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Study of the interaction of Zinc sulfide with Europium (III) fluoride by spectroscopic methods

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A study was conducted on the interaction of Zinc sulfide, obtained by the method of self-propagating high-temperature synthesis, and purified from oxygen with Europium (III) fluoride. The optical properties of the obtained systems were studied. The luminescence spectra show a decrease in its intensity for the samples after their heat treatment, which occurs due to the possible reaction with partial disappearance of Europium (III) fluoride. A hypothesis was proposed regarding the redox mechanism of interaction between the reagents with the formation of Europium (II) fluoride and other compounds.

Keywords: Europium fluoride, Zinc sulfide, IR spectroscopy, photoluminescence spectroscopy.

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Introduction

Zinc sulfide is one of the most common and widely used materials for interference optics in the infrared (IR) spectrum range [1-3], due to its manufacturability and the high performance parameters of the coatings obtained from it. Additionally, Zinc sulfide, doped with metal additives (Ag, Ln (Ln – La ÷ Lu) [4], exhibits interesting luminescent properties, making this material important for practical applications. However, Zinc sulfide has certain drawbacks related to the presence of Zinc oxide impurities in its compound, which deteriorate the properties of the resulting thin films [5]. We proposed approaches that allow partial mitigation of the harmful effects of the mentioned impurity, in particular, through the use of additives such as lanthanide sulfides [6].

In this regard, one can distinguish the work of a Japanese author [7], which established the continuous nature of the change in the refractive index of the coating with the composition of the CeF_3–ZnS system, which is quite interesting from the perspective of regulating optical properties. Similar works using fluorides of other lanthanides have not been found in the current scientific literature. Instead, a significant number of publications have emerged concerning the synthesis, study, and potential application of Zinc sulfide nanoparticles doped with lanthanide compounds, mainly Europium [8-11] and Cerium [12]. This is because such objects exhibit interesting spectral properties and can be used in various optical devices. For instance, in the work [8], it was established that doping with Europium leads to a decrease in the band gap from 4.2 eV to 3.9 eV compared to undoped ZnS parts. With excessive doping from 10 to 20%, the Europium compound transforms into Eu_2O_3. Interestingly, the authors of [9] found the presence of a doping impurity in the Eu^{2+} valence state in ZnS nanowires, confirmed by electron paramagnetic resonance. A similar result regarding the Eu^{2+} valence state in Europium-doped Zinc sulfide was obtained by the authors of [10] based on the study of the effect of the oxidizing environment on luminescence spectra, specifically, the disappearance of the broad band characteristic of intra-ionic transitions in the Eu^{2+} ion with a maximum near 530 nm and its replacement by the characteristic "toothed" band of Eu^{3+} [10]. However, the author notes that this phenomenon is observed only in doped nanoparticles and is absent in the bulk material ZnS. A significant number of publications are devoted to the study of the electronic structure and optical properties using first-principles methods, an example of which is the article by M. Hedjar [11] for a series of Zinc sulfide samples doped with Sm, Eu, Gd, and Er. The work, which is considered very promising, based on spin-polarized density functional theory, predicts the properties of materials based on the mentioned systems. The photoluminescent properties of CeF_3–ZnS nanocomposite systems with varying compositions (from 1:1 to 1:7 by mass) were studied and presented by the authors [12]. Due to the overlap of the emission and absorption spectra of ZnS, there is an enhancement of energy transfer from CeF_3 to ZnS nanoparticles. The influence of core-shell type nanostructures on luminescence is anticipated. In considering compounds as candidates for the role of an additive, Europium fluoride (III) stands out. This lanthanide is prone to change its valence state from Eu(III) to Eu(II) under inert atmosphere conditions, high temperatures, and the presence of a reducing agent, which ZnS itself plays. Similarly, attention can be given to the ZnS–CeF_3 system, which contains Cerium fluoride, an element capable of exhibiting oxidation states (III) and (IV). The task of this study is to determine the nature of the interaction between Europium fluoride and Zinc sulfide by spectroscopic methods. It is planned to carry out redox reactions (1-5) by high-temperature treatment in an inert environment.

$$\text{ZnS (g.)} + 2EuF_3 \xrightarrow{T,\ Ar} ZnF_2 + 2EuF_2 + S\uparrow, \quad (1)$$

$$2\text{ZnS (g.)} + 2EuF_3 \xrightarrow{T,\ Ar} 2ZnF_2 + EuS + EuF_2 + S\uparrow, \quad (2)$$

$$\text{ZnS (y.)} + 2EuF_3 \xrightarrow{T,\ Ar} ZnF_2 + 2EuF_2 + S\uparrow, \quad (3)$$

$$2ZnO + 4EuF_3 \xrightarrow{T,\ Ar} 2ZnF_2 + 4EuF_2 + O_2\uparrow, \quad (4)$$

$$4ZnO + 4EuF_3 \xrightarrow{T,\ Ar} 4ZnF_2 + 2EuF_2 + 2EuO + O_2\uparrow. \quad (5)$$

and establish their mechanism.

For this purpose, IR transmission spectroscopy in the far (up to 200 cm^{-1}) IR range of the spectrum and solid-state photoluminescence spectroscopy of powders in the range from 300 to 750 nm should be used. Additionally, the change in the mass of the samples after high-temperature (900 °C) annealing will be determined. The obtained composites have the potential to be used as materials for interference coatings, recognizing their optical and operational properties. Conclusions will be drawn regarding the influence of oxide impurities in ZnS on the processes occurring between EuF_3 and ZnS, and the feasibility of their identification and possible elimination.

I. Experimental part

We prepared samples of the ZnS–EuF_3 system in a molar ratio of 1:2 by calcination at 900 °C of a fine dispersion mixture of reagents, pressed into tablets with a diameter of 8 mm and a thickness of 10 mm. The raw materials were purchased from JV «New Materials and Technologies (Odessa)». Zinc sulfide was obtained by the method of self-propagating high-temperature synthesis from a mixture of zinc and sulfur powders, taken in a molar ratio of 1:1 as described in [3]. According to the content of heavy metal impurities (Cu, Fe, Ni, etc.), the synthesis product met the qualification of pure analytical grade, however, the oxygen content was not standardized. One of the initial products of the ZnS synthesis was subjected to treatment to remove oxide impurities according to the methodology described in [4]. They were designated as ZnS (y.) and ZnS (g.), respectively; this is related to the fact that the first sample had a white with yellowish tint coloration, while the second had a grayish tint. Europium fluoride, EuF_3, was synthesized by the interaction of Eu_2O_3 with a fluorinating agent - ammonium fluoride, NH_4F, followed by the melting of the product in an induction furnace. It was qualified as a pure analytical grade preparation. The samples were studied using spectroscopic methods, namely, IR transmission spectroscopy [13, 14] and luminescent spectroscopy [13].

IR spectra were recorded in the coordinates $T = f(\tilde{\nu})$, where T denotes transmittance and $\tilde{\nu}$ - wavenumber, using a Fourier transform IR spectrophotometer Frontier Perkin-Elmer (Perkin-Elmer Inc., Waltham, MA, USA) in the wavenumber range of 4000-200 cm^{-1} [13]. IR transmission spectra were recorded for samples of the batch and tablets ground into powder, pressed into a matrix of pre-dehydrated heating at 180 °C CsI of analytical reagent grade (produced by the Institute of Single Crystals NAS of Ukraine, Kharkiv) in a mass ratio of sample: matrix = 1:20 [14]. For IR transmission spectroscopy, the spectral range was 4000-200 cm^{-1}, and the instrument's resolution was about 0.4 cm^{-1}; the wavelength reproducibility was approximately 0.008 cm^{-1}; and the signal/noise ratio exceeded 50 000:1 [13]. Luminescence and excitation spectra were recorded on a Fluorolog FL3-22 spectrofluorimeter (HORIBA Jobin Yvon Inc, Longjumeau Cedex, France). The excitation source was a 450 W xenon lamp (model 1907). For the visible region of the spectrum, an R928P photomultiplier was used as the emission detector. The excitation wavelength range was from 240 to 600 nm, and the luminescence wavelength range was from 290 to 850 nm. The photomultiplier registered the emission intensity by counting individual light photons, maintaining proportionality in the range of 1000 to 2 000 000 counts per second (CPS). Based on this sensitivity range, the instrument's input and output slits were adjusted accordingly. Luminescence measurements were carried out in a specialized cuvette for solid powder materials with a depth of 1.5 mm and a surface area of 70мmm^2. Before registering the luminescence spectrum, the crystalline sample was ground into a homogeneous fine powder [13].

The IR spectra of the initial compounds ZnS and EuF_3 significantly differ from each other (Fig. 1). Similarly, the same applies to the ZnS (y.) and ZnS (g.) samples. Both ZnS samples are characterized by a distinct absorption band with a maximum near 300 cm^{-1}. In this case, the absorption band of ZnS (g.) is less pronounced; however, the ZnS (y.) transmission spectrum contains an absorption band at 415 cm^{-1}, reflecting the presence of ZnO impurity.

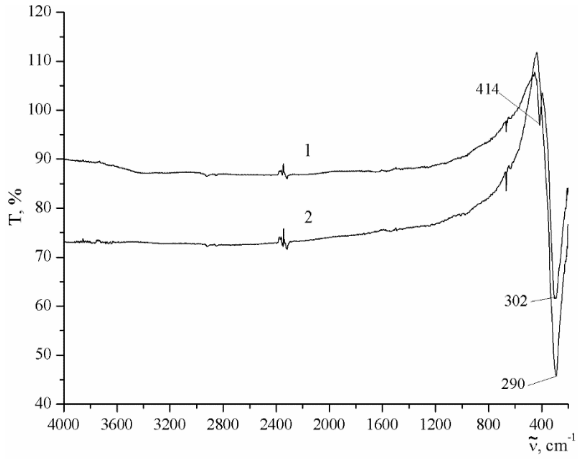

Fig. 1. Infrared transmission spectra of ZnS (y.) (1) and ZnS (g.) (2) in the range of 4000-200 $cm^{-1.}$

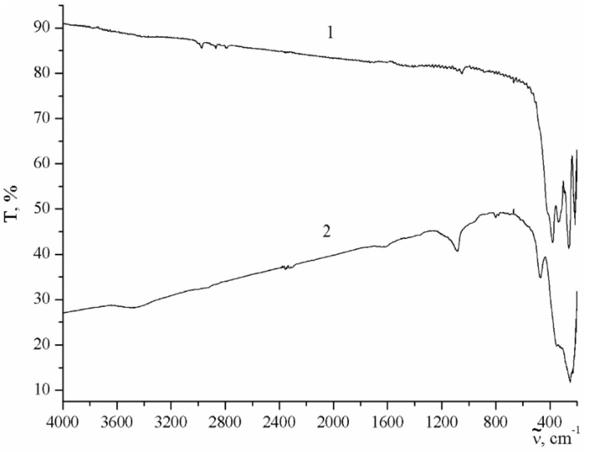

Fig. 2. Infrared transmission spectra of EuF_3 (1) and EuF_2 (2)

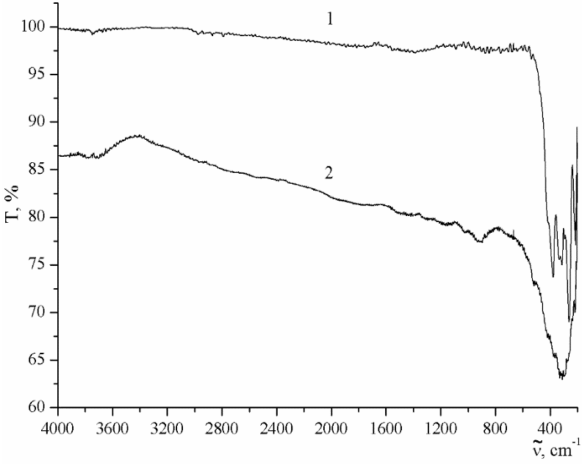

Fig. 3. Infrared transmission spectra of the ZnS (y.) – EuF_3 system: 1 - mechanical mixture; 2 - sample after heat treatment

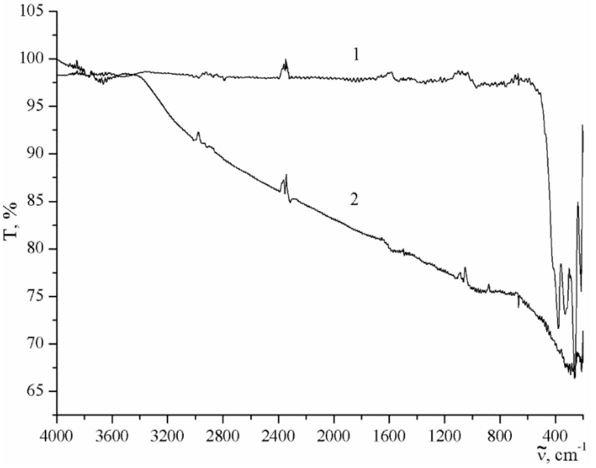

Fig. 4. Infrared transmission spectra of the ZnS (g.) – EuF_3 system: 1 - mechanical mixture; 2 - sample after heat treatment

When EuF_3 is added to ZnS, the intensity of the absorption bands of the former changes insignificantly, while the intensity of the main ZnS band in the IR transmission spectrum sharply decreases, and, in this respect, this band occupies almost the last place among all the bands of the mixture. At the same time, its position undergoes a noticeable hypsochromic shift. These changes are still unclear in terms of the optics of finely dispersed materials.

The changes in the IR transmission spectra of the sintered ZnS – EuF_3 sample compared to the mechanical mixture are even more significant. The absorption band generally remains, but the peaks change their position and intensity. Some absorption peaks of the initial EuF_3 compound remain, while the absorption peaks of ZnS for both samples almost entirely disappear.

The luminescence spectra presented in Figures 5 - 10 turned out to be very rich in informational content and, at the same time, quite complex to interpret.

The shape of the luminescence spectra of ZnS (y.) and ZnS (g.) samples (Fig. 5) differs significantly from that of EuF_3 (Fig. 6). They are very broad bands in the wavelength range of 400-700 nm for luminescence spectra and 275-425 nm for excitation spectra (the latter are significantly narrower).

Naturally, the highest intensity is observed in the luminescence bands corresponding to the 4f-4f electronic transitions in Eu^{3+} ions (EuF_3), specifically, in the wavelength range of 575-625 nm for luminescence and 275-425 nm for excitation.

In Figures 7 and 8, the bands of the excitation and luminescence spectra, respectively, have a similar arrangement to each other, but differ significantly in intensity and are completely different from the spectra shown in Figures 9 and 10. It appears that the arrangement of the bands of the excitation and luminescence spectra of the latter are similar, but their shapes are quite different, and the intensity differs by a factor of approximately 2.

II. Experimental results and their discussion

The obtained results show significant changes in the nature of the spectra of different types, with the most significant occurring at the stage of conversion from batch to alloy (sinter). This undoubtedly indicates certain chemical transformations during the sintering process. Additionally, it should be noted that the ZnS (g.) – EuF_3 sample lost 3.05% of its weight after sintering ZnS (y.) – EuF_3 – 4.54%. Of all possible volatile products at 900 °C, sulfur is the one that can exhibit such volatility, as indicated by the appearance of a nearly white deposit on the cold parts of the reactor by reactions (1-3). The above-mentioned weight loss (considering only sulfur loss) is calculated to be 6.2% of the total weight of the tablet. Thus, the relative weight loss does not exceed 48.3%, that is, about half; this fact of preserving a significant part of the sample in its original form is confirmed by the data of all types of spectroscopy, except possibly IR transmission spectroscopy. The addition of ZnS (g.) leads to a significant (30%) decrease in the luminescence intensity of EuF_3, likely due to reflection and scattering caused by the dilution effect of the luminescent substance with a non-luminescent one. An even greater effect (up to 50%) is caused by the addition of ZnS (y.). This may be related both to the higher dispersibility of the material and to the presence of a certain content of oxide impurity. At the same time, the effect of intensity reduction is more noticeable in the excitation spectrum compared to the luminescence spectrum. Finally, the most noticeable

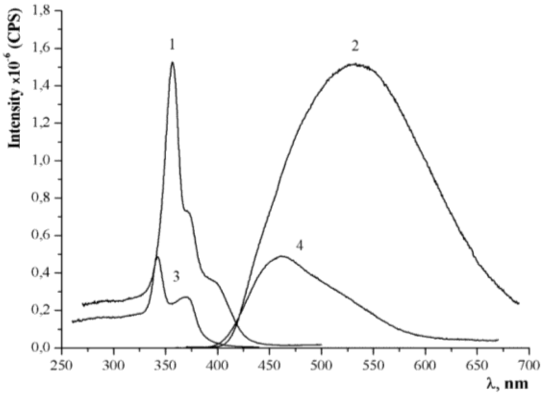

Fig. 5. Excitation and luminescence spectra of ZnS (y.) (1, 2) and ZnS (g.) (3, 4), slit 5-1 nm: 1 - excitation spectrum at λ_{em} = 531 nm, 2 - luminescence spectrum at λ_{exc} = 357 nm; 3 - excitation spectrum at λ_{em}=461 nm, 4 - luminescence spectrum at λ_{exc} = 342 nm

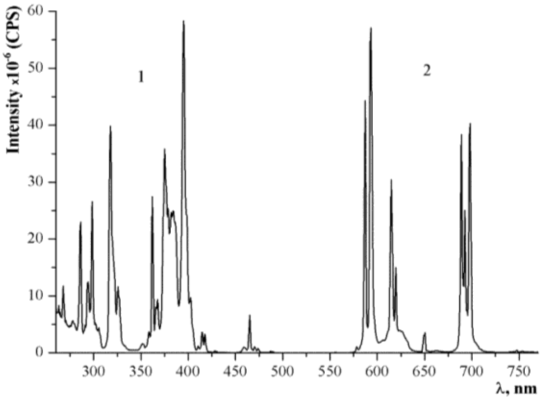

Fig. 6. Excitation and luminescence spectra of EuF_3 with a slit of 1-1 nm: 1 - excitation spectrum at λ_{em} = 593 nm, 2 - luminescence spectrum at λ_{exc} = 395 nm

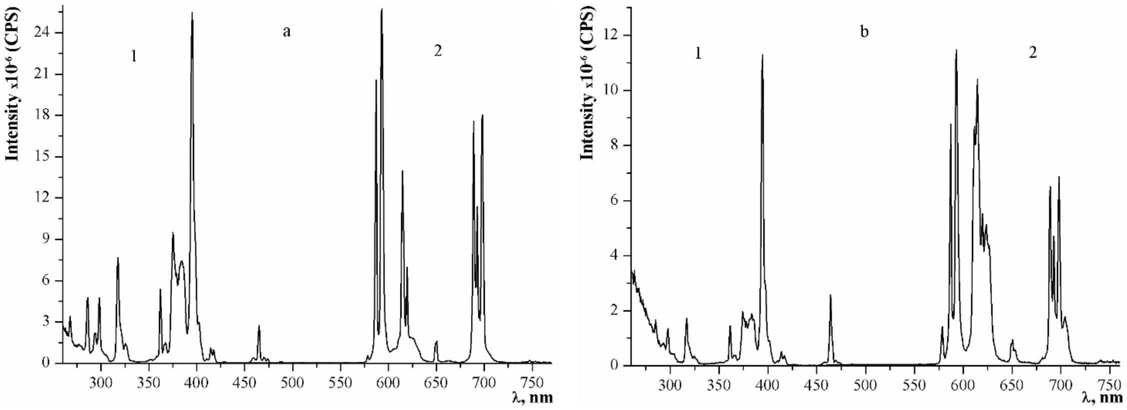

Fig. 7. Excitation and luminescence spectra of EuF_3 in the ZnS (y.) – EuF_3 system with a slit of 1.5-1 nm: (a) - mechanical mixture; (b) - heat-treated sample; 1 - excitation spectrum at λ_{em} = 593 nm, 2 - luminescence spectrum at λ_{exc} = 395 nm

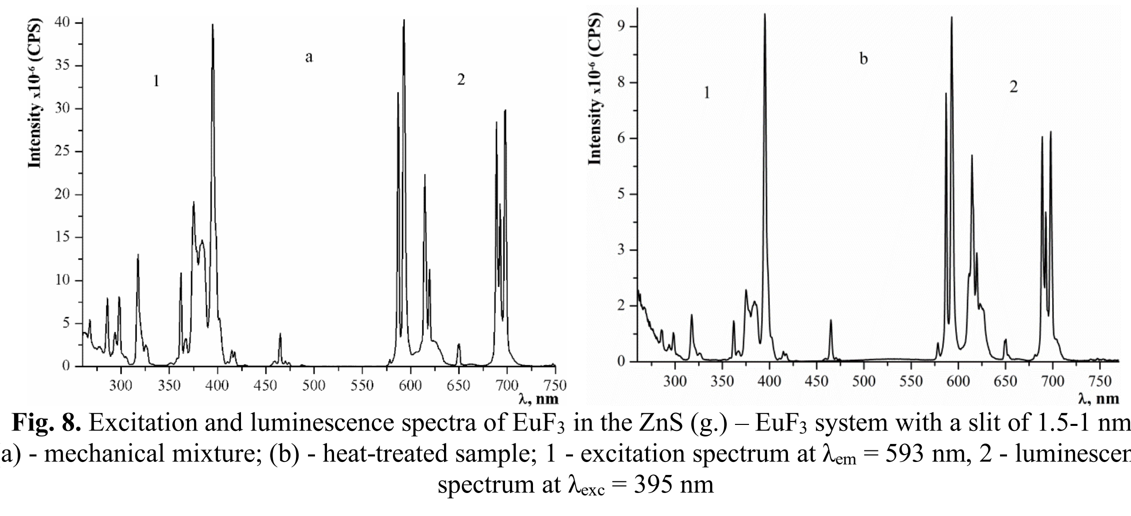

Fig. 8. Excitation and luminescence spectra of EuF_3 in the ZnS (g.) – EuF_3 system with a slit of 1.5-1 nm: (a) - mechanical mixture; (b) - heat-treated sample; 1 - excitation spectrum at λ_{em} = 593 nm, 2 - luminescence spectrum at λ_{exc} = 395 nm

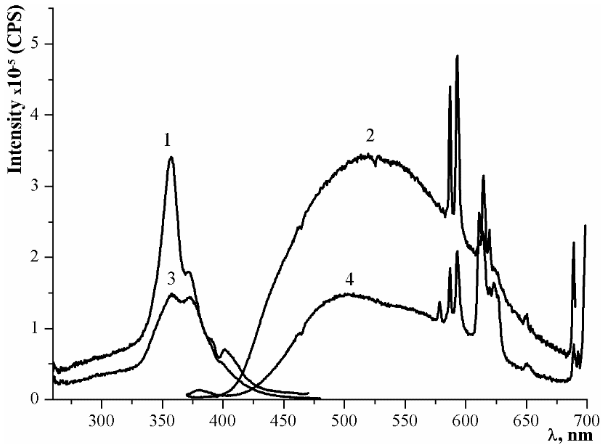

Fig. 9. Excitation and luminescence spectra of ZnS (y.) in the system: ZnS (y.) – EuF_3, mechanical (1, 2) and heat-treated (3, 4) mixtures, slit 5-1 nm: 1 - excitation spectrum at λem = 520 nm, 3 - excitation spectrum at λ_{em}=504 nm; 2, 4 - luminescence spectra at λ_{exc}=357 nm.

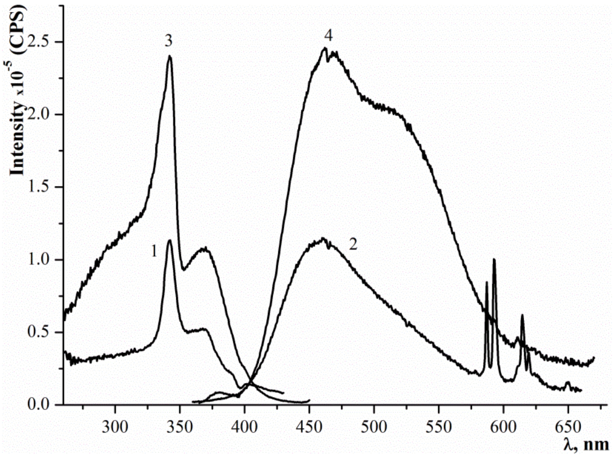

Fig. 10. Excitation and luminescence spectra of ZnS (g.) in the system: ZnS (g.) – EuF_3, mechanical (1, 2) and heat-treated (3, 4) mixtures, slit 5-1 nm: 1, 3 - excitation spectra at λ_{em} = 461 nm; 2, 4 - luminescence spectra at λ_{exc} = 342 nm

effect on the luminescence spectra of EuF_3 is the calcination of the batch, which results in a 75 – 80% decrease in luminescence intensity, except for ZnS (g.). In this case, the reason for the decrease is most likely the chemical interaction between the components with the conversion to other Europium compounds, in particular, EuF_2, which does not emit at all [5]. In addition, the formation of other Europium compounds that are not active in emission cannot be ruled out. The luminescence intensity of ZnS is significantly lower – several times and tens of times compared to EuF_3. At the same time, unlike EuF_3, the nature of the luminescence and its mechanism for ZnS is not fully understood [5]. It is undeniable that the luminescence intensity of ZnS (y.) is several times higher (Fig. 9) compared to that of ZnS (g.) (Fig. 10), which suggests that the main source of emission is most likely the impurity of the oxygen-containing compound ZnO. As with the other component, EuF_3, a several-fold decrease in intensity is observed for ZnS samples when added to the mixture (dilution effect). The calcination of the mixture significantly affects the luminescence intensity (a twofold decrease) compared to the initial component rather than their mixture; therefore, it has not yet been possible to unequivocally determine which effect more significantly affects the luminescence intensity – dilution or interaction. At the same time, the luminescence intensity of the thermally treated sample of the ZnS (g.) – EuF_3 system is, on the contrary, higher than that of the mechanical mixture, which currently seems somewhat paradoxical. The absence of Eu(II) luminescence was somewhat unexpected, however, it is known that EuF_2, which is formed, in our opinion, as a result of reactions (1-5), does not possess luminescent properties itself [5].

Conclusions

As a result of the analysis of the ZnS–EuF_3 systems by infrared and luminescence spectroscopy methods, data were obtained indicating the course of the reaction according to a likely redox mechanism with the formation of Europium (II) compounds. This is also indicated by such signs as a noticeable weight loss and a significant decrease in the intensity of luminescence of the mechanical mixture after its heat treatment, with the exception of the heat-treated sample of the ZnS (g.) – EuF_3 system. It was found that the luminescence of the initial sample of the ZnS (y.) – EuF_3 system has a greater intensity than the sample of the ZnS (g.) – EuF_3 system under the same conditions. Obviously, this phenomenon occurs due to the ZnO impurity in the initial ZnS (y.), the presence of which is confirmed by infrared spectra. Given the nature and composition of the interaction products in the ZnS–EuF_3 system, it is possible to predict its prospects for use as a base material for optics in the IR range of the spectrum.

Conflicts of interest:

The authors declare no conflict of interest.

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Дослідження взаємодії Цинку сульфіду з Європію (III) фторидом спектроскопічними методами

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Проведено дослідження взаємодії сульфіду Цинку, одержаного методом самопоширюваного високотемпературного синтезу та очищеного від кисню, з фторидом Європію (III). Вивчено оптичні властивості отриманих систем. На спектрах люмінесценції спостерігається зменшення її інтенсивності для зразків після їх термообробки, що відбувається через можливий перебіг реакції з частковим зникненням фториду Європію (III). Висунуто припущення щодо окисно-відновного механізму взаємодії між реагентами з утворенням фториду Європію (II) та інших сполук.

Ключові слова: фторид Європію, сульфід Цинку, ІЧ спектроскопія, фотолюмінесцентна спектроскопія.