

FEATURES OF MANGANESE DIFFUSION IN ZnS POWDERS

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The diffusion of manganese ions in powder-like zinc sulfide after its thermal doping with Mn has been studied. Photoluminescence (PL) and Raman scattering (RS) of light were measured at various times after doping having been completed, which allowed us to trace the process of Mn diffusion in ZnS. It has been shown that the processes of diffusion and incorporation of Mn ions into the crystal lattice of a ZnS specimen practically come to the end after the 240-h holding of the specimens under ambient conditions at $T = 300$ K.

1. Introduction

Thermal doping of powder-like zinc sulfide with manganese is, from the technological point of view, one of the simplest and cheapest methods of producing powder-like luminophors which emit light in the red-orange range of the spectrum. Therefore, the interest in those luminophors has not been relaxing for more than half a century. Some aspects of the luminescent center properties formed with the assistance of manganese [1–10], as well as other impurities [11–13], in zinc sulfide have been studied so completely that there is a possibility to monitor the behavior of impurity atoms in ZnS, making use of the PL method. The authors of works [14–16] have demonstrated a successful usage of the PL method for monitoring the behavior of implanted atoms in the specimens at various treatments of the latter after implantation.

It is known well that a Mn impurity in ZnS forms two groups of luminescent centers. The first group includes Mn_{Zn} ; it constitutes about 90% of the total concentration of Mn in ZnS. The second one involves Mn ions at interstitial positions and at places of defect accumulation — mainly near dislocations [1, 4]. The emission properties of luminescent centers formed by Mn^{2+} ions, which have replaced Zn^{2+} ones isovalently, depend very strongly on the ion environment. The probability of radiative transitions in Mn^{2+} ions is low, because the latter reside in the

cubic field of the T_d -symmetry, where the radiative transitions in Mn are forbidden. A reduction of the intracrystalline field symmetry from T_d to C_{3v} increases the probability of radiative transitions in the Mn^{2+} ion itself. But in order that this ion may emit light, it is necessary that a sensitizer should be present near the dot center. In this case, a radiative transition ($\lambda_{max} = 557$ nm) of one of the $3d$ -electrons takes place from the first excited state ${}^4T_1({}^4G)$ to the ground one ${}^6A_1({}^6S)$ [2, 7, 9]. The authors of works [2, 7, 9] showed that the PL band with $\lambda_{max} = 557$ nm is caused by emissions of several luminescent centers (one cubic center, two axial ones, and a hexagonal center) which are situated at the tetrahedral nodes of the crystalline lattice of zinc sulfide with defects.

As a rule, the most intense luminescence connected with the Mn impurity in ZnS is distributed between the elementary bands with $\lambda_{max} = 578$ and 600 nm [1]. The luminescent centers, which are responsible for those bands, are located at the defective sites of the ZnS crystal lattice, where the symmetry of the intracrystalline field is low. The same places, as a rule, are the centers of accumulation of various defects which are capable to fulfill the functions of luminescence sensitizers. The authors of works [1, 7] considered the PL band with $\lambda_{max} = 635$ nm to be connected with the emission in the α -Mn phase, when such a phase is formed in zinc sulfide at high concentrations of Mn.

This work sums up the results of the series of experiments dealing with the researches of structural transformations in the ZnS:MnS system after its annealing at $T = 800^\circ\text{C}$.

2. Experimental Object and Method

The Zn powder (ETO.035.295 TU) was annealed in the presence of (β)MnS. Annealing was carried on in quartz

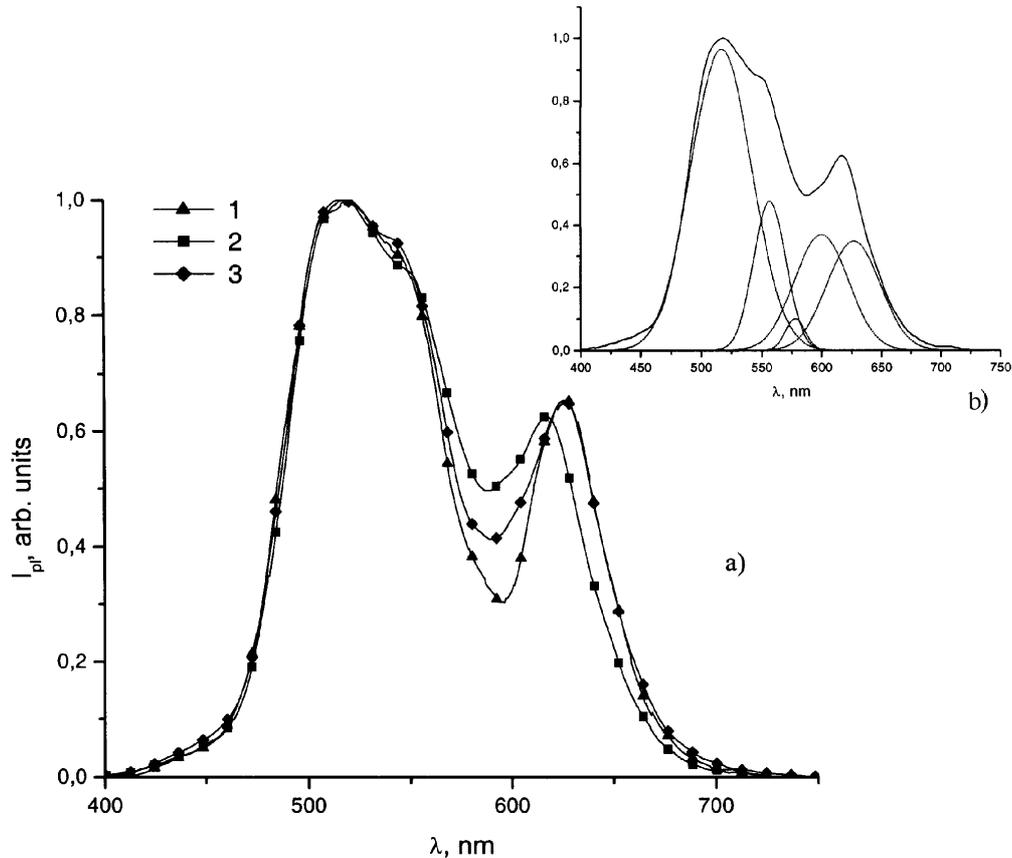


Fig. 1. *a* — PL spectra of the ZnS:Mn powder recorded after 1.6 (1), 9.1 (2), and 24 h (3) after its thermal doping; *b* — decomposition of a typical PL spectrum of the specimens of the first group into its components

test tubes at a temperature of 800°C during 180 min. The concentration of Mn in ZnS amounted to 0.02 g of Mn per 1 g of ZnS. In order to impede the air access to powders in the course of annealing, we used, in all cases, a gas gate fabricated of granulated activated coal which covered ZnS:MnS with a 3-cm layer. After annealing, the doped powder was kept at ambient temperature and provided the free access of air.

The PL spectra were measured on a KSVU-23 installation at $T = 300$ K. Photoluminescence was excited by the emission of a nitrogen laser ($\lambda = 337.1$ nm). The RS spectra were recorded making use of a DFS-24 double monochromator. The line $\lambda = 514.5$ nm of a 100-mW argon laser was used for excitation. The spectra were recorded in the 45-degree geometry. After the powder having been cooled down to $T = 300$ K, the PL and RS spectra were recorded at certain time intervals.

3. Experimental Results and Their Discussion

The PL spectra of the ZnS:Mn powder subjected to thermal doping are shown in Figs. 1–3. They are involved contours which consist of 3–5 bands. To define the parameters of those bands which compose the PL spectra, we used a procedure that included a consecutive subtraction of the next PL spectra. This allowed us to decompose the PL spectra into their components. The band parameters, determined in such a way, correlate well with the literature data [1–10]; therefore, we used these values in our further considerations (see Figs. 1, *b*; 2, *b*; and 3, *b*).

The PL spectra obtained in this work can be divided by their forms, which are connected to the specimen's prehistory, into three groups. In Fig. 1, *a*, the PL spectra of the powders from the first group, which were recorded within the time interval 0–24 h after the end of doping the specimens with manganese, are depicted. From Fig. 1, *b*, one can see that the PL spectra of the powder,

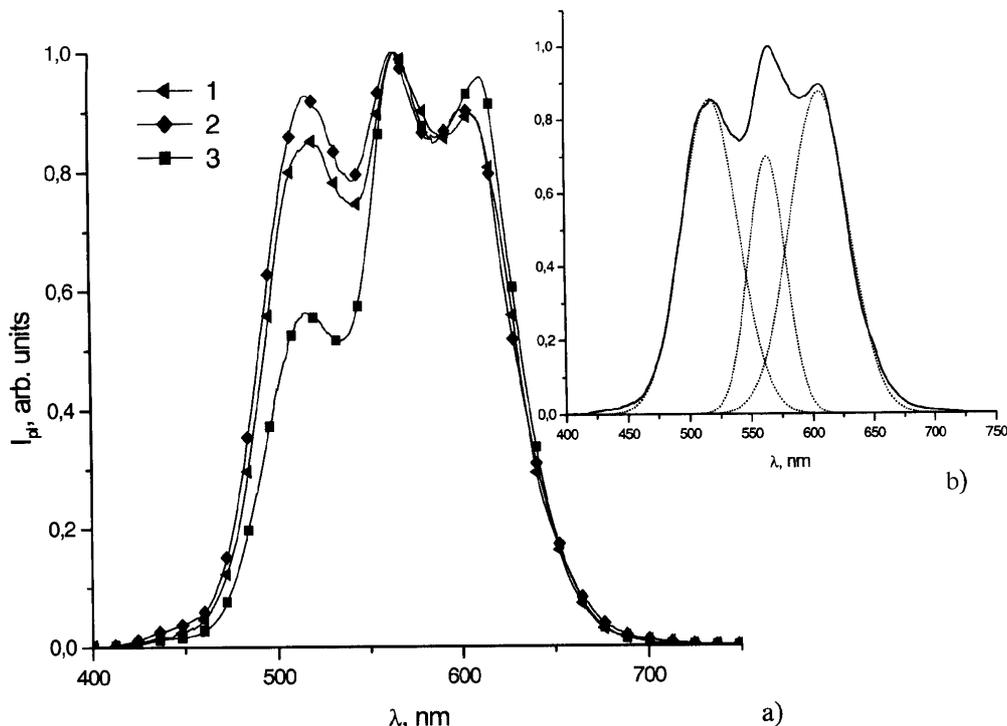


Fig. 2. *a* — PL spectra of the ZnS:Mn powder recorded after 24 (1), 26 (2), and 72 h (3) after its thermal doping; *b* — decomposition of a typical PL spectrum of the specimens of the second group into its components

which has been residing in the open air for no more than 24 h, contain a series of PL bands: two strongly overlapping bands with $\lambda_{\max} \approx 517$ and 557 nm in the short-wave range and two bands with $\lambda_{\max} \approx 600$ and 630 nm in the long-wave one. We note that holding the luminophor obtained by us in air for 9 h resulted mainly in the variations in the long-wave side of the spectrum. From Fig. 1, *a*, one can see that, in this spectral range, there occurs a redistribution of intensities among the bands with $\lambda_{\max} \approx 578$, 600, and 630 nm, which manifests itself in the spectrum, first, as a displacement of the maximum of the 630-nm band by 10 nm towards the short-wave side (curve 2), and, then, as its return to the previous position (curve 3).

Concerning the PL bands with $\lambda_{\max} \approx 517$, 557, and 630 nm, holding the luminophor for 24 h in air after its thermal doping had practically no effect on their intensities. In works [17, 18] devoted to studying the band in pure ZnS at 510–520 nm, it was shown that the emission of this band is caused by a deep acceptor which is a doubly ionized vacancy of sulfur. According to this model, the radiative transition is exerted from the valence band onto the defect level. The PL bands with the maxima at 557 and 630 nm are connected with Mn

ions located at the sites of the crystal lattice and with MnS dissolved in the ZnS lattice, respectively [1].

The analysis of the intensity ratio between the bands $\lambda_{\max} = 578$ and 600 nm allowed us to assume that, during the indicated time, a transfer of interstitial Mn to the localization region of dislocations takes place in the material obtained [1, 5].

Fig. 2, *a* displays the PL spectra of the specimens from the second group. The holding period for them after their annealing amounted to from 24 to 72 h. The spectra of the specimens of this group differ considerably from those of the first group. They are all composed of three distinctly resolved PL bands with the maxima at 517, 564, and 606 nm (see Fig. 2, *b*). As is seen from Fig. 2, *a*, the main modification of the spectrum that occurs within this time interval is a 40% reduction of the 517-nm band intensity with respect to the maximum of the spectrum ($\lambda_{\max} = 564$ nm) after a 30-h holding of the luminophor in air. It may be connected to a decrease of the sulfur vacancy concentration owing to the diffusion of oxygen in ZnS, as well as to the ultimate dissolution of the MnS phase in zinc sulfide.

Fig. 3, *a* presents the third group of the PL spectra which have been obtained from specimens after their

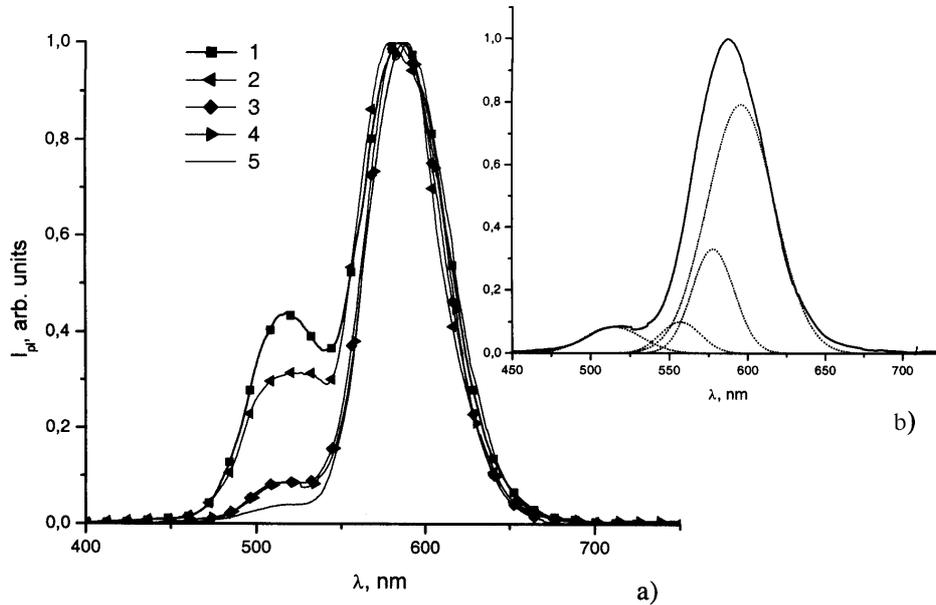


Fig. 3. *a* – PL spectra of the ZnS:Mn powder recorded after 11 (1), 25 (2), 30 (3), 153 (4), and 275 days (5) after its thermal doping; *b* – decomposition of a typical PL spectrum of the specimens of the third group into its components

holding in air during the period from 11 days to 9 months. The spectra of this group of specimens consist of two bands with the maxima at 517 and 585 nm (and a halfwidth of 60 nm). It should be emphasized that the increase of the period of passivation of the powder in air and holding the specimens after their thermal doping for 270 days result in the practically total fading of the PL band with the maximum at 517 nm. According to the literature data, the broad emission band with the maximum at 580–590 nm is a cumulative result of the luminescence of the bands at 578, 553, and 600 nm (see Fig. 3,*b*). Confronting the intensity of emitted energy and probable values of the factors of the intracrystalline field at various places of the ZnS crystal, the authors of works [1,5] drew a conclusion that the band at 557 nm is connected with Mn ions located at the crystal lattice sites, while the bands at 578 and 600 nm with Mn ions situated in the vicinity of dislocations and at octahedral interstitials, respectively.

The measured RS spectra are presented in Fig. 4. As is seen from the figure, they include the lines that correspond only to phonons in ZnS. This fact testifies to that a macroscopical ZnO phase was not formed in our material, despite the long stay of the latter in air.

4. Conclusions

Thus, the results obtained allowed us to draw a conclusion that, within the first 24 h after annealing,

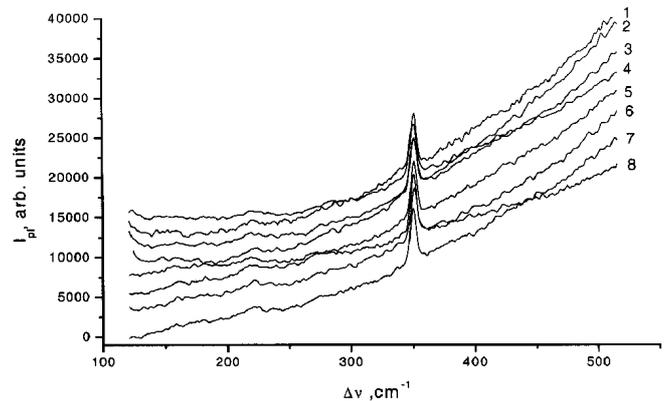


Fig. 4. Raman spectra of the ZnS:Mn powders Zn:Mn recorded after 0 (1), 3.6 (2), 22.5 (3), 27.5 (4), 52 (5), 94 (3), 196 (4), and 261 h (5) after their thermal doping

the diffusion of Mn from the near-surface regions into the bulk of the specimen and its transfer from interstitial positions, first, to the localization region of dislocations and, afterwards, to the lattice sites, with Zn ions being substituted, take place. At the second stage, i.e. within the period of 24–72 h, the diffusion of Mn from the surface to the bulk of ZnS practically comes to the end. The main part of the manganese impurity occupies the sites of the ZnS crystal lattice, having replaced zinc isovalently. Starting from 30 h, the sulfur vacancy concentration decreases, owing probably to a prolonged

access of oxygen. However, as the RS studies showed, this does not result in the formation of the ZnO phase in zinc sulfide. The reported results testify to that the processes of diffusion and incorporation of Mn atoms into the ZnS crystal lattice practically comes to the end after 240 h, provided the free access of air.

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ОСОБЛИВОСТІ ДИФУЗІЇ МАРГАНЦЮ В ПОРОШКАХ ZnS

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Резюме

Проведено дослідження дифузії Mn в порошкоподібному сульфіді цинку після його термолегування. Результати вимірювання фотоломінесценції і комбінаційного розсіяння світла у сульфіді цинку, проведені через різні проміжки часу після його легування Mn, дозволили прослідкувати процес дифузії Mn в сульфіді цинку. Показано, що процеси дифузії і вбудовування Mn в кристалічну ґратку ZnS практично закінчилися через 240 год після його термолегування і зберігання при температурі $T = 300$ К в умовах вільного доступу повітря