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LUMINESCENCE AND THE FORMATION OF ELECTRON-HOLE TRAPPING CENTERS IN CaSO4–Bi PHOSPHOR

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The mechanisms of creation of a new combined electron-emissive state at 2.95 eV, 3.1 eV, 2.6–2.7 eV and 2.25–2.4 eV, which is a pre-decay state for energy transfer from the matrix to the emitters, were investigated in the $CaSO_4 - Bi$ phosphor. Combined electron-emissive states are formed from intrinsic $SO_4^{3-} - SO_4^-$ and impurity $Bi^{2+} - SO_4^-$ electron-hole trapping centers according to studying via spectroscopic and thermal activation methods. In turn, the intrinsic and impurity electron-hole trapping centers are created during excitation of the anionic complex SO_4^{2-} as a result of charge transfer from the matrix to impurities ($O^{2-} - Bi^{3+}$) and neighboring anions ($O^{2-} - SO_4^{2-}$). It is shown that the energy accumulated in the intrinsic matrix during external irradiation in the form of a combined electron radiative state of SO_4^{3-} and Bi^{2+} decays as a result of the recombination process and is transferred to impurities.

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

INTRODUCTION

Luminescent properties of alkali halide, alkaline earth oxides, sulfates, phosphates, tungstates, borates and other compounds activated by Bi ions have been studied since the 1960s [1–13]. Phosphors activated by ions Bi^{3+}, Bi^{2+} are used in practice as sources of visible radiation. Phosphors with Bi^{2+} impurities are also used to obtain radiation in the infrared region of the spectrum, which are used in medicine for visualization of human tissue.

According to experimental data, Bi^{3+} and Bi^{2+} ions in phosphors emit in the ultraviolet, visible, and infrared regions of the spectrum. In the studies by authors [14–16], emissions were observed at 4.08–4.09 eV in $La_3Al_5O_{12} - Bi$, $Y_3Al_5O_{12} - Bi$ and $Lu_2SiO_5 - Bi$ at low temperatures T<100 K. The authors suggest that the appearance of ultraviolet emission is associated with the transition of an electron from a metastable 3p$_0$ level to the ground state. As the temperature increases T>100 K, this emission fades.

The authors in [17] observed ultraviolet emission spectra at 242 nm (5.1 eV) in the $YPO_4 - Bi$ phosphor at room temperature, excited by 227 nm (5.4 eV). The emission band at 242 nm (5.1 eV) is attributed to intra-center emission from the Bi^{3+} ion. Visible emission associated with the electronic transition 3p$_1$→1s$_0$ in the Bi^{3+} ion has been investigated in the works of authors [14–16] across various phosphors.

In the work [18], it was shown that the appearance of a broad emission band at 448 nm (2.75 eV) in the $CaSnO_3 - Bi^{3+}$ phosphor is associated with the 3p$_1$→1s$_0$ transition in Bi^{3+}, which is excited by photon energies of 262 nm and 308 nm (4.02 eV). The authors suggest that the 448 nm (2.75 eV) emission is excited as a result of charge transfer from the matrix ($O^{2-} - Bi^{3+}$) to the Bi^{3+} centers.

Visible emissions at 377 nm (3.3 eV) and 390 nm (3.2 eV) were observed in the $CaO - Bi$ phosphor when excited by of 300 nm (4.1 eV) and 354 nm (3.5 eV), as reported by the authors in [19]. Numerous experimental studies have demonstrated that the ground state of the Bi^{3+} ion is located above the valence band within the transparency region of the phosphor matrix at the 1s$_0$ level, while the excited state is 6s^{1}6p^1.

Absorption bands associated with transitions 1s$_0$3p$_1$ and 1s$_0$1p$_1$ have been identified in the spectral range of 250–400 nm (3.1–4.9 eV). Intra-center emission of Bi^{3+} arises from the decay of the excited 3p$_0$ and 3p$_1$ states, which may be mixed depending on the matrix temperature.

In contrast to Bi^{3+} emission, the luminescence of Bi^{2+} (with the 6s^{2}6p^{1}configuration) is less studied due to its instability. Bi^{2+} luminescence is attributed to an intra-configurational p-p transition, which is forbidden by parity rules. Due to spin-orbit coupling in the electronic configuration of the Bi^{2+} ion, with a configuration of 6s^{2}6p^1, the Bi^{2+} ion splits into a ground state 2p$_{1/2}$ and an excited state 2p$_{3/2}$.

The study by the authors [20] demonstrated that the luminescent material $CaAl_4O_4 - Bi$ exhibits emission from Bi^{2+} in the deep red and near-infrared regions (720–850 nm), associated with the 2p$_{3/2}$→2p$_{1/2}$ transition. It was established that this luminescence is dominant in radioluminescence and thermoluminescence spectra. Such phosphors are widely used in biomedicine.

In the phosphor $CaF_2 - Bi$, photoluminescence has been observed in the energy range of 380–800 nm, corresponding to the 2p$_{3/2}$→2p$_{1/3}$ transition, which is excited by 266 nm [21].

The work by the authors [22] identified infrared emissions at 627 nm (1.9 eV), which are excited in the spectral regions of 260 nm (4.7 eV), 452 nm (2.75 eV), and 592 nm (2.09 eV). It is suggested that in $BaSO_4$, the Bi^{2+} ion is responsible for the emission at 627 nm (1.9 eV), which is excited by the transition of electrons from the ground state $2p_{1/2}\rightarrow 2s_{1/2}$ (260 nm) to the excited state $2p_{1/2}\rightarrow 2p_{3/2}$ (452 nm).

Thus, in phosphors activated by Bi ions, excitation by ionizing radiation leads to emissions in the ultraviolet, visible, and infrared spectral regions. The resulting energy of intrinsic electronic excitations is transformed to the emitter through the mechanisms described above. In the present work, the possibility of transforming the energy of electronic excitations to emitters through the formation of intrinsic and impurity trapping centers is considered in the $CaSO_4 - Bi$ phosphor.

METHODS

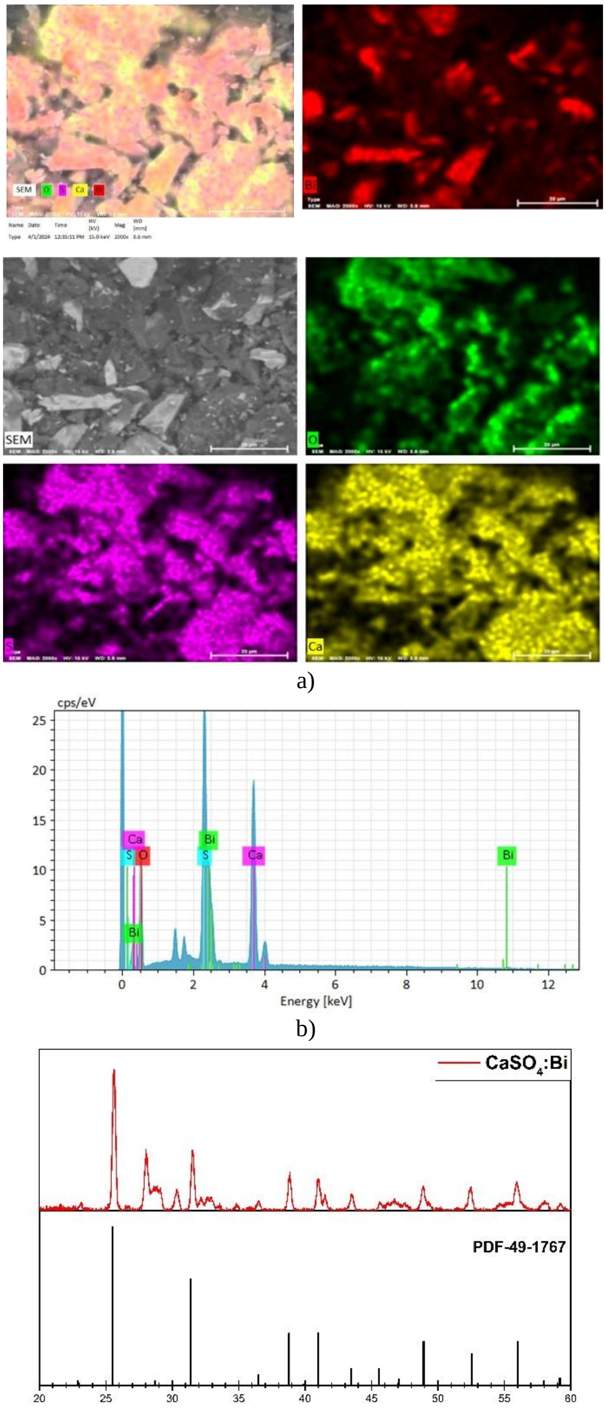
The samples under investigation were prepared using a wet chemical synthesis method. High-purity powders of $CaSO_4$ and Bi_2O_3 were used in the synthesis process. Initially, $CaSO_4$ and Bi_2O_3 (with a 0.2% g/mol impurity concentration) were thoroughly mixed and dissolved in concentrated H_2SO_4 (3–4 drops).The resulting solution was then evaporated at a temperature of 250 °C. After the evaporation of the acid, the powder was washed with double distilled water and subsequently dried at 70 °C. The final powders were pressed into tablets with a diameter of 8–9 mm and a thickness of 1–2 mm.

The structure and purity of the samples were monitored using microscopic and energy-dispersive elemental analysis techniques. The analyses were conducted using an energy-dispersive X-ray spectrometer (EDS) and a scanning electron microscope (SEM). Specifically, a Hitachi TM4000Plus II SEM was employed, paired with a BRUKER EDS system. The SEM operated at an accelerating voltage of 10 kV. X-ray diffraction (XRD) analysis was performed using a D6 PHASER diffractometer (BRUKER).

Photoluminescence characteristics were measured with a Solar SM2203 spectrofluorimeter (Belarus) which has a spectral resolution of 0.3 nm. Low-temperature investigations (down to 77 K) and temperature-dependent studies were conducted using a thermoactivation setup, which included a cryostat with three quartz windows and one beryllium oxide window, monochromators for excitation and detection (from OKB "Spektr MDR-41" and MDR-23U, respectively), and a photomultiplier tube (Hamamatsu 1P28). The system was evacuated to a pressure of 10^{-2} Pa and cooled using liquid nitrogen. To account for potential measurement uncertainties, the spectral resolution of the system was taken into consideration when analyzing the emission linewidths and peak positions. The uncertainty in wavelength calibration was estimated to be within ±0.5 nm, and the signal-to-noise ratio was optimized by adjusting the slit widths and integration times. Additionally, background signal subtraction and dark noise corrections were performed to enhance the accuracy and reliability of the obtained spectra.

RESULTS

SEM images reveal particles of varying sizes in the $CaSO_4 - Bi$ powder. The overall image indicates the presence of large particles ranging from 9 to 18 μm and smaller particles ranging from 0.1 to 2 μm (Figure 1).



a)

b)

c)

Figure 1. SEM (a), EDS (b) and XRD (c) images of the $CaSO_4 - Bi$ phosphor

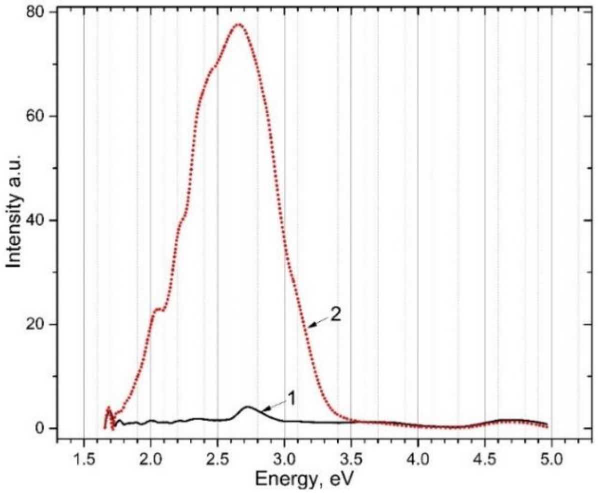
The images also show that the impurity components of the powder appear brighter than the main substance. This difference in brightness is due to the difference in atomic numbers between the Bi impurities and the main $CaSO_4$ matrix.

Elemental analysis (EDS) confirmed that the sample consists primarily of the $CaSO_4$ matrix and bismuth impurities, with no other uncontrolled impurities present. Additionally, the XRD pattern corresponds well to the reference PDF 49-1762, confirming the presence of the $CaSO_4$ phase. The structural analysis further indicates that the sample crystallizes in both tetragonal (P-421c, a = 7.7314 Å, c = 5.6361 Å) and orthorhombic (Bbmm, a = 6.2300 Å, b = 6.9800 Å, c = 6.9700 Å) modifications, with a calculated density of 2.980 g/cm³.

Next step is investigating of the optical properties of the irradiated $CaSO_4-Bi$ phosphor.

In the phosphor irradiated with photons possessing energies greater than the [23] bandgap of $CaSO_4-Bi$, as in other Bi -activated compounds, ultraviolet, visible, and orange-red emissions are expected to appear.

Figure 2 presents the emission spectra of the $CaSO_4-Bi$ phosphor irradiated with an energy of 5.64 eV at temperatures of 300 K and 77 K.



1 – at 300 K; 2 – at 77 K

Figure 2. Emission spectra of the $CaSO_4-Bi$ phosphor irradiated with an energy of 5.64 eV

From the figure, it can be observed that ultraviolet emissions associated with Bi^{3+} impurities appear in the 4.65–4.75 eV range, visible emissions at 2.7 eV, and red-orange emissions at 1.9–2.03 eV. Similar emission bands have been identified in the works of authors [17, 18, 21–22]. The ultraviolet $CaSO_4-Bi$ bands, which are detected at low temperatures T<100 K, are associated with electronic transitions from hybrid states $3p_1$ and $3p_0$ to the ground state $^1s_0$. The emission bands at 2.7 eV correspond to Bi^{3+} emissions, arising from the $3p_1 \rightarrow {}^1s_0$ electron transition.

The red-orange emission band around 1.9–2.03 eV is attributed to Bi^{2+} ions.

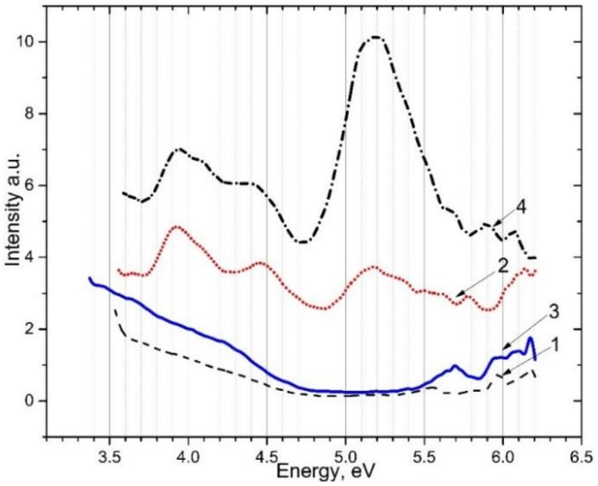
At a temperature of 77 K, after irradiation with photons of the same energy, in addition to the main intracenter emissions, new groups of emission bands appear at 3.1 eV, 2.9 eV, 2.7 eV, 2.6 eV, 2.4 eV, 2.2 eV, and 2.03 eV, 1.92 eV, 1.89 eV. These emission bands can be divided into three groups: the first group, which is the most intense, appears at 2.9–3.1 eV; the second group of bands appears at 2.6–2.7 eV; and the third group appears at 2.2–2.4 eV. These groups of bands have been discussed in the works of authors [23–26] and are associated with recombination emissions that occur due to the recombination of electrons with non-equivalently located localized holes SO_4^- in three crystallographic directions. These recombination emissions correspond to electron-hole trapping centers within the bandgap of the matrix. The emission bands at 1.9–2.03 eV, as suggested by the authors [22], are likely related to intracenter emission of Bi^{2+} ions in the $BaSO_4$ matrix.

The appearance of new recombination emission bands is likely related to the interaction of impurities with intrinsic electronic excitations, specifically electron-hole pairs, which arise as a result of charge transfer from an excited anion to impurities [$O^{2-} \rightarrow Bi^{3+}$] and to neighboring anions in the matrix [$O^{2-} \rightarrow SO_4^{2-}$] [18]. This charge transfer process leads to the formation of electron trapping centers such as Bi^{2+} and SO_4^{3-}. It is well known that in ionic crystals with introduced impurities, electron-hole pairs are more efficiently excited near the impurities. During the excitation of the matrix, a 2p oxygen electron from the valence band transitions to the conduction band and is captured by Bi^{3+} impurities, forming the Bi^{2+} ion. The hole generated near the impurity becomes localized above the valence band in the vicinity of the $Bi^{3+}-SO_4^-$ complex.

At the final stage, as a result of these relaxation processes, intrinsic $Bi^{2+}-SO_4^-$ and impurity $SO_4^{3-}-SO_4^-$ electron-hole trapping centers are formed. The decay of these trapping centers in the matrix results in three types of recombination emissions at 2.9–3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV [23–26]. In order to clarify the nature of these recombination or tunneling emissions, the excitation spectrum of these emissions were measured.

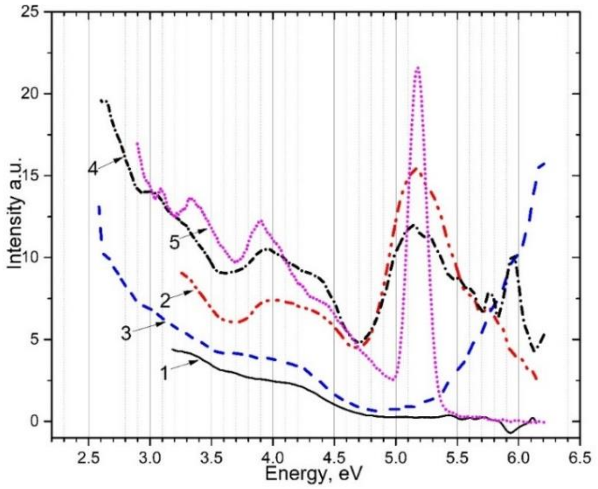
Figure 3 shows the excitation spectra of the newly formed emission bands at 3.1 eV and 2.9 eV at 77 K (curves 2 and 4, respectively). The figure indicates that these bands are excited by photons with energies of 3.95–4.1 eV, 4.4–4.5 eV, 5.15–5.2 eV, as well as above 5.9–6.18 eV.

Figure 4 presents the excitation spectra for the newly formed recombination emission bands in the second and third groups at 2.6–2.7 eV and 2.25–2.4 eV at 77 K (curves 2 and 4, respectively). It is evident that these groups of bands are also excited by photons of 3.0–3.35 eV, 3.95–4.1 eV, 4.4–4.5 eV, and more intensely at 5.15–5.2 eV.



1 – at 3.1 eV at 300 K; 2 – at 3.1 eV at 77 K;
3 – at 2.95 eV at 300 K; 4 – at 2.95 eV at 77 K

Figure 3. Excitation spectra of $CaSO_4 - Bi$ *at 3.1 eV and 2.9 eV*



1 – at 2.6-2.7 eV at 300 K; 2 – at 2.6-2.7 eV at 77 K;
3 – at 2.25-2.4 eV at 300 K; 4 – at 2.25-2.4 eV at 77 K;
5 – excitation spectrum of *CaSO4* at 2.75 eV at 77 K

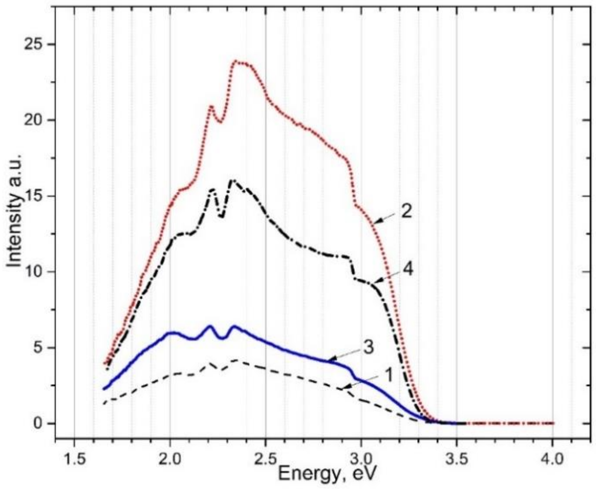
Figure 4. Excitation spectra of $CaSO_4 - Bi$ *at 2.6-2.7 eV and 2.25-2.4 eV*

In the same Figure **4,** the excitation spectra of the presumed intracenter emission at 2.75 eV at 77 K (curve 5) are also shown. It can be observed that this emission band is effectively excited by photon energies of 5.15–5.2 eV, as well as by 3.95–4.1 eV and 4.4–4.5 eV.

To investigate the interaction between the two groups of recombination emissions and the excitation spectrum at 3.95–4.1 eV and 4.4–4.5 eV at 77 K, it is hypothesized that the appearance of recombination or tunneling emissions is likely connected to the formation of electron-hole trapping centers in $CaSO_4 - Bi$. These centers are formed during irradiation with photons whose energy exceeds the bandgap, leading to the creation of new electron-hole trapping centers.

The $CaSO_4 - Bi$ phosphor with induced trapping centers was re-excited by photons with energies of 3.95–4.1 eV and 4.4–4.5 eV at 77 K, resulting in the appearance of recombination emissions.

Figure 5 shows the recombination or tunneling emissions of $CaSO_4 - Bi$.



1 – at 4.4–4.5 eV at 300 K; 2 – at 4.4–4.5 eV at 77 K;
3 – at 3.95–4.1 eV at 300 K; 4 – at 3.95–4.1 eV at 77 K

Figure 5. Emission spectra of $CaSO_4 - Bi$ *irradiated with photon energies of 4.4–4.5 eV and 3.95–4.1 eV*

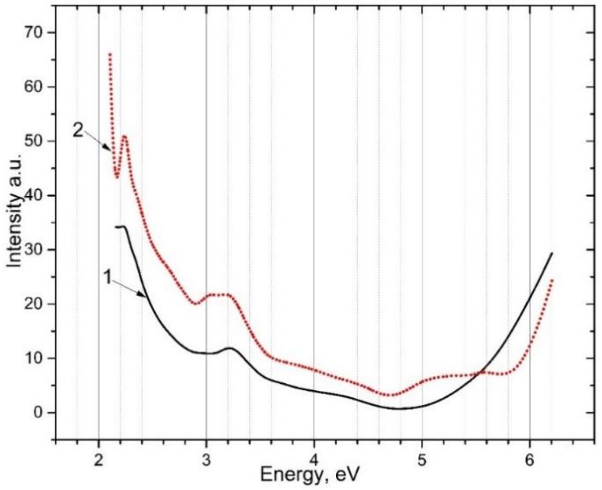
From Figure 5 (curves 2 and 4), it is evident that at 77 K, emission bands appear at 2.95–3.1 eV, 2.6–2.7 eV, and 2.25–2.4 eV. Additionally, in the same figure, emissions corresponding to Bi^{2+} ions are observed at 2.03–1.8 eV, which are excited by photons with energies of 3.95–4.1 eV and 4.4–4.5 eV.

It is also important to note that the bands at 2.7–2.75 eV, corresponding to the intracenter emission of Bi^{3+}, are excited at these energies (curve 5).

Figure 6 presents the excitation spectra for the emission bands at 2.03–1.9 eV corresponding to Bi^{2+} ions in the $CaSO_4 - Bi$ phosphor. From the figure, it is clear that these bands are excited by photon energies of 2.2–2.4 eV, 2.6–2.75 eV, 2.95–3.1 eV, and above 5.1–6.2 eV.

To clarify the nature of the new recombination emissions, the intensity of these emissions was measured as a function of temperature (77–450 K) under excitation by photons with an energy of 5.64 eV. This energy was found to be optimal for generating all observed emission bands.

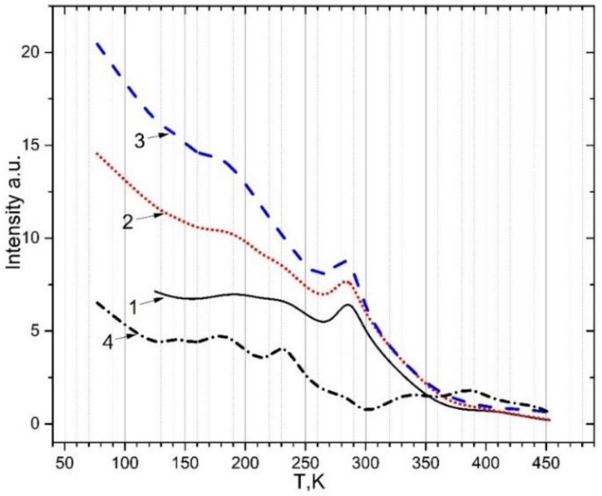
Figure 7 shows the temperature dependence of the intensity of the main recombination emission bands at 3.1 eV and 2.9 eV, as well as the intracenter emissions of Bi^{3+} and Bi^{2+} impurities at 2.75 eV and 1.9 eV, in the $CaSO_4 - Bi$ phosphor. The figure indicates that the intensity of the recombination emissions at 3.1 eV and 2.95 eV, as well as the intracenter emissions at 2.75 eV and 1.9 eV, gradually decreases over the temperature range from 100 K to 250 K.



1 – at 300 K; 2 – at 77 K

Figure 6. Excitation spectra of $CaSO_4-Bi$ *at 2.03–1.9 eV*

In the temperature range of 250–330 K, the emissions at 3.1 eV, 2.95 eV, and 2.75 eV exhibit a marked increase in intensity before monotonically decreasing to minimal levels. The observed increase in emission intensity is likely associated with an intense process of emission band decay.



1 – at 3.1 eV; 2 – at 2.95 eV; 3 – at 2.75 eV; 4 – at 1.9 eV

Figure 7. Temperature dependence in the $CaSO_4-Bi$ *phosphor*

DISCUSSION

The primary objective of this study is to establish the regularity of energy transfer from the matrix to the emitters, specifically demonstrating that energy transfer occurs through the formation of intrinsic and impurity electron-hole trapping centers. Based on the experimental data obtained, it is hypothesized that the new groups of recombination emission bands at 3.1 eV, 2.95 eV, 2.6–2.7 eV, and 2.2–2.4 eV are generated upon irradiation with photons whose energy exceeds the bandgap of the matrix, resulting in the creation of electron-hole pairs. The trapping centers that generate emissive electronic states are formed when free electrons are captured by impurities or anionic complexes, according to the reactions $Bi^{3+}+e^{-}\rightarrow Bi^{2+}$ [17, 19, 22] and $SO_4^{2-}+e^{-}\rightarrow SO_4^{3-}$ $[27]$. These electron trapping centers, Bi^{2+} and SO_4^{3-}, can be created as a result of charge transfer from the excited anionic complex SO_4^{2-} to impurities such as Bi^{3+} or to anions such as , following the reactions ($O^{2-}-Bi^{3+}$) or ($O^{2-}-SO_4^{2-}SO_4^{2-}$).

The hole component formed during the transition of an electron to the conduction band is expected to localize above the valence band as a radical, SO_4^{-}.

Thus, the created electron trapping centers form, with their complementarily localized holes SO_4^{-}, intrinsic $SO_4^{3-}-SO_4^{-}$ and impurity $Bi^{2+}-SO_4^{-}$ trapping centers. The electron components of the trapping centers Bi^{2+} and SO_4^{3-}, located below the conduction band, create induced or combined electronic emissive states, which are localized in the transparency region of the matrix, complementarily with the hole states located above the valence band.

When electrons from the combined electronic emissive state recombine with hole components, new bands of recombination emissions appear at 3.1 eV, 2.95 eV, 2.6–2.75 eV, and 2.2–2.4 eV. These electron-hole emissive states are excited by photon energies of 4.4–4.5 eV and 3.9–4.1 eV, primarily at 77 K.

Another important aspect is the experimental detection of the presence of both impurity and intrinsic electronic states in the pair within the combined electronic emissive state. This is evidenced by the measurement of the temperature dependence of the intensity of intrinsic recombination emissions at 3.1 eV and 2.95 eV, along with impurity intracenter emissions of Bi^{3+} and Bi^{2+}. These findings support the idea that both impurity and intrinsic electronic states coexist in the combined emissive states, contributing to the observed luminescence behavior.

From Figure 7, it is evident that the intensity of both intrinsic and recombination emissions at 3.1 eV and 2.95 eV, as well as the intracenter emissions at 2.75 eV and 2.03–1.9 eV, decreases monotonically up to temperature of 250 K. In the temperature range of 250–330 K, the recombination emissions at 3.1 eV and 2.95 eV, along with the intracenter emissions of Bi^{3+} at 2.75 eV, increase sharply, followed by a decrease to a minimal value at 450 K. The intensity of the intracenter emission of Bi^{2+} significantly decreases within this temperature range.

In this temperature range, the combined emissive states undergo decomposition. The band diagram shows that the ionization energy of the electronic emissive states Bi^{2+} and SO_4^{3-} is proportional to $kT\approx 250-330$ K, with a maximum at around 300 K (where Eu represents the ionization energy of the electron). The resulting free electron recombines with a hole near the Bi^{3+} impurity, thereby exciting the impurity. Another portion of the electrons recombines with holes, leading to the appearance of recombination emissions at 3.1 eV and 2.95 eV. The "burning out" of the three emission bands can be explained as follows: the increase in intensity of the two recombination emission bands at 2.95 eV and 3.1 eV is associated with the recombination of the ionized electron from SO_4^{3-} and Bi^{2+} with the SO_4^- hole localized in two nonequivalent crystallographic directions. The nonequivalent positions of the holes lead to different energies relative to the top of the valence band, which in turn affects the recombination processes and the resulting emission bands.

The increase in the intensity of the intracenter emission of Bi^{3+} at 2.75 eV is related to the rise in the concentration of Bi^{3+} centers due to the ionization process $Bi^{2+} \rightarrow Bi^{3+} - e^-$ in this temperature range.

The decrease in the radiation intensity of 2.03–1.9 eV Bi^{2+} ion is associated with a decrease in their concentration as a result of ionization $Bi^{2+} \rightarrow Bi^{3+} - e^-$.

The energy accumulated by the matrix itself during UV irradiation in the form of Bi^{2+}-center and SO_4^{3-} combined radiative state is transferred to the impurities of the main emitter of the phosphor Bi^{3+} center. The band diagram on the left side of the figure shows the ground and excited states of the anionic complex SO_4^{2-} and the local states of the formed electron-emitting state SO_4^{3-}, which are formed by the capture of electrons by the anionic complexes SO_4^{2-} located under the conduction band $E_u = kT$ (activation energy).

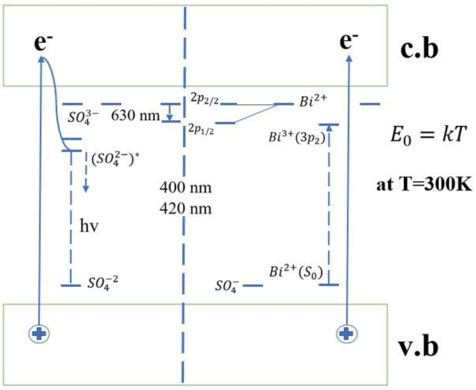


Figure 8. Band diagram

The right part of the band diagram shows the ground $^1s_0$ states of the Bi^{3+} impurity near the localized hole, and the $^3p_1$ excited state of the Bi^{3+} ion. The impurity electron-emitting states of Bi^{2+} are formed upon the capture of electrons $Bi^{3+} + e^- \rightarrow Bi^{2+}$ (^{2}p state). According to the authors of [22], the ^{2}p state is split due to the spin-orbit interaction into $^2p_{1/2}$ (ground) and $^2p_{3/2}$ (excited) states. The emission of Bi^{2+} at 2.03–1.9 eV occurs upon the transition of an electron from $^2p_{3/2} \rightarrow {}^2p_{1/2}$ [22].

CONCLUSIONS

In the irradiated $CaSO_4 - Bi$, new combined electronic emissive states at 3.1 eV, 2.95 eV, 2.6–2.75 eV, and 2.25–2.4 eV are formed from intrinsic and impurity electron-hole trapping centers, specifically $Bi^{2+} - SO_4^-$ and $SO_4^{3-} - SO_4^-$. It has been demonstrated that the energy accumulated in the intrinsic matrix during external irradiation, in the form of combined electronic emissive states $Bi^{2+} - SO_4^-$, is transferred to the Bi^{3+} impurities through the recombination process.

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$CaSO_4$–Bi ФОСФОРДАҒЫ ЛЮМИНЕСЦЕНЦИЯ ЖӘНЕ ЭЛЕКТРОНДЫҚ КЕМТІКТЕРДІ ҚАРМАУ ОРТАЛЫҚТАРЫНЫҢ ҚАЛЫПТАСУЫ

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$CaSO_4 - Bi$ люминофорында 2,95 эВ, 3,1 эВ, 2,6–2,7 эВ және 2,25–2,4 эВ энергия деңгейлерінде жаңа аралас электронды-кемтіктік күйдің түзілу механизмдері зерттелді, бұл күй матрицамен сәулелендіргіштер арасында энергияны беру алдындағы күй болып табылады.

Комбинацияланған электронды-кемтіктік күйлер $SO_4^{3-} - SO_4^-$ және қоспалы $Bi^{2+} - SO_4^-$ электронды-кемтіктік қармау орталықтарынан спектроскопиялық және жылулық активация әдістерімен зерттеулер негізінде қалыптасады. Өз кезегінде, өздік және қоспалы электронды-ткемтіктік қармау орталықтары SO_4^{2-} анионды кешенін қоздырған кезде, матрицадан қоспаларға ($O^{2-} - Bi^{3+}$) және көршілес аниондарға ($O^{2-} - SO_4^{2-}$) заряд тасымалдануы нәтижесінде түзіледі.

Сыртқы сәулелену кезінде өздік матрицада жинақталған энергия SO_4^{3-} және Bi^{2+} электронды-сәулелендіргіш біріктірілген күйі түрінде рекомбинация процесі арқылы ыдырап, қоспаларға берілетіні көрсетілді.

Түйін сөздер: *сульфат; электрон; рекомбинациялық эмиссия; меншікті эмиссия; тесік; қозу.*

ЛЮМИНЕСЦЕНЦИЯ И ОБРАЗОВАНИЕ ЭЛЕКТРОННО-ДЫРОЧНЫХ ЦЕНТРОВ ЗАХВАТА В ЛЮМИНОФОРЕ $CaSO_4$–Bi

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В люминофоре $CaSO_4 - Bi$ исследованы механизмы создания нового комбинированного электронно-дырочного состояния при 2,95 эВ, 3,1 эВ, 2,6–2,7 эВ и 2,25–2,4 эВ, которое является предраспадным состоянием для передачи энергии от матрицы к излучателям.

По данным исследования спектроскопическими методами и методами термической активации комбинированные электронно-дырочные состояния формируются из собственных $SO_4^{3-} - SO_4^{-}$ и примесных $Bi^{2+} - SO_4^{-}$ электронно-дырочных центров захвата. В свою очередь, собственные и примесные электронно-дырочные центры захвата создаются при возбуждении анионного комплекса SO_4^{2-} в результате переноса заряда с матрицы на примеси ($O^{2-} - Bi^{3+}$) и соседние анионы ($O^{2-} - SO_4^{2-}$).

Показано, что энергия, накопленная в собственной матрице при внешнем облучении в виде объединенного электронного излучательного состояния SO_4^{3-} и Bi^{2+}, распадается в результате процесса рекомбинации и передается примесям.

Ключевые слова: *сульфат; электрон; рекомбинационная эмиссия; собственная эмиссия; дырка; возбуждение.*