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Научная статья

## Recombination emission in the phosphor $\text{CaSO}_4 - \text{Pb}^{2+}$

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**Abstract.** Optical methods were used to investigate the formation of combined or induced electronic emissive states in irradiated  $\text{CaSO}_4 - \text{Pb}^{2+}$  phosphor at 2.9 eV and 3.1 eV. The combined electronic emissive state consists of electronic states of impurity  $\text{Pb}^+ - \text{SO}_4^-$  and intrinsic  $\text{SO}_4^{3-} - \text{SO}_4^-$  trapping centers. The impurity electronic states are formed by capturing free electrons of conduction band by  $\text{Pb}^{2+}$  impurities and localizing electrons resulting from charge transfer from the excited anion complex  $\text{SO}_4^{2-}(\text{O}^{2-} - \text{Pb}^{2+})$  impurities by reaction  $\text{Pb}^{2+} + (\text{e}^- + \text{SO}_4^-) \rightarrow \text{Pb}^+ - \text{SO}_4^-$ . The intrinsic electronic states are formed by capturing free electrons of conduction band by anion complexes or by localizing electrons resulting from charge transfer from the excited anion complex  $\text{SO}_4^{2-}(\text{O}^{2-} - \text{SO}_4^{2-})$  to neighboring anion complexes by reaction  $\text{SO}_4^{2-} + (\text{e}^- + \text{SO}_4^-) \rightarrow \text{SO}_4^{3-} - \text{SO}_4^-$ . The combined electronic emissive states at 2.9 eV and 3.1 eV are excited by photons of 3.9-4.0 eV and 4.5 eV. It was also experimentally shown that in the phosphor with induced trapping centers, recombination emissions at 2.9 eV and 3.1 eV are regenerated upon excitation by photons of 3.9-4.0 eV and 4.5 eV. Thus, energies of 3.9-4.0 eV and 4.5 eV are the excitation and absorption energies between the electronic and hole trapping centers located in the transparency region of  $\text{CaSO}_4 - \text{Pb}^{2+}$  phosphor.

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

## Introduction

CaSO<sub>4</sub> compounds, whether in the form of crystals or pressed powders, activated by rare earth and transition metals, are widely used in dosimeters and as emission sources in phosphors. It is well-known that phosphors activated by rare earth ions are significantly more expensive than those activated by transition metals or other non-rare earth ions.

In the work by the authors [1], ZnB<sub>2</sub>O<sub>4</sub> – Pb<sup>2+</sup> powdered phosphors emitting ultraviolet radiation were studied. It was shown that these phosphors emit blue light at 3.1 эВ (388 nm) when excited by photons with an energy of 4.08 эВ (304 nm). ZnB<sub>2</sub>O<sub>4</sub> – Pb<sup>2+</sup> phosphors are good candidates for wavelength converters used in various UV radiation applications.

In phosphors [2,3] based on SrB<sub>2</sub>O<sub>4</sub> – Pb<sup>2+</sup> and MAI<sub>2</sub>B<sub>2</sub>O<sub>7</sub> – Pb<sup>2+</sup>, intra-center emissions of Pb<sup>2+</sup> impurities were observed at room temperature at 3.4 эВ (363 nm) and 2.9 эВ (420 nm) when excited by photons with energies of 4.5 эВ (270 nm) and 4.4 эВ (277 nm), respectively.

In the work by [4] on Pb<sup>2+</sup> activated aluminates and gallates, two types of intra-center luminescence of impurities were discovered. The first type of emission is associated with intra-center transitions <sup>3</sup>P<sub>1</sub> – <sup>1</sup>S<sub>0</sub> in the Pb<sup>2+</sup> ion. The second type of emission is linked to the so-called C-D level transition of Pb<sup>2+</sup> impurities in the matrix, associated with the transition of an electron to an activator disturbed by the excitonic state of the matrix.

In the phosphor [5] SrMgBO<sub>3</sub>Pb<sup>2+</sup> – Gd<sup>3+</sup>, under the influence of mercury radiation at 4.8 эВ (254 nm), two emission spectra were observed: one line at 3.9 эВ (313 nm) and another emission band at 3.7 эВ (330 nm). It is suggested that this phosphor can be used as a phototherapeutic material for UVB therapy.

In the work [6] have shown that the position of intra-center Pb<sup>+</sup> emission in ZnTiO<sub>3</sub> nanocrystals is strongly influenced by its interaction with the lattice. An increase in Pb<sup>2+</sup> concentration significantly affects the maximum emission band. Red emission at 2 эВ (620 nm) observed by the authors is associated with charge transfer between Pb<sup>2+</sup> ions and the ZnTiO<sub>3</sub> matrix.

In the CaAlBO<sub>4</sub> phosphor [7] doped with Pb<sup>2+</sup>, Dy<sup>3+</sup>, and Sm<sup>3+</sup>, photoluminescent properties at 300 K were studied. It was shown that CaAlBO<sub>4</sub> – Pb<sup>2+</sup> phosphor emits a broad band at 339 nm when excited by photons with an energy of 4.5 эВ (272 nm). CaAlBO<sub>4</sub> – Pb<sup>2+</sup> Dy<sup>3+</sup>, Sm<sup>3+</sup> phosphors are optical materials for developing new optical display systems and sensitizers for recombination emissions in the red spectral region.

In the work by the authors [8], the optical properties of the Ca<sub>2</sub>La<sub>8</sub>SiO<sub>4</sub>6O<sub>2</sub> – Pb<sup>2+</sup> phosphor were studied. The luminescence of Pb<sup>2+</sup> ions in apatites, which can be used in X-ray imaging devices, low-pressure lamps, and high-energy physics, was shown.

In the SrZnO<sub>2</sub> – Pb phosphor obtained by the sol-gel method, broadband emissions with a maximum at 2.7 эВ (451 nm) were discovered, excited by photons with energies of 4.3 эВ (283 nm) and 3.9 эВ (317 nm). The matrix band gap is 3.4 eV. Emissions are associated with combined impurity-excitonic states [9].

Recombination emissions related to the creation of electron-hole trapping centers were previously studied [10-13] in CaSO<sub>4</sub> and CaSO<sub>4</sub>-Mn. It was shown that in CaSO<sub>4</sub> and CaSO<sub>4</sub>-Mn, intrinsic and impurity electron-hole trapping centers created during recombination decay emit intrinsic recombination or tunneling emissions, as well as impurity emissions of Mn<sup>2+</sup> ions.

By analyzing the works of the authors [5-6,9] as well as [10-14], the following conclusion can be drawn: in irradiated phosphors with photons whose energy exceeds the band gap [11], intrinsic and impurity trapping centers are formed. As a result of their recombination decay, intrinsic recombination emissions, as well as intra-center impurity emissions, occur.

This work examines the nature of recombination emissions in  $\text{CaSO}_4 - \text{Pb}^{2+}$  phosphor arising when irradiated with photons whose energy exceeds the band gap of the matrix.

## Experimental part

For the experiments, highly pure calcium sulfate (99.99% purity, Sigma Aldrich) and lead sulfate powders (Sigma Aldrich) were used.  $\text{CaSO}_4 - \text{Pb}^{2+}$  samples were obtained by the slow evaporation method. A stoichiometrically calculated amount of  $\text{CaSO}_4$  was mixed with a pre-calculated amount of  $\text{PbSO}_4$  impurity. Concentrated sulfuric acid was used to dissolve the mixture. After complete dissolution, the solution was washed several times with distilled water and dried at  $70^\circ\text{C}$ . The samples were then sintered at  $400^\circ\text{C}$  for 5 hours in an argon atmosphere. The annealed powder was slowly cooled over several hours. The final samples were pressed at 0.05 MPa.

The samples were analyzed using fundamental and thermally stimulated spectroscopy methods. The structure and purity were analyzed using microscopic and energy-dispersive elemental analysis. Primary photoluminescent measurements were conducted with a Solar SM2203 spectrofluorimeter (Belarus). Corrections to the Solar SM2203 spectrofluorimeter graphs are included in the software.

Studies at low temperatures down to 77 K and temperature dependence measurements were performed in a thermally activated complex consisting of a cryostat with three quartz windows and one beryllium oxide window, excitation and registration monochromators (OKB "Spektr MDR-41" and MDR-23U, respectively), and a photomultiplier (Hamamatsu 1P28). The system was vacuumed to a pressure of  $10^{-2}$  Pa and cooled with liquid nitrogen.

For the study of thermally stimulated luminescence (TSL), the samples were irradiated with X-rays. After irradiation, the samples were heated at a constant rate of 0.1-0.2 degrees per second, and the integral TSL was recorded by a photomultiplier.

An energy-dispersive X-ray spectrometer (EDS) and a scanning electron microscope (SEM) were used for analysis. SEM: Hitachi TM4000Plus II EDS: BRUKER. SEM working condition: EHT 10 kV. X-ray structural analysis was performed on a D6 PHASER diffractometer from BRUKER.

## Results

In previous studies of authors [15] on  $\text{Na}_2\text{SO}_4 - \text{Pb}$  and  $\text{K}_2\text{SO}_4 - \text{Pb}$  phosphors, the mechanisms creation and their recombination decay of trapping centers over a wide temperature range were investigated.

In order to determine the purity of the samples, the microstructure and elemental analysis of the obtained samples were performed. The microstructure of pure  $\text{CaSO}_4 - \text{Pb}$  powder samples was examined using a scanning electron microscope (SEM) (Fig. 1 a) and energy-dispersive

X-ray spectroscopy (EDS) (Fig. 1 b). The SEM image shows that the micro-powder sizes range from 0.5 to 15  $\mu\text{m}$ , with particles predominantly measuring 2-8  $\mu\text{m}$ .

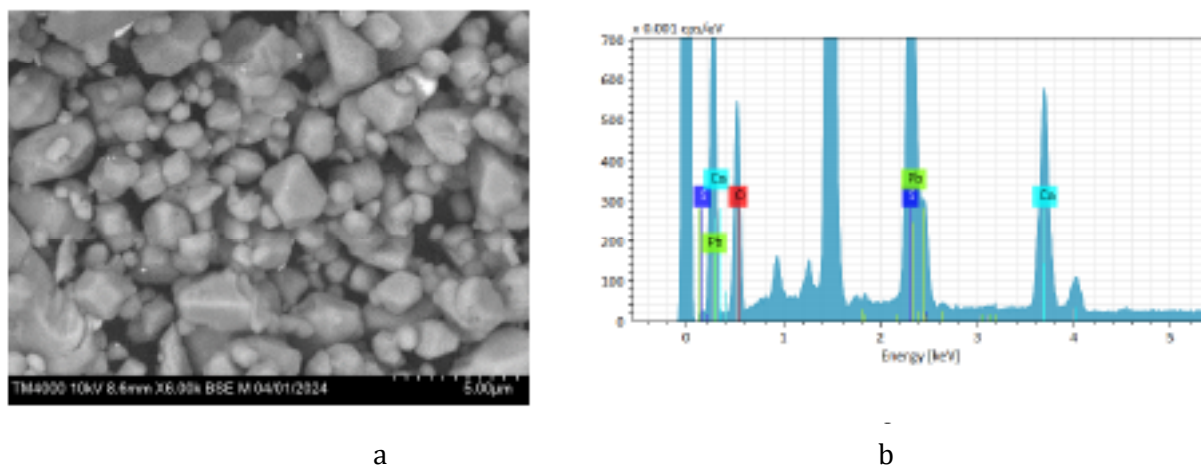


Figure 1. (a) SEM image, (b) EDS elemental analysis of irradiated  $\text{CaSO}_4$ -Pb phosphor

The elemental analysis (EDS) indicated that the sample consists of the main matrix of  $\text{CaSO}_4$  and lead impurities, with no other specific impurities present.

Next step is investigating the optical properties of irradiated  $\text{CaSO}_4$ -Pb phosphor.

In Fig. 2 (curve 1 and curve 2), the emission spectra of irradiated  $\text{CaSO}_4$ -Pb phosphor at 300 K (curve 1) and 77 K (curve 2) excited by photons with an energy of 6.2 eV are shown. The same figure (curve 3 and curve 4) presents the emission spectra of irradiated  $\text{CaSO}_4$ -Pb phosphor at 300 K (curve 3) and 77 K (curve 4) excited by photons with an energy of 5.64 eV.

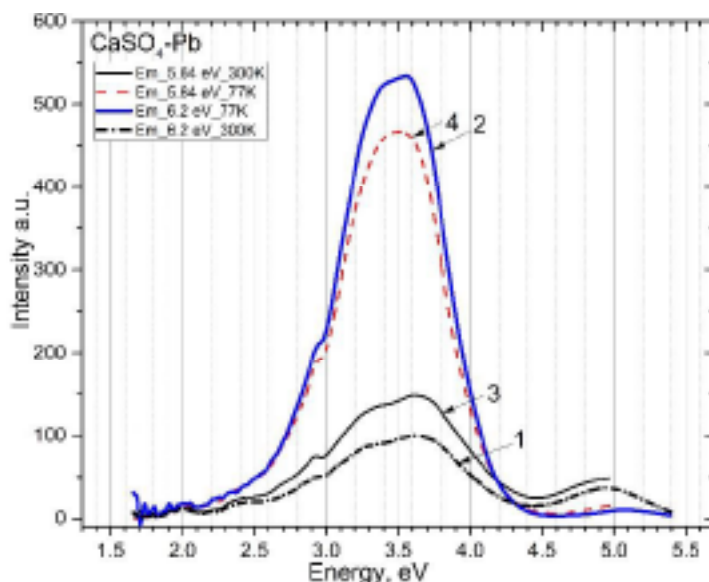


Figure 2. Emission spectra of  $\text{CaSO}_4$ -Pb excited by photons with energy: 6.2 eV at 300 K (curve 1); 6.2 eV at 77 K (curve 2); 5.64 eV at 300 K (curve 3); 5.64 eV at 77 K (curve 4)

From Fig. 2 (curves 1 and 3), it is evident that at 300 K, a broad emission with a maximum at 3.65 eV corresponding to  $\text{Pb}^{2+}$  impurities is more effectively created [15]. At low temperatures of 77 K, due to the appearance of new emission centers, the overall broad emission band shifts (Fig. 2 curves 2 and 4) to the longer wavelength region with a maximum at 3.4 eV.

Similar to other pure sulfates and those with impurities [16-22], after irradiation at 77 K, induced emission bands appear at 2.9 eV and 3.1 eV.

In Fig. 3, the excitation spectra of the 3.1 eV emission band (curve 1) and the 2.9 eV band (curve 3) at 300 K, as well as the 3.1 eV emission band (curve 2) and the 2.9 eV band (curve 4) at 77 K, are presented.

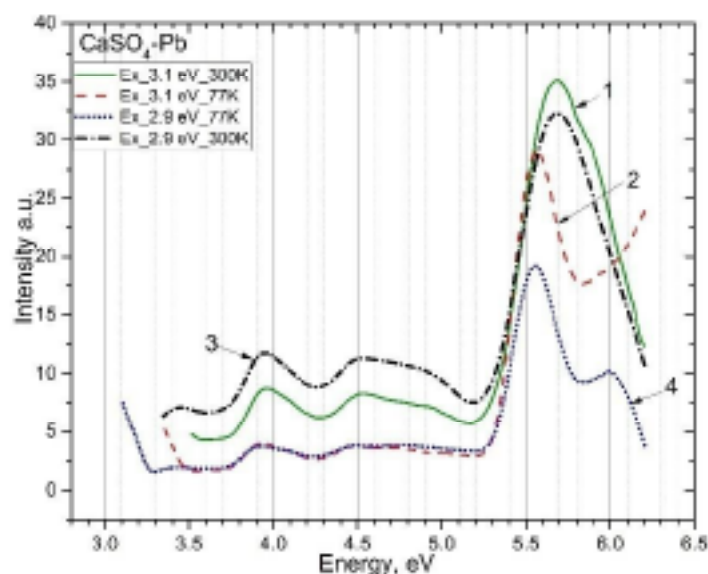


Figure 3. Excitation spectra of  $\text{CaSO}_4 - \text{Pb}$  for emission bands: 3.1 eV at 300 K (curve 1); 3.1 eV at 77 K (curve 2); 2.9 eV at 300 K (curve 3); 2.9 eV at 77 K (curve 4)

From Fig. 3 (curves 1 and 3), it is evident that recombination emissions are excited at 300 K (curves 1 and 3) and 77 K (curves 2 and 4) at 5.6 eV, 5.9 eV, 4.5 eV, and 3.9 eV. Thus, these recombination emission bands are excited or created in the fundamental region of the matrix at 5.5-6.2 eV and in the transparency region of the  $\text{CaSO}_4$  matrix at 4.5 eV and 3.9 eV.

In Fig. 4 (curves 1-3), the excitation spectra of the main intra-center emission of  $\text{Pb}^{2+}$  impurities at 3.65 eV and 3.4 eV at 300 K and 77 K are presented.

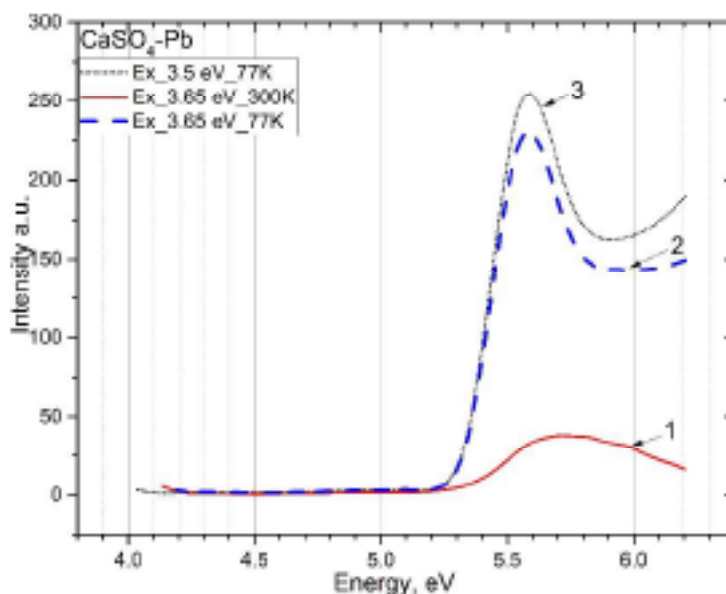


Figure 4. Excitation spectra of  $\text{Pb}^{2+}$  impurity emission bands at: 3.65 eV at 300 K (curve 1); 3.4 eV at 77 K (curve 2); 3.4 eV at 77 K (curve 3)

From Fig. 4 (curves 2 and 3), it can be seen that the 3.4 eV emission is excited by photons with an energy of 5.57 eV. At 300 K (Fig. 4 curve 1), the 3.65 eV emission is excited over a broad spectral range from 5.5 eV to 5.9 eV, meaning that the  $\text{Pb}^{2+}$  impurity at 300 K is excited by intra-center absorption of  $\text{Pb}^{2+}$  at 5.5 eV [23], as well as in the fundamental region of the matrix.

Thus, intra-center emission is excited in the spectral region corresponding to  $\text{Pb}^{2+}$  ion absorption in the matrix.

New recombination emission at 3.1 eV and 2.9 eV is excited in the fundamental absorption edges at photon energies of 4.5 eV and 3.9 eV.

In Fig. 5, the emission spectra of recombination emission upon excitation by 4.5 eV photons at 300 K (curve 1) and 77 K (curve 2) are presented. The same figure (curves 3 and 4) presents the recombination emissions upon excitation by 3.9 eV photons.

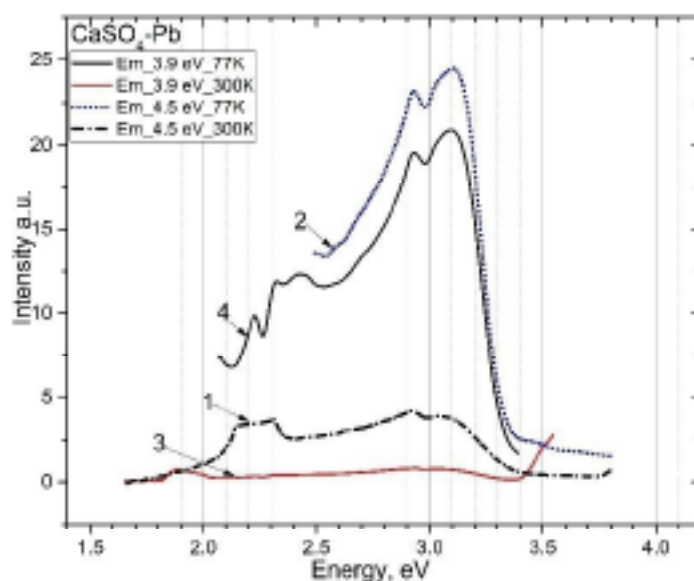


Figure 5. Emission spectra of  $\text{CaSO}_4\text{-Pb}$  excited by photons with energy: 4.5 eV at 300 K (curve 1); 4.5 eV at 77 K (curve 2); 3.9 eV at 300 K (curve 3); 3.9 eV at 77 K (curve 4)

It can be seen that in both cases, recombination emissions of 3.1 eV and 2.9 eV appear (intensity upon excitation at 77 K is much higher than at 300 K). The experimental [13] result shows that photons with energies of 3.9 eV and 4.5 eV are the excitation spectra of the new recombination emission.

To determine the nature of the recombination and intra-center emissions arising from the corresponding excitations, the changes in their emission intensity depending on temperature from 77 K to 450 K were measured. In Fig. 6 (curves 1-4), the changes in the intensity of intra-center emissions at 3.4 eV (curve 1) and 3.65 eV (curve 2), and the new induced emission at 3.1 eV (curve 3) and 2.9 eV (curve 4), are presented.

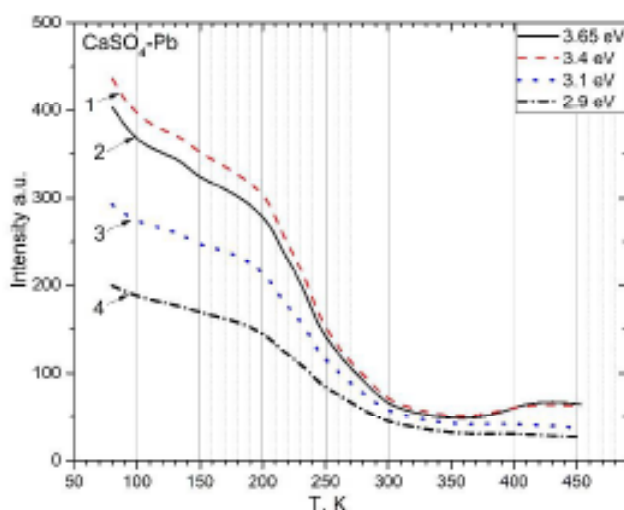


Figure 6. Temperature dependence of intra-center emission of  $\text{CaSO}_4\text{-Pb}$  at: curve 1 – 3.4 eV; curve 2 – 3.65 eV; curve 3 – 3.1 eV; curve 4 – 2.9 eV

From Fig. 6, it can be seen that the intensity of the induced emission at 3.1 eV (curve 3) and 2.9 eV (curve 4) gradually decreases to a minimum value from 200 K to 300 K, then slowly decreases. The intensity of intra-center emission at 3.65 eV and 3.4 eV, overlapping with the new induced emissions, also decreases from 200 K to 350 K, then gradually increases to 450 K.

In Fig. 7, the thermally stimulated luminescence (TSL) glow curve of irradiated  $\text{CaSO}_4\text{-Pb}$  at liquid nitrogen temperature is presented.

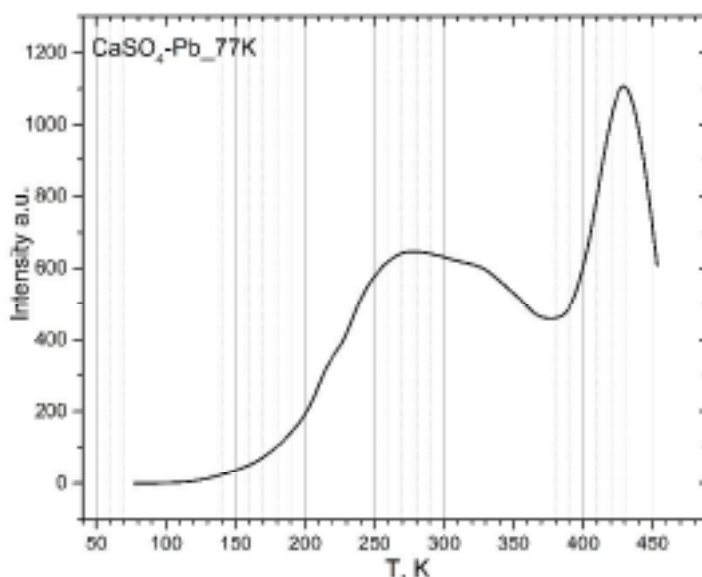


Figure 7. Thermally stimulated luminescence glow curve of  $\text{CaSO}_4\text{-Pb}$  irradiated by X-rays for 1 minute at 77 K

It can be seen that the TSL maxima fall in the temperature range of 200-350 K, where the decay of the combined emissive state at 2.9-3.1 eV occurs. The high-temperature TSL at 430 K corresponds to the increase in  $\text{Pb}^{2+}$  emission intensity.

## Discussion

The main research question of this study is the formation of a new combined emissive electronic state and to show that as a result of the recombination decay of the electronic state, the energy of electronic excitations of the matrix is transferred to the emitters, i.e., impurities.

In this work, when irradiated with photons whose energy exceeds the band gap or due to charge transfer from the excited  $\text{SO}_4^{2-}$  anion complex to  $\text{Pb}^{2+}$  impurities or neighboring  $\text{SO}_4^{2-}$  ions, free electrons are formed, which are captured by impurities or neighboring  $\text{SO}_4^{2-}$  ions of the matrix. Electron trapping centers are created according to the reactions  $e^- + \text{Pb}^{2+} \rightarrow \text{Pb}^+$  and  $e^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{3-}$ , and hole centers in the form of  $\text{SO}_4^{\cdot-}$ .

It is assumed, as shown in the band diagram (Figure 8), that the  $\text{SO}_4^{3-}$  and  $\text{Pb}^+$  trapping centers below the conduction band should correspond to local states, and their complementary  $\text{SO}_4^{\cdot-}$  hole component is located above the valence band. Thus, these complementary trapping centers in



the fundamental absorption edges correspond to local states. During the recombination decay of these intrinsic and impurity trapping centers, recombination and tunneling emissions at 2.9 eV and 3.1 eV are observed. Measurements have shown that these recombination emissions at 2.9 eV and 3.1 eV correspond to the excitation spectrum at 3.9 eV and 4.5 eV. Experimentally, it has been shown that the  $\text{CaSO}_4$ -Pb phosphor with induced trapping centers, when excited by photons of 4.5 eV and 3.9 eV, re-emits recombination emission at 2.9 eV and 3.1 eV.

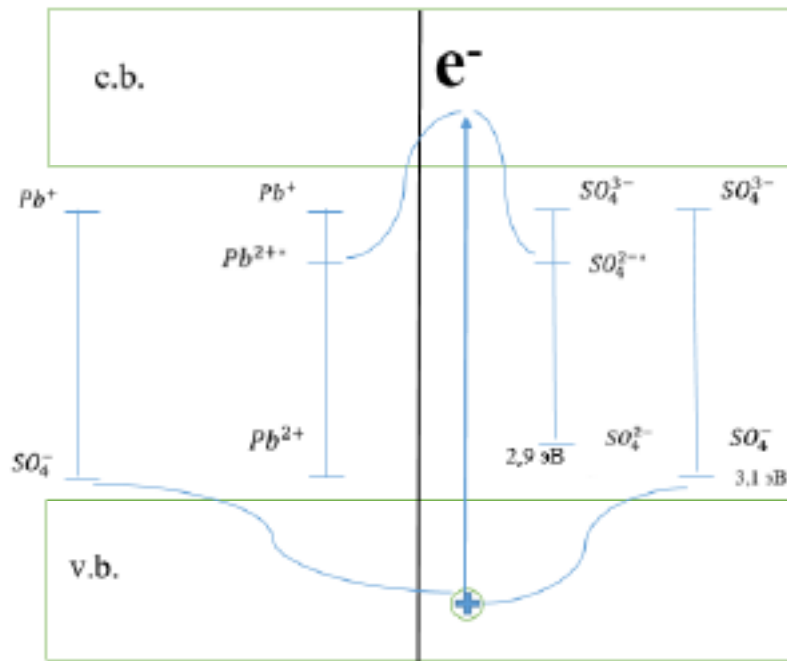


Figure 8. Band diagram of calcium sulfate with lead impurity.  $\text{Pb}^{2+*}$ -excited state of impurity;  $\text{SO}_4^{2-*}$ - excited state of the anion

Regarding the presence of  $\text{Pb}^+$  ions in the composition of  $\text{Pb}^+ - \text{SO}_4^-$ -trapping centers, it can be observed when measuring the temperature dependence of combined and impurity emission. From Fig. 5, it can be seen that the intensity of combined emission (curves 3 and 4) in the temperature range of 200-350 K monotonically decreases, i.e., decays during the ionization of  $\text{Pb}^+$  to  $\text{Pb}^{2+} + e^-$ . Above 350 K, the intensity of intra-center  $\text{Pb}^{2+}$  emission in the temperature range of 350-450 K increases, i.e., the electronic states of  $\text{Pb}^{2+}$  are restored due to the ionization of the  $\text{Pb}^+$  center. The increase in  $\text{Pb}^{2+}$  emission can be explained by the following processes: during the ionization of  $\text{Pb}^+$ , an electron is released. This electron recombines with a hole in  $\text{SO}_4^-$  located near the  $\text{Pb}^{2+}$  ion. The energy released during this recombination is transferred to the  $\text{Pb}^{2+}$  impurity ions, leading to their excitation. This process can be interpreted as a reabsorption mechanism, where the transferred energy excites the  $\text{Pb}^{2+}$  centers. After relaxation from the excited state,  $\text{Pb}^{2+}$  emits light, resulting in the observed increase in emission intensity. In this process, during the recombination of electron-hole pairs of the matrix, energy is transferred from the matrix to the impurities. This demonstrates an elementary mechanism of energy

transfer from the matrix to the impurities. In this experiment, due to the overlap of impurity emission and induced emission bands, the energy transfer process is not clearly identified.

The second question regarding the appearance of two intra-center emission bands at 3.65 eV and 3.4 eV, as well as the appearance of two combined emission bands, is associated with the anisotropic properties of alkali and alkaline earth metal sulfates.

In the works [24], it has been shown that two types of  $SO_4^-$  holes (A and B) are formed in  $CaSO_4$  crystals after irradiation due to the anisotropic properties of the crystal. Theoretical studies by the authors [25] have shown that the ground state of an unpaired electron in  $SO_4^-$  in different crystallographic directions has different energies relative to the top of the valence band. Therefore, during the recombination decay of the induced electronic state at 2.9 eV and 3.1 eV, an electron arising after ionization recombines with holes located at different distances from the top of the valence band, resulting in different energies of recombination emission.

Now regarding the two intra-center emissions at 3.4 eV and 3.65 eV. The formation of two types of  $SO_4^-$  radicals in the lattice is associated with Ca cations in the matrix in different ways. During the substitution of such cations by  $Pb^{2+}$  impurities, different binding energies of  $Pb^{2+}$  with  $SO_4^{2-}$  anion complexes are formed. It is assumed that the appearance of two emission bands of impurities is due to the anisotropic properties of the matrix.

## Conclusion

In  $CaSO_4$ - $Pb^{2+}$  phosphors, as in other matrices activated by  $Pb^{2+}$  ions, intracenter emissions occur in the energy ranges of 3.4 eV and 3.65 eV. The novelty of this work lies in the appearance of new electronic emissive states that emit recombination emission at 2.9 eV and 3.1 eV. These new emissive states arise from the capture of impurities and anions of the matrix by free zonal electrons formed during excitation by photons with energy exceeding the bandgap of the  $CaSO_4$  matrix through the reactions  $Pb^{2+} + (e^- + SO_4^-) \rightarrow Pb^+ - SO_4^-$  and  $SO_4^{2-} + (e^- + SO_4^-) \rightarrow SO_4^{3-} - SO_4^-$ . The new electronic emissive states consist of the electronic states of the trapping centers  $Pb^+ - SO_4^-$  and  $SO_4^{3-} - SO_4^-$  in the  $CaSO_4$ - $Pb^{2+}$  matrix. During the recombination decay of these combined electronic states ( $Pb^+$  and  $SO_4^{3-}$ ), recombination emission occurs at 2.9 eV and 3.1 eV, along with emissions from the restored  $Pb^{3+}$ . At the moment of recombination decay of the combined emissive state, the energy of the intrinsic electronic excitations ( $e^- + SO_4^-$ ) is transferred to the emitters or impurities in the luminescent lamps used, as well as in modern phosphors with semiconductor chips.

The formation of two intracenter emission bands at 3.4 eV and 3.65 eV is associated with the substitution of  $Pb^{2+}$  impurities for the  $Ca^{2+}$  cations in the base, with different binding energies to the anionic complex.

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### The author's contribution

**Shamiyeva R.K.** – results calculation, writing the text and critically revising its content, approval of the final version of the article for publication

**Balapanov M.H.** – approval of the final version of the article for publication, agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

**Salikhodzha Zh.M.** – writing the text and critically revising its content, approval of the final version of the article for publication, agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

**Kainarbay A.Zh.** – approval of the final version of the article for publication, agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

**Sadykova B.M.** – approval of the final version of the article for publication, agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

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**Karibay B.A.** – agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

**Batisheva A.T.** – agreement to be responsible for all aspects of the work, proper examination and resolution of issues related to the reliability of the data

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### $\text{CaSO}_4\text{-Pb}_{2+}$ люминофорындағы рекомбинациялық сәулелену

**Андатпа.** Оптикалық әдістермен  $\text{CaSO}_4\text{-Pb}^{2+}$  люминофорында пайда болған комбинирленген немесе индуцирленген электрондық сәулелену 2,9 эВ және 3,1 эВ тең күйінің түзілуі зерттелді. Комбинирленген электрондық сәулелену күйі  $\text{Pb}^+\text{-SO}_4^-$  қоспа орталықтарының электрондық күйлерінен және матрицаның  $\text{SO}_4^{3-}\text{-SO}_4^-$  меншікті қармау орталықтарының электрондық күйлерінен тұрады. Қоспа қармау орталықтарының электрондық күйлері еркін зоналық электрондардың  $\text{Pb}^{2+}$  қоспасымен қармалуы кезінде немесе қоздырылған аниондық комплекстен  $\text{SO}_4^{2-}\text{-O}^{2-}\text{-Pb}^{2+}$  қоспаға заряд тасымалдау нәтижесінде түзілген электрондардың локализациялануы кезінде  $\text{Pb}^{2+} + (\text{e} + \text{SO}_4^-) \rightarrow \text{Pb}^+\text{-SO}_4^-$  реакциясы бойынша түзіледі. Меншікті қармау орталықтарының электрондық күйлері еркін зоналық электрондардың аниондық комплекстермен қармалуы немесе қоздырылған аниондық комплекстен  $\text{SO}_4^-(\text{O}^{2-}\text{-SO}_4^{2-})$  көрші аниондық комплекстерге заряд тасымалдау нәтижесінде түзілген электрондардың локализациялануы кезінде  $\text{SO}_4^{2-} + (\text{e} + \text{SO}_4^-) \rightarrow \text{SO}_4^{3-}\text{-SO}_4^-$  реакциясы бойынша түзіледі.

Өлшеулер көрсеткендей, 2,9 эВ және 3,1 эВ кезіндегі комбинирленген электрондық сәулелену күйлері 3,9-4,0 эВ және 4,5 эВ фотон энергияларымен қоздырылады. Сондай-ақ эксперименталды түрде көрсетілгендей, қармау орталықтары индуцирленген люминофорларда 3,9-4,0 эВ және 4,5 эВ фотондармен қоздырылған кезде 3,1 эВ және 2,9 эВ рекомбинациялық сәулеленулер қайта түзіледі. Осылайша, 3,9-4,0 эВ және 4,5 эВ фотон энергиялары  $\text{CaSO}_4\text{-Pb}^{2+}$  люминофор матрицасының мөлдірлік аймағында орналасқан электрондық және кемтіктік қармау орталықтары арасындағы қоздыру және сіңіру энергиялары болып табылады.

**Түйін сөздер:** сульфат, электрон, рекомбинациялық сәулелену, меншікті радиация, кемтік, қозу.

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### Рекомбинационное излучение в люминофоре $\text{CaSO}_4\text{-Pb}^{2+}$

**Аннотация.** Оптическими методами исследовано образование комбинированного или индуцированного электронного излучательного состояния в облученном люминофоре  $\text{CaSO}_4\text{-Pb}^{2+}$  при 2,9 эВ и 3,1 эВ. Комбинированное электронное излучательное состояние состоит из электронных состояний примесных центров  $\text{Pb}^+\text{-SO}_4^-$  и электронных состояний  $\text{SO}_4^{3-}\text{-SO}_4^-$  собственных центров захвата матрицы. Примесные электронные состояния центров захвата образуются при захвате свободных зонных электронов примесью  $\text{Pb}^{2+}$  или при локализации электронов созданного в результате переноса заряда от возбужденного анионного комплекса  $\text{SO}_4^{2-}\text{-O}^{2-}\text{-Pb}^{2+}$  к примесям  $\text{Pb}^{2+}$  по реакции  $\text{Pb}^{2+} + (e^- + \text{SO}_4^-) \rightarrow \text{Pb}^+ \text{-SO}_4^-$ . Собственные электронные состояния центров захвата образуются при захвате свободных зонных электронов анионными комплексами или локализации электронов созданного в результате переноса заряда от возбужденного анионного комплекса  $\text{SO}_4^-(\text{O}^{2-}\text{-SO}_4^{2-})$  к соседним анионным комплексам по реакции  $\text{SO}_4^{2-} + (e^- + \text{SO}_4^-) \rightarrow \text{SO}_4^{3-}\text{-SO}_4^-$ .

Измерением показано, что комбинированные электронно-излучательные состояния при 2,9 эВ и 3,1 эВ возбуждаются при энергиях фотона 3,9-4,0 эВ и 4,5 эВ. Также экспериментально показано, что в люминофоре с наведенными центрами захвата при возбуждении фотонами 3,9-4,0 эВ и 4,5 эВ обратно образуются рекомбинационные излучения при 3,1 эВ и 2,9 эВ. Таким образом, энергия фотона при 3,9 -4,0 эВ и 4,5 эВ является энергией возбуждения и поглощения между электронными и дырочными центрами захвата расположенного в области прозрачности матрицы люминофора  $\text{CaSO}_4\text{-Pb}^{2+}$ .

**Ключевые слова:** сульфат; электрон; рекомбинационное излучение; собственное излучение; дырка; возбуждение.

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