

## INFLUENCE OF DEFECT COMPOSITION ON OPTICAL ACTIVITY OF $\text{Mn}^{2+}$ IONS IN ZnS CRYSTALS

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The  $\text{Mn}_{\text{Zn}}^{2+}$  ion intracentred luminescence in ZnS crystal ( $\lambda_{\text{max}}=590\text{nm}$ , FWHM=160-210meV) and its relation to the native, impurity (the background and aluminum) defects formed at the crystal annealing in the bismuth melt at  $950^\circ\text{C}$  during 100hrs was studied. The luminescence of the aluminum doped and undoped ZnS single crystals, before and after annealing, were studied. The aluminum presence on the one hand creates sensitizing centers (the radiation bands close to 400nm and 450nm) and on the other hand makes difficult Mn doping of the crystal. It is supposed that the temperature influence on the  $\text{Mn}_{\text{Zn}}^{2+}$  ion is determined by the position of the electron and hole Fermi cuazi-levels relative to the deep levels, acting as recombination radiative and nonradiative centers the nature of which is determined by the type of crystal lattice defects. The relation between blue centers of recombinative radiation and Mn bands was shown

In the optical absorption and luminescence spectra of II-VI compound crystals doped with the atoms having uncompleted 3d-shell the intracentered transitions in the impurity atoms reveal themselves. The study of such ions and, particularly, of two-valence manganese ions is of practical interest, as  $\text{ZnS:Mn}^{2+}$  luminophor is the most efficient electroluminescent phosphorous [1-5]. Two types of the electron excitation: band to band and intracentered one bring their contribution to the luminescence, often considerably interacting with one another. The main subject of the given paper is the investigation of the optically excited (PL) and intracentered luminescence (IL) of the  $\text{Mn}_{\text{Zn}}^{2+}$  ions and its relation with the inherited and impurity (the background and aluminum) defects in ZnS crystals after their annealing in bismuth melts. On the formation of photoluminescence (PL) spectra of  $\text{ZnS:Mn}^{2+}$  a considerable influence is exercised by the local symmetry of the crystalline field [1,6,7]. In the PL process the  $\text{Mn}^{2+}$  ions absorb the radiation from the manganese characteristic absorption region. For to enhance the luminescence efficiency a sensitization impurity is introduced into the crystal the radiation of which leads to the resonance excitation of  $\text{Mn}^{2+}$  ions due to dipole-quadrupole interaction. The use of  $\text{Mn}^{2+}$  as a sonde impurity at ZnS PL studies allows us to get information about the peculiarities of the inherited and impurity defects leading to the appearance of self-activated luminescence (SAL). The effect of sondage using  $\text{Mn}^{2+}$  ions is determined by the fact that manganese is a paramagnetic impurity. The ion intracentred transitions reveal themselves in ZnS as a characteristic radiation close to 590nm, depending on the symmetry of the local crystalline field. The radiation from this region of spectrum related to the other known inherited and impurity defects reveals itself rather weakly. Proceeding from this the ZnS single crystals with the background impurities and aluminum doped, before and after the annealing were investigated. The annealing was carried out in the silica ampoules at  $950^\circ\text{C}$  during 100 hrs in the Bi melts and bismuth melts with the addition of 5at.% of Mn or  $6 \cdot 10^{-3}$  and  $1 \cdot 10^{-2}$  at% Al with the subsequent tempering outside the furnace. The temperature variation of the PL spectra from a crystal cleavage perpendicular

to the surfaces contacting with the melt during the annealing was studied both in the crystal volume and subsurface region as well in the temperature range from 77 up to 300K.

At 77K the luminescence spectrum of the parent crystal with the background impurities is represented by two bands with the maxima situated at 390nm and 650nm accordingly. At 300K the spectrum consists of a single band with the maximum situated close to 470nm. In the PL spectra of the starting samples, containing aluminum the two radiation bands with the maxima at 445nm, 650nm (77K) and 480nm, 660nm (300K) accordingly were observed.

After the annealing of the both types of starting crystals in the Bi without any additions in their PL spectra at 77K the PL spectrum consists of two bands with the maxima situated at 400nm (SAL) and 650nm. At 300K a band centered at 595nm with the FWHM of 160meV predominates.

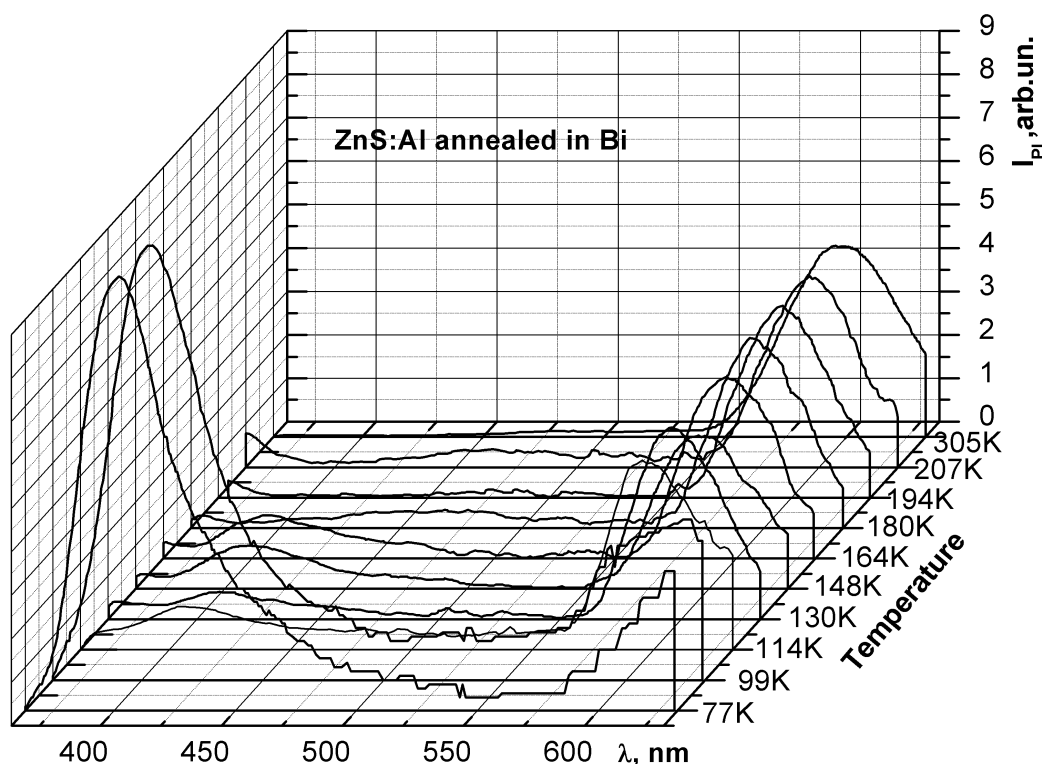


Fig.1. The PL spectra at different temperatures of ZnS: AL crystal annealed in Bi melt.

The analysis of PL spectra temperature evolution had shown that beginning from approximately 105K a peculiarity close to 590nm reveals itself, which at about 115K is formed into a predominant band. At 300K this band remains as a single one in the PL spectrum (Fig1). This band FWHM temperature dependence in the  $T^2$  scale (Fig.2) is linear, which along with the preservation of its maximum position in the temperature interval 100K...300K can indicate the intracentred character of the radiative electron transitions responsible for its appearance in the PL spectrum.

So the PL band with the maximum close to 590nm in the studied crystals can be attributed to the manifestation of the radiation on  $Mn^{2+}$  ions. The bursting of the band at 590nm is accompanied by the quenching of the SAL violet radiation at 390nm (Fig1). The last fact can indicate the participation of the given radiation in the excitation of the manganese

band, i.e. the given centre is a sensitization one and its radiation energy corresponds to the  $\text{Mn}_{\text{Zn}}^{2+}$  characteristic radiation  $\approx 3,20\text{eV}(393\text{nm})$  at 300K) [1,7].

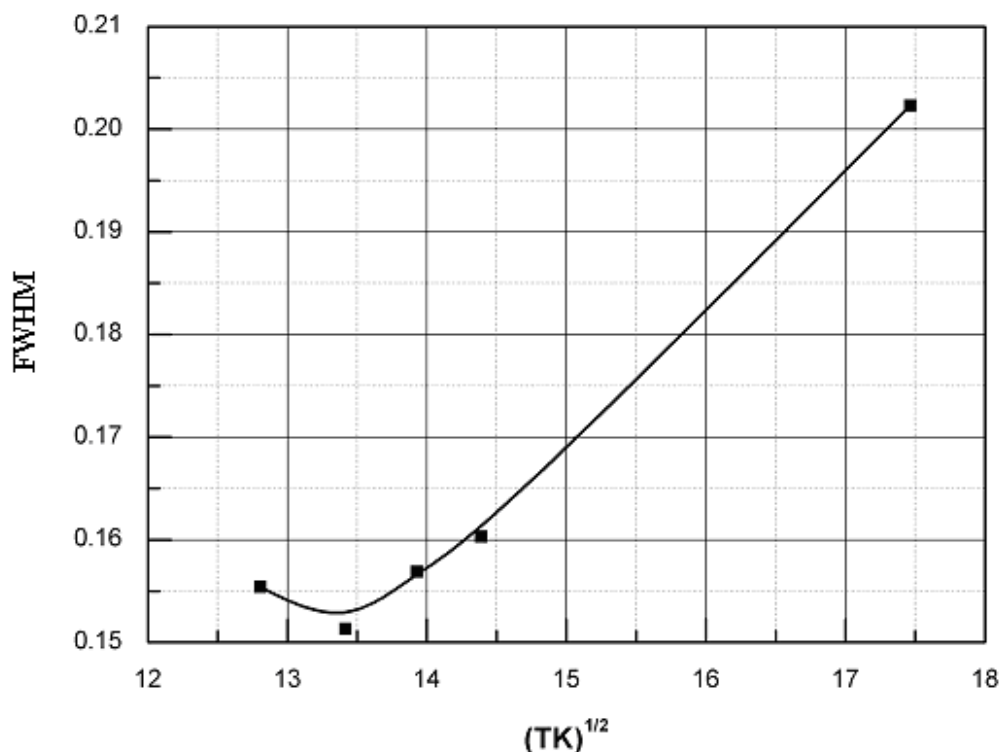


Fig2. The band FWHM temperature dependence in the  $T^2$  scale.

After the ZnS annealing in  $(\text{Bi}+10^{-2}\text{ at.\%Al})$  melt the PL spectrum at 77K consists of two bands with the maxima situated at 460nm and 540nm. Beginning with the temperatures of 105K (Fig3) the formation of the radiation band with the maximum close to 590nm is observed. At 127K this band predominates in the PL spectrum and then in the temperature range of 210-305K sharply quenches and remains only as a peculiarity on a long wavelength slope of the fundamental band with the maximum at 540nm. One should observe the fact of the absence at 77K of the radiation with the maximum situated close to 400nm. The appearance of the manganese radiation is accompanied by the decrease of the radiation intensity with the maximum close to 460nm.

After ZnS:Al crystals annealing in the Bi melt with the addition of  $6 \cdot 10^{-3}\text{ at.\%Al}$  the PL spectrum at 77K consists of a wide band with the maximum at 400nm and a shoulder close to 450nm. At the measurement temperature increase at 133K the band with the maximum at 590K emerges which at 245K disappears almost entirely.

After ZnS:Al crystals annealing in the Bi melt with the addition of 0,5at.%Mn in the whole measurement temperature range the predominating radiation with the maximum close to 590nm and a FWHM of  $\approx 210\text{eV}$  is observed (Fig.4). This value is higher than for a sample where Mn centers were formed at the crystal fabrication and the manganese is uniformly distributed in the whole volume. So, one can suppose, that in the subsurface region the lattice defectness is higher than in the second case

According to the temperature behavior of this band and its spectral position, one can relate its appearance to the intracentered transitions in the manganese ion. The considerable increase of this band FWHM comparable with the previous case, when in the bismuth melt the manganese was not added, is related, apparently, to the fact that the tempering after

annealing with the manganese additions increases the crystal defectness, and, hence, local disorder of the crystal field, which enlarges the  $\text{Mn}^{2+}$  ion radiation band occurs.

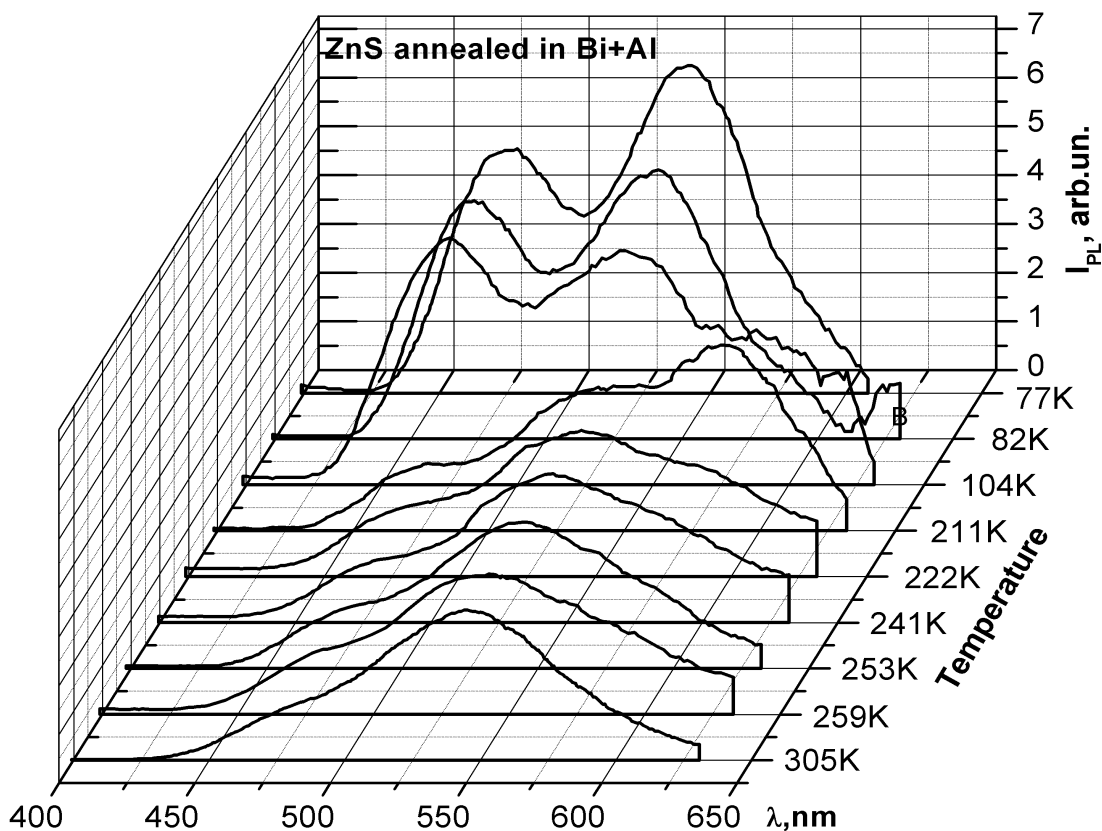


Fig3. The PL spectra at different temperatures of ZnS crystal annealed in Bi+Al melt.

Along with this, due to the high concentration of the manganese centers the formation of Mn-Mn pairs is possible [8]. The appearance of the manganese pairs in the crystal lattice leads to the decrease of PL intensity in the  $\text{Mn}_{\text{Zn}}^{2+}$  ions radiation band in the luminescence spectra, i.e. to its quenching. The same influence on the PL spectrum will have the radiative and non-radiative centers appearing at the atoms recharging, through which a competing with intracentred dissipation of the energy, excited by the ZnS crystal electron subsystem occurs. The named centers recharging at the temperature variation are related to the electron and hole Fermi cuazi-levels displacement, A transformation of the deep levels, which are sensitizers of the intracentred transitions, from recombination levels into the non-equilibrium carrier capture levels and vice-versa, occurs. In its turn this manifests itself in the appearance in the Pl spectra at certain temperatures of the Mn band and its quenching. Earlier [9] we established that interphase interaction at the bismuth melt – ZnS crystal interface generates Zn vacancies. In the subsurface region this enhances the Mn inculcation with the ion formation, occurring according to the bipolar vacancy-hopping diffusion and leads to the impediment of the further manganese doping of the ZnS crystal, due to the formation of, apparently, immobile local charged regions in the dislocation vicinity appearing at the tempering after annealing in bismuth melts. The aluminum presence in the melt, possibly, decreases the efficiency of the manganese doping, as aluminum also occupies the zinc knots of the crystal lattice and from this point of view is competing with the manganese.

It was shown that the starting set of the background, impurity and native defects before the annealing determines the possibilities and the level of ZnS crystal doping from the

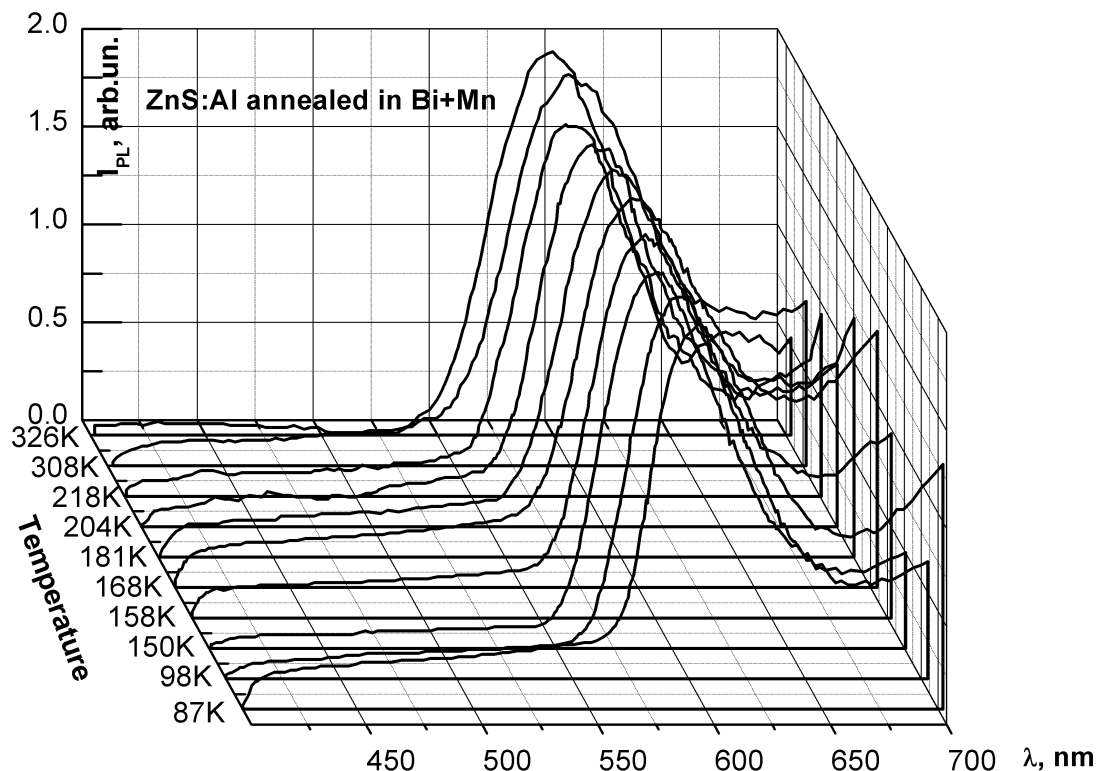


Fig.4. The PL spectra at different temperatures of ZnS:AL crystal annealed in Bi+Mn melt.

bismuth melt. The aluminum presence on the one hand creates sensitizing centers, and on the other hand makes difficult Mn doping of the crystal. The intracentred radiation of  $\text{Mn}_{\text{Zn}}^{2+}$  ion, after crystal doping from Bi melt, is concentrated at the crystal surface and due to the formation of the immobile local regions in the defect vicinity. It is supposed that the temperature influence on the  $\text{Mn}_{\text{Zn}}^{2+}$  ion is determined by the position of the electron and hole Fermi cuazi-levels relative to the deep levels, acting as recombination radiative and nonradiative centers.

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