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## COMPOSITION DEPENDENCE OF PHOTOLUMINESCENCE SPECTRA IN $Zn_{1-x}Mg_xSe$ MIXED CRYSTALS<sup>†</sup>

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$Zn_{1-x}Mg_xSe$  mixed crystals with  $x$  ranging from 0 to 0.56 were obtained by high pressure Bridgman method. It has been found that a phase transition from sphalerite structure to wurtzite one occurs at  $x = 0.185 \pm 0.03$ . The crystals exhibit blue-violet and yellow-green (depending on  $x$ ) luminescence in the temperature range from 40 K to room temperature. An attempt has been also made to dope  $Zn_{1-x}Mg_xSe$  crystals with Al. The incorporation of Al produces a strong green photoluminescence in the temperature range from 40 K to 300 K but almost completely quenches the near-band-edge emission.

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Mixed crystals of II-VI binary compounds with Mg chalcogenides have recently attracted much attention which result from the possibility of tuning of band gap energies and lattice constants of these materials by adjusting Mg content in the alloy. This paper deals with the study of photoluminescence spectra of a series of  $Zn_{1-x}Mg_xSe$  crystals with  $x$  up to 0.56.

Crystals were grown by the high pressure Bridgman method [1]. The starting material was formed using a powder mixture of ZnSe and magnesium. For some samples selenium powder was added. In the case of aluminium doping an appropriate content of Al metal was admixed. The crucible charge was preheated first at the temperature 970 K for 6 hours for preliminary mixing and next it was kept at the temperature 1830 K for several hours. Thereafter the crucible was moved out of the heating zone with the lowering speed of 4 mm/h. It was found that the obtained crystals have a gradient of Mg content along the growth direction. For

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investigations the crystals were cut into 1 mm thick slides, mechanically polished and chemically etched as described in [1].

Electron-probe microanalysis was applied for determination of the composition. The measurements were performed in wave dispersion mode exploiting  $K_\alpha$  lines of Zn, Mg and Se. Pure elements were used as standards. X-ray diffraction experiments were done using a Bragg-Brentano powder diffractometer, Ni-filtered Cu  $K_\alpha$  radiation and a proportional counter. For  $\text{Zn}_{0.94}\text{Mg}_{0.06}\text{Se}$  sample the full width at half maximum of the rocking curve of  $31.5''$  was obtained. Phase transition from sphalerite structure to wurtzite has been found to occur at  $x = 0.185 \pm 0.03$ .

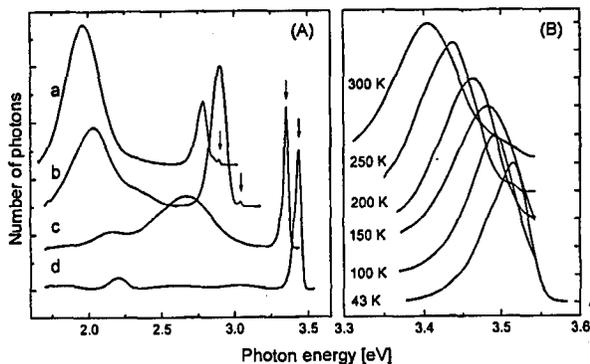


Fig. 1. Photoluminescence spectra of  $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$  crystals: (A) for different concentration of magnesium:  $x = 0.08$  (a),  $x = 0.21$  (b),  $x = 0.48$  (c) and  $x = 0.53$  (d); (B) the temperature evolution of the high energy part of the spectrum for  $\text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}$ .

The photoluminescence of investigated crystals was excited with a He-Cd laser. Figure 1A presents photoluminescence spectra of  $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$  crystals for different  $x$  values. Typical spectrum consists of near-band-edge (excitonic), shallow D-A pairs (edge) and deep level emission bands. It can be noticed that a relatively strong edge emission is observed only for low concentration of magnesium. With increasing of the Mg content, a rise of the ratio of the intensities of near-band-edge to deep level bands is observed. For higher Mg concentrations the composition disorder induces broadening of the emission bands. For the highest obtained  $x$  value ( $x = 0.56$ ) the full width at half maximum of the near-band-edge line is about 62 meV which is considerably larger than that in ZnSe. Figure 1B shows the temperature evolution of the ultraviolet part of photoluminescence spectrum for  $\text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}$ . It must be noticed that the line of highest photon energy is observed up to room temperature for the whole investigated range of composition. In Fig. 2 the peak energy of near-band-edge emission is plotted as a function of the composition. The linear fit to the experimental data gives a band gap variation about 13 meV per percent of Mg content in the alloy. All as-grown  $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$  crystals with  $x > 0.3$  exhibit high electrical resistivity that does not decrease substantially after annealing in liquid zinc or zinc vapour. According to Chadi [2],

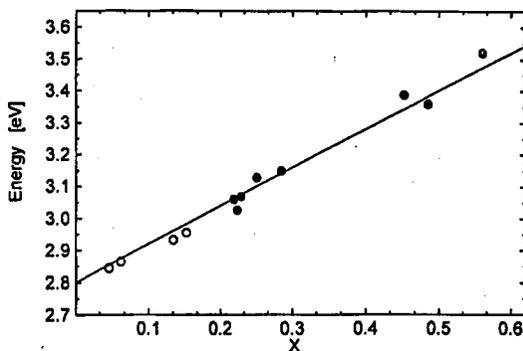


Fig. 2. Composition dependence of energy of the position of the near-band-edge emission line derived from PL spectra at  $T = 40$  K; open circles — sphalerite structure; full circles — wurtzite structure.

the  $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$  alloy could be successfully  $n$ -type doped by Al because it should not create localized deep donor state in ZnSe and MgSe and the formation process of DX centres for Al is endothermic. To check this prediction a first attempt was made to dope the mixed crystals with aluminium. Our preliminary results show that incorporation of Al into  $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$  gives strong “green” photoluminescence in whole range of temperature from 40 K to 300 K but almost completely quenches the near-band-edge emission. The photoluminescence spectra obtained for the  $\text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}:\text{Al}$  crystal at several different temperatures are given in Fig. 3. The luminescence centre responsible for the “green” band is probably of

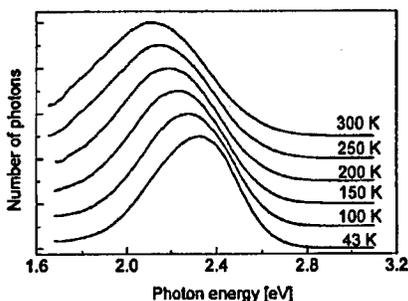


Fig. 3. Photoluminescence spectra of  $\text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}:\text{Al}$  at different temperatures.

the same kind as the one responsible for the self-activated luminescence in ZnS and ZnSe. The emission results from the recombination of donor–acceptor pairs which consist of an isolated IIIb group element on Zn site (shallow donor) and acceptor which is a complex of cation vacancy and the nearest neighbour IIIb group element (i.e.  $\text{V}_{\text{Zn}}\text{Al}$  or  $\text{V}_{\text{Mg}}\text{Al}$ ).

The obtained  $\text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}:\text{Al}$  crystals are also of high resistivity as the undoped ones. This suggests that the compensation process occurs in the inves-

tigated mixed crystals similarly as in ZnSe. According to Aven et al. [3, 4], in Al doped  $n$ -type ZnSe the major compensating defect is the  $V_{Zn}Al$  centre. Recently, Chadi [5] suggested that the donor and acceptor impurity compensation in II-VI semiconductors is caused by dopant induced bond instabilities. On the basis of the available data no positive identification of the mechanism responsible for compensation can be given now.

Present experimental findings on Al doping reported in this paper seems not to confirm the prediction of Chadi. Our latest observations indicate [6] that iodine could be a more suitable dopant.

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