapping centers at 77 K during irradiation with photons whose energy exceeds the band gap, allowing the creation of new electron–hole trapping centers within the transparency region of the matrix.

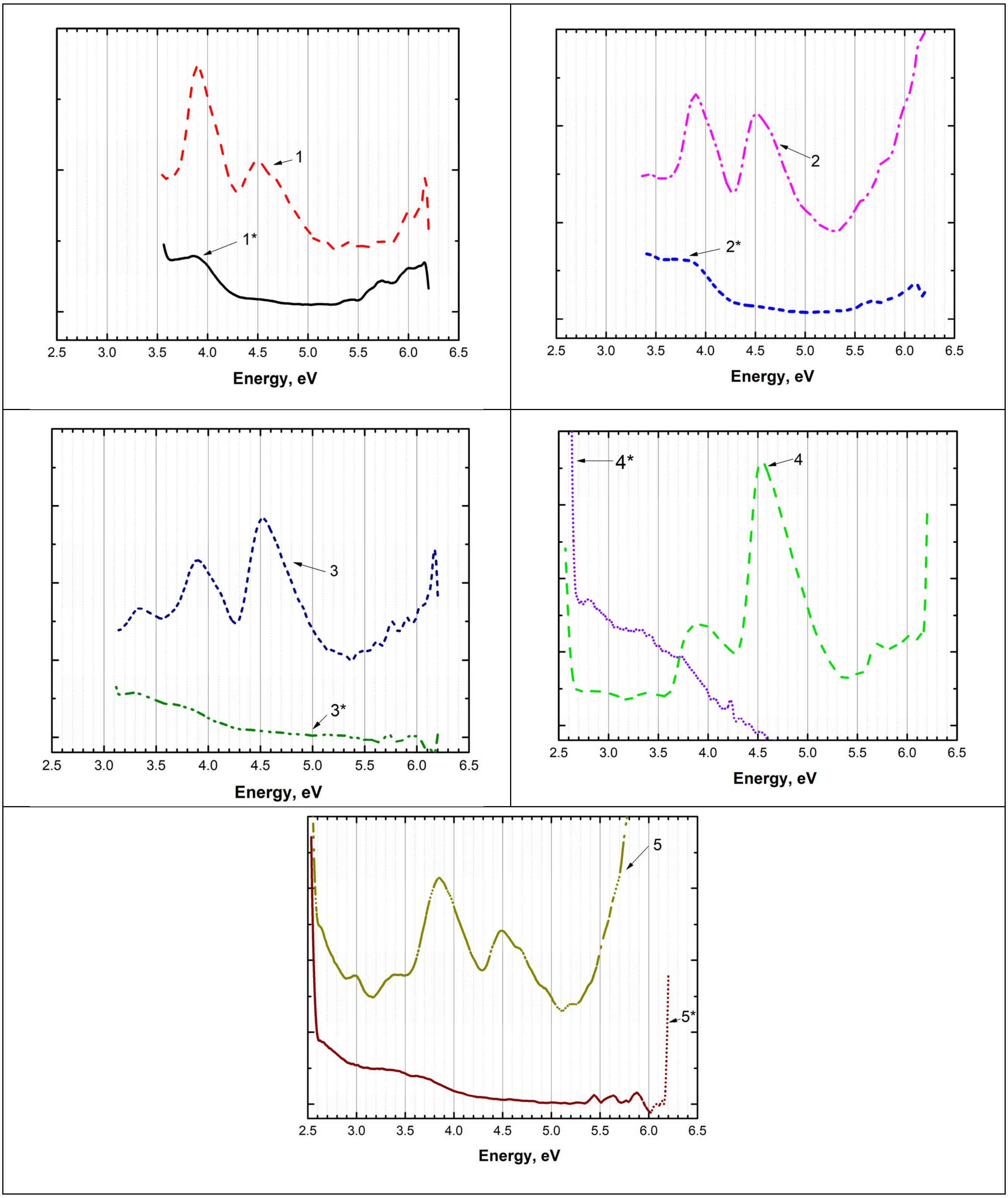


Figure 3. Excitation spectra of pre-irradiated $BaSO_4$-Bi phosphor: 1—for the emission band at 3.1 eV at 300 K (curve 1*) and at 77 K (curve 1); 2—for the emission band at 2.95 eV at 300 K (curve 2*) and at 77 K (curve 2); 3—for the emission band at 2.75 eV at 300 K (curve 3*) and at 77 K (curve 3); 4—for the emission band at 2.4 eV at 300 K (curve 4*) and at 77 K (curve 4); 5—for the emission band at 2.34 eV at 300 K (curve 5*) and at 77 K (curve 5).

Table 1 presents the measured band maximum energies and their corresponding full width at half maximum (FWHM) for the investigated curves. Specifically, the band maximum energies range from 4.0 eV to 6.20 eV. Notably, for the curve labeled 1*, the band maximum energy is 4.0 eV with a FWHM of 1.38 eV. For curves 1 and 2*, the band maximum energies are 6.17 eV and 6.20 eV with FWHMs of 2.05 eV and 1.55 eV, respectively. Several entries exhibit a significantly narrower FWHM, such as 0.16 eV for curve 2 and 0.03 eV for curve 4*. Curves 3, 4, and 5* display band maximum energies of 5.74 eV, 6.2 eV, and 6.2 eV, respectively.

Table 1. Band maximum energy and FWHM data of the curves.

Curve	Band Maximum Energy	FWHM
1*	4.0 eV	1.38 eV
1	6.17 eV	2.05 eV
2*	6.20 eV	1.55 eV
2	6.14 eV	0.16 eV
3*	6.17 eV	0.17 eV
3	5.74 eV	1.12 eV
4*	6.17 eV	0.03 eV
4	6.20 eV	1.14 eV
5*	6.20 eV	-
5	5.8 eV	-

Figure 4 shows the recombination or tunneling emissions of $BaSO_4$-Bi after excitation. As can be seen from the figure, at 77 K, all five groups of recombination emissions appear at 3.18–3.1 eV, 2.95–2.92 eV, 2.75–2.72 eV, 2.4 eV, and 2.34 eV. The same figure also displays the emissions corresponding to Bi^{2+} ions at 1.97 eV, indicating that, along with the recombination emissions, the intracenter emissions of Bi^{2+} ions are also excited.

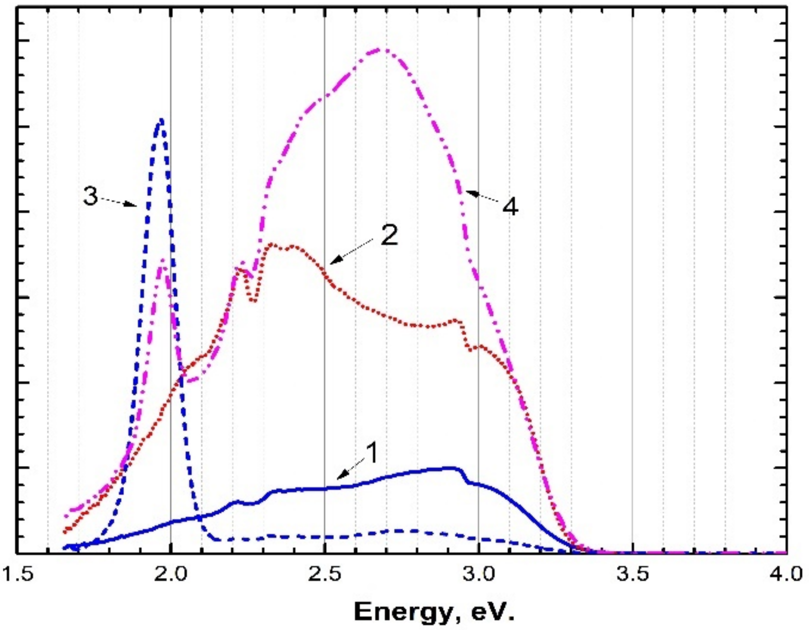


Figure 4. Emission spectra of the BaSO4-Bi phosphor under excitation with photons of 3.9 eV (1—at 300 K, 2—at 77 K) and with photons of 4.6 eV (3—at 300 K, 4—at 77 K).

In Figure 5, similar to other studies [5], short-wavelength ultraviolet emission bands are observed at 4.77 eV. These emission bands are associated with intracenter emissions of the Bi^{3+} ion, corresponding to the transitions $1S_0 \rightarrow 3P_{0.1}$.

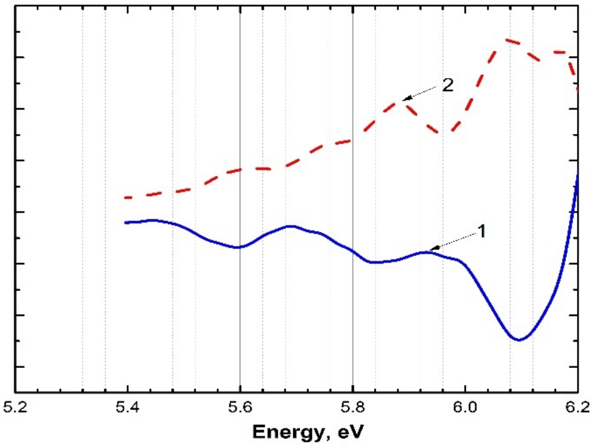


Figure 5. Excitation spectra of the pre-irradiated $\mathrm{BaSO_4}$-Bi phosphor for the emission band at 4.77 eV at 300 K (curve 1) and at 77 K (curve 2).

Figure 5 presents the excitation spectra of the ultraviolet emission bands at 4.77 eV. The figure shows that the ultraviolet emission band is excited in the spectral range from 5.71 eV to 6.2 eV in the form of several narrow excitation bands. These excitation bands are likely associated with intracenter transitions in the Bi^{3+} ion, corresponding to the $1S_0 \rightarrow 3P_{1,0}$, transitions. Additionally, the Bi^{3+} ion can also be excited within the fundamental absorption region of the matrix.

Figure 6 shows the excitation or formation spectra for the emission band corresponding to the Bi^{2+} ion in the spectral range from 2.1 eV to 6.2 eV at 300 K and 77 K. As seen from Figure 6, Bi^{2+} ions are formed as follows:

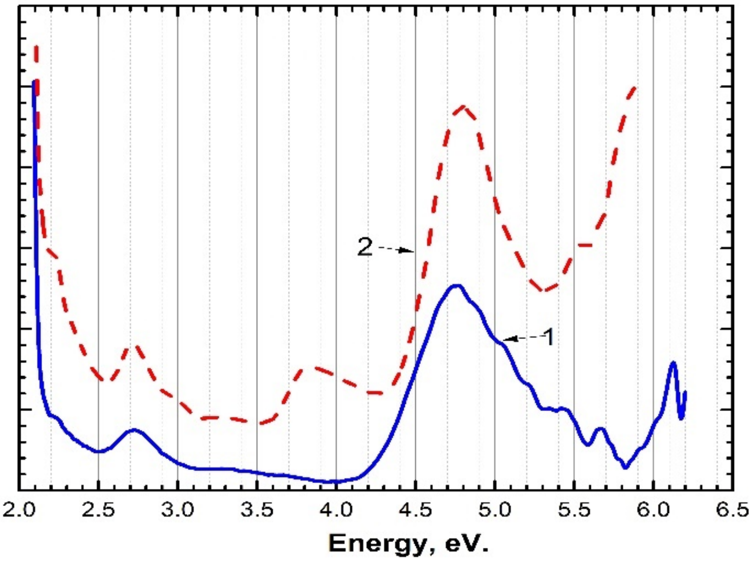
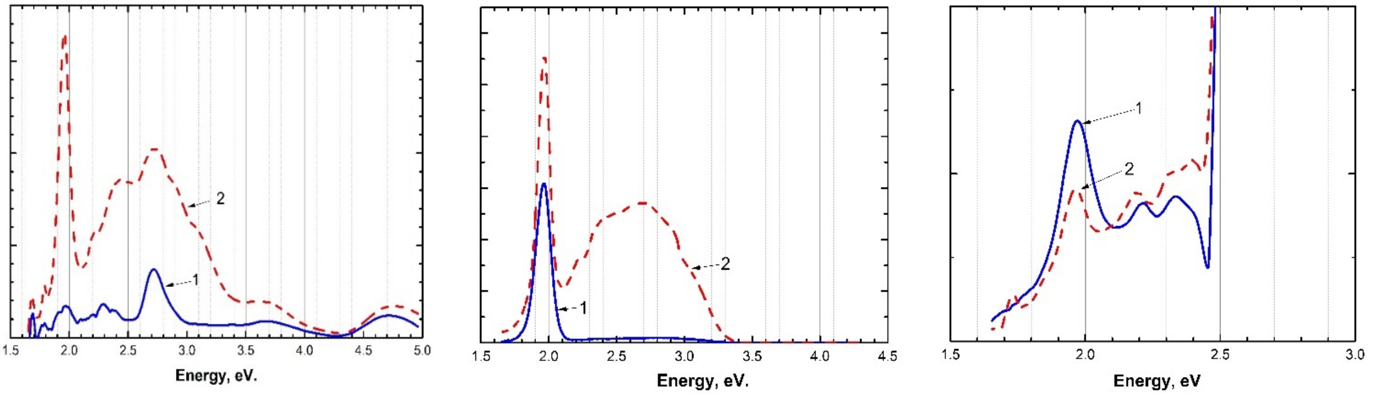


Figure 6. Excitation and formation spectra of the pre-irradiated $\mathrm{BaSO_4}$-Bi phosphor under excitation with photons of 1.96 eV (1—at 300 K, 2—at 77 K).

- In the spectral interval of 2.2–2.75 eV, where combined electronic states consisting of electron and hole trapping centers decay.
- At 3.76 eV and 4.77 eV, where SO_4^{2-} anions of the matrix are excited, and charge transfer occurs from the excited SO_4^{2-} anion to the impurity ($O^{2-} - Bi^{3+}$), resulting in the formation of Bi^{2+} ions.
- In the fundamental spectral region above 5.5 eV up to 6.2 eV, where electron–hole pairs are generated, new intrinsic and impurity-related electron trapping centers are created, which can lead to the formation of Bi^{2+} ions.

Figure 7 presents the emission spectra of the $BaSO_4$-Bi phosphor under excitation in the spectral region where the bands corresponding to Bi^{2+} ion emission are regenerated. As seen from Figure 7, Bi^{2+} ion emissions are formed at the following photon energies:



(**a**) (**b**) (**c**)

Figure 7. (**a**) Emission spectra of the $BaSO_4$-Bi phosphor under excitation with photons of 5.64 eV (1—at 300 K, 2—at 77 K). (**b**) Emission spectra of the $BaSO_4$-Bi phosphor under excitation with photons of 4.77 eV (1—at 300 K, 2—at 77 K). (**c**) Emission spectra of the $BaSO_4$-Bi phosphor under excitation with photons of 2.76 eV (1—at 300 K, 2—at 77 K).

- At 5.64 eV, where electron–hole pairs are generated; upon electron capture by Bi^{3+} ions, Bi^{2+} ions are formed according to the reaction $Bi^{3+} + e^- \rightarrow\ Bi^{2+}$.
- At 4.77 eV, where the intracenter excitation of the Bi^{3+} ion occurs, and Bi^{2+} ions may form as a result of charge transfer.
- At 2.76 eV, where recombination emissions are excited near the Bi^{3+} impurity centers.

Figure 8 shows the temperature dependence of the intensity for three recombination emission bands at 2.76 eV, 3.1 eV, and 2.94 eV, as well as the Bi^{2+} ion emission at 1.96 eV. The intensity of all three recombination emission bands decreases monotonically. However, two temperature intervals around 200 K and between 280 and 320 K exhibit a noticeable rise (flare up) in recombination emission.

We assume that the observed increase in recombination luminescence in these temperature ranges is associated with an increased concentration of recombining electrons released from trapping centers.

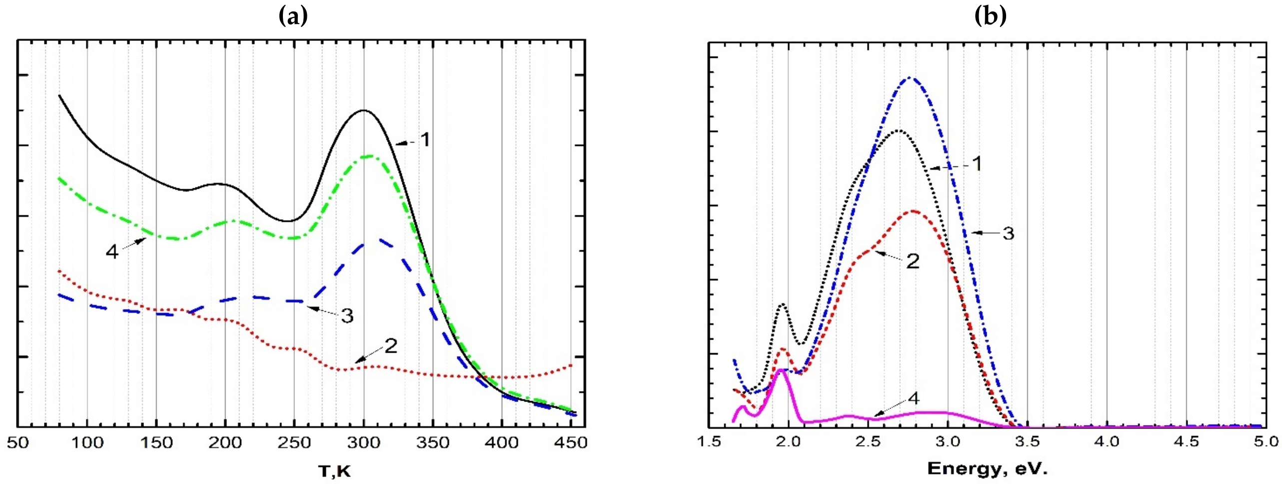


Figure 8. Temperature dependence of the recombination emission intensity of $BaSO_4$-Bi: (**a**) at 2.76 eV (1), 1.96 eV (2), 3.1 eV (3), 2.94 eV (4); (**b**) at 103 K (1), 250 K (2), 308 K (3), 453 K (4).

4. Discussion

The main objective of this study is to clarify the nature of intracenter emission and the formation of combined electronic states, the decay of which gives rise to visible recombination emissions as well as emission associated with Bi^{2+} ions. It was experimentally shown that four types of recombination emissions are generated in irradiated phosphors, which are associated with the decay of electron–hole trapping centers, along with emission at 1.97 eV corresponding to the intracenter transitions of the Bi^{2+} ion. In the work [20], it was shown that in $BaSO_4$ and $BaSO_4$-Mn, these recombination emissions are excited by photon energies of 4.0 and 4.5 eV and are associated with electron–hole trapping centers localized within the transparency region of the $BaSO_4$ matrix. Electron–hole trapping centers are formed through the localization of electrons on anionic complexes according to the reaction: $SO_4^{2-} + e^- \rightarrow SO_4^{3-}$. The holes are localized above the valence band [21]. Similarly, impurity electron trapping centers are formed when electrons are captured by Bi^{3+} ions according to the reaction: $Bi^{3+} + e^- \rightarrow Bi^{2+}$ as reported in [5].

Thus, from Figure 1, it can be seen that in the $BaSO_4$-Bi phosphor, upon irradiation with photons in the fundamental spectral region, four types of recombination emissions are generated at 2.95–2.92 eV, 2.75–2.72 eV, 2.4 eV, and 2.34 eV. The appearance of four types of recombination emissions is associated with the anisotropic properties of sulfates [22]. In sulfates, in three crystallographic directions, the hole represented in its ground state as an unpaired electron in the form of SO_4^- is localized at different energy levels above the valence band within the matrix [22]. During the recombination of a localized electron with such holes, recombination emissions are generated within a specific spectral energy interval.

Figure 2 shows that all four recombination emissions are excited by photons with energies of 3.85–3.9 eV and 4.5–4.53 eV.

To clarify the relationship between the four recombination emission groups and their excitation spectra, we assumed that the appearance of these emissions is linked to excitation by photons with energies of 3.85–3.9 eV and 4.5–4.53 eV. In other words, the phosphor with pre-induced trapping centers was re-excited by photons at 77 K. From the figure, it can be seen that these four recombination emission groups reappear in the emission spectrum after excitation. It is also noteworthy that emission corresponding to the Bi^{2+} ion is observed as well.

Thus, it should be particularly noted that upon excitation with photons of 4.5–4.53 eV in the phosphor containing pre-induced trapping centers, the groups of recombination emissions and emission from Bi^{2+} ions simultaneously appear.

To investigate the relationship between the recombination and ultraviolet intracenter emission of Bi^{3+} and the emission of Bi^{2+} ions, we measured the creation (or excitation) spectrum of the Bi^{2+} ion at 1.97 eV in the phosphor with pre-induced electron–hole trapping centers.

Bi^{2+} ions were shown to form in the following spectral regions:

- In the spectral interval of 2.2–2.75 eV, where combined electronic states decay.
- At 3.76 eV and 4.77 eV, where SO_4^{2-} anions are excited, and the charge transfer from the excited SO_4^{2-} anion to impurity centers ($O^{2-} - Bi^{3+}$) leads to the formation of Bi^{2+} ions.
- In the fundamental spectral region above 5.5 eV up to 6.2 eV, where electron–hole pairs are generated, forming combined electronic states that subsequently result in the formation of Bi^{2+} ions.

Thus, in irradiated $BaSO_4$-Bi, the interaction of a conduction band electron with Bi^{3+} ions or an electron formed as a result of the charge transfer from an excited SO_4^{2-} anion ($O^{2-} - Bi^{3+}$) to an impurity leads to the creation of Bi^{2+} impurity electron trapping centers. A similar mechanism [20] also results in the formation of intrinsic electron trapping centers via the reaction $SO_4^{2-} + e^- \rightarrow SO_4^{3-}$. The hole component of the electron–hole trapping centers is localized above the valence band within the transparency region of the matrix. We assume that the Bi^{2+} and SO_4^{3-} electron trapping centers form combined states just below the conduction band. Upon the decay of these combined states ($Bi^{2+} - SO_4^-$, $SO_4^{3-} - SO_4^-$), four groups of recombination emissions and the emission from Bi^{2+} ions are generated (as illustrated in Figures 3 and 9—the band diagram).

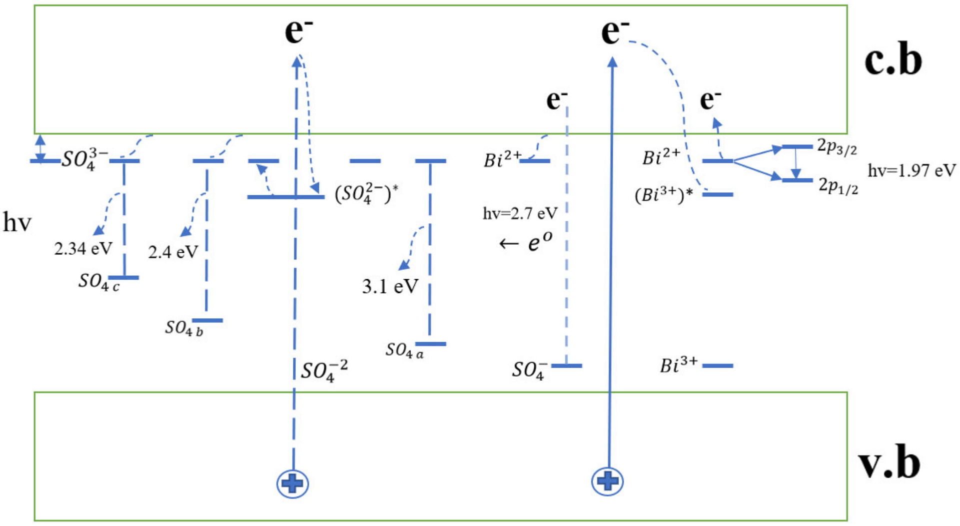


Figure 9. Band diagram of the formation and decay of the combined state in $BaSO_4 - Bi$.

Let us discuss the relationship between the ultraviolet and visible recombination emissions and the emission of Bi^{2+} ions observed in many compounds. In the work by the authors [8], it was shown that the ultraviolet emission in the phosphors $Y_3Al_5O_{12} - Bi$ and $Lu_3Al_5O_{12} - Bi$, occurring at 4.00 eV and 4.05 eV, respectively, at 85 K, is excited by photon energies of 4.5 eV, 5.3 eV and 4.55 eV, 5.3 eV. This UV emission is associated with Bi^{3+} ions and corresponds to the transitions $S_0 \leftrightharpoons 3P_{1,0}$.

In compounds such as phosphates, garnets, and sulfates [1–6], the mechanisms of formation and the electronic transitions in Bi^{2+} ions are well identified.

The emission band we observed at 1.97 eV in $BaSO_4$-Bi is, in our view, associated with Bi^{2+} ions. Based on the creation spectra of Bi^{2+} ion emission, we also identify spectral features corresponding to Bi^{3+} ions.

Only the excited Bi^{3+} ions can lead to the formation of Bi^{2+} through the charge transfer from an excited Bi^{3+} ion $\left(Bi^{3+}\right)^*$ to a neighboring Bi^{3+} ion.

Figure 5 shows that the emission of Bi^{2+} ions is formed in the excitation bands at 3.76 eV and 4.77 eV, which correspond to Bi^{3+} ions. The emissions at 3.76 eV and 4.77 eV are excited within the spectral range from 6.05 eV to 5.71 eV (as shown in Figure 5). Regarding the nature of the visible emission at 2.75–2.72 eV, the authors of works [8,10] attributed this emission to the excitons localized near Bi^{3+} impurity centers. It appears to us that the emission at 2.75 eV corresponds to the decay of a combined electronic state.

Figure 4 shows that upon the excitation of the combined electronic state with photons of 3.9–4.0 eV and 4.6 eV corresponding to their excitation and absorption, groups of recombination emissions and Bi^{2+} ion emissions are generated, which are components of the combined electronic state. The emission at 2.75 eV may arise during the ionization of intrinsic and impurity trapping centers via the processes: $SO_4^{3-} \rightarrow SO_4^{2-} + e^-$ and $Bi^{2+} \rightarrow Bi^{3+} + e^-$. The free electron then recombines with a hole located near a Bi^{3+} ion, forming a decaying excitonic state in the vicinity of the Bi^{3+} impurity. It is also possible that the energy from this process is transferred to impurity centers, resulting in the simultaneous observation of impurity-related emission from Bi^{3+} ions.

From the temperature dependence of the 2.75 eV emission, it is evident that, in the temperature range of 280–300 K, there is a flare up of emission corresponding to a recombination process. As seen in the temperature dependence presented in Figure 8b, in this same temperature interval (280–300 K), the intensity of the Bi^{2+} ion emission decreases ($Bi^{2+} \rightarrow Bi^{3+} + e^-$) while the 2.75 eV emission increases (curves 1 and 3 in Figure 8b).

Thus, the visible emission is likely associated with the radiative decay of a combined electronic state, which subsequently forms an excitonic state near a Bi^{3+} impurity. It is also possible that part of this energy is transferred to the Bi^{3+} impurity centers. Figure 9 illustrates the mechanism of combined state formation and its recombination decay in the band diagram.

During irradiation, electron–hole pairs are created. Electrons can be captured by anions of the matrix or by impurities. As a result, electron trapping centers are formed, such as $SO_4^{2-} + e^- \rightarrow SO_4^{3-}$ and $Bi^{3+} + e^- \rightarrow Bi^{2+}$. The holes become self-trapped above the valence band in the form of SO_4^-. According to the authors' calculations in [22], the radical SO_4^- with an unpaired electron in anisotropic crystals is localized in three arbitrary directions, a, b, and c, at different energy distances from the valence band maximum: $SO_{4.a}^-$, $SO_{4.b}^-$, and $SO_{4.c}^-$ (Figure 9). During the recombination of electrons ionized from electron trapping centers SO_4^{3-}, recombination emissions are created at 3.1 eV ($SO_{4.a}^-$), 2.4 eV ($SO_{4.b}^-$), and 2.34 eV ($SO_{4.c}^-$).

5. Conclusions

1. In the irradiated $BaSO_4$-Bi phosphor, when excited with photon energies exceeding the bandgap, not only are ultraviolet intracenter emissions from Bi^{3+} ions generated, but also several recombination emissions and emissions from Bi^{2+} ions.
2. The recombination luminescent states and the emission from Bi^{2+} ions together form a combined electronic state located below the conduction band of the matrix.
3. For the first time, it has been shown that excitation with photons of 4.5–4.6 eV leads to the formation of a combined state that produces both recombination emissions and Bi^{2+} ion emission, which are its constituent components.

4. The recombination emissions at 2.34 eV, 2.4 eV, and 3.1 eV are associated with the recombination of electrons with non-equivalently localized SO_4^- hole centers within the matrix lattice.
5. The visible emission at 2.7 eV is related to the decay of an exciton formed during the recombination of an electron with a hole localized near a Bi^{3+} impurity ion.

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