ABSTRACT

Zn$_{1-x}$Mg$_x$Se crystals were grown in the range extending up to $x = 0.615$ and characterized using the X-ray diffraction and electron probe microanalysis. Below $x = 0.2$ there is a phase transition from sphalerite to wurtzite. The lattice constants are found to exhibit linear dependence on $x$ for both, the sphalerite and wurtzite structure types. For compositions close to the phase transition, the formation of 4H and 8H polytypes as main or secondary phases is observed. The energy gap in the investigated composition range is higher than that reported for thin Zn$_{1-x}$Mg$_x$Se layers on GaAs substrate.

INTRODUCTION

Solid solutions of II-VI compounds have found numerous applications in electronics. The general formula of cation substituted II-VI compounds is (A, X)$_2$B$_6$W$_4$, where the most often studied X metals are manganese and, only recently, magnesium. The investigated Mg-substituted compounds usually do not cover Mg-rich solid solutions, because MgS, MgSe and MgTe are unstable in air, and MgS and MgSe are of not tetrahedral NaCl structure type. Wide gap binary II-VI compound ZnSe (mineral name: stilleite) is the basis of solid solutions (such as Zn$_{1-x}$Mg$_x$Se$_{1-y}$S$_y$) which have potential applications in design of light-emitting diodes and lasers operating in green and blue wavelength range. The green II-VI semiconductor laser diodes based on (Zn,Cd)Se active layer surrounded by Zn(S,Se) guiding and (Zn,Mg)(S,Se) cladding layers with a room temperature continuous wave operating lifetime exceeding 100 hours have been already successfully fabricated. The construction of semiconductor lasers operating in the short wavelength region is an important step towards increasing the density of optical recording.

Development of the technology of Zn$_{1-x}$Mg$_x$Se$_{1-y}$S$_y$ requires first to determine the structural and physical properties of bulk Zn$_{1-x}$Mg$_x$Se and bulk Zn$_{1-x}$Mg$_x$Se$_{1-y}$S$_y$. In earlier structural studies, the Zn$_{1-x}$Mg$_x$Se solid solutions in the form of thin layers on ZnSe [1,2] and epitaxial layers on GaAs and InAs [3-6] have been investigated, in some cases [3,4] as a part of studies of quaternary Zn$_{1-x}$Mg$_x$Se$_{1-y}$S$_y$ system.

Zn$_{1-x}$Mg$_x$Se layers fabricated by Mg diffusion into ZnSe single crystals have probably been the first subject of studies of Zn$_{1-x}$Mg$_x$Se luminescent properties [1,2]. The authors of [1] have concluded that this material seems to be a suitable candidate for narrow band emitters for a range of wavelengths in the violet-ultraviolet. The results obtained in [1] have supported the postulate expressed in [7] to use (Zn,Mg)(S,Se) in optoelectronic devices. Immediately, studies of structural [3] and optical [8] properties of (Zn,Mg)(S,Se) thin layer systems followed. Investigation of structural [9-12] and optical [13,14] properties of bulk Zn$_{1-x}$Mg$_x$Se crystals have indicated similarities and differences between bulk crystals and thin layers of Zn$_{1-x}$Mg$_x$Se. This paper deals with the powder X-ray characterization of Zn$_{1-x}$Mg$_x$Se crystals grown from the melt in the range $0 < x < 0.615$, including some results...
This document was presented at the Denver X-ray Conference (D XC) on Applications of X-ray Analysis.

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briefly reported elsewhere [9-11]. This study is completed by a comparison of the energy gap obtained for the bulk crystals with that of thin layers.

EXPERIMENTAL

Zn$_{1-x}$Mg$_x$Se crystals were grown at N.Copernicus University by the high-pressure Bridgman method under pressure of 11 MPa. More details of the growth conditions may be found in [9,10]. Selected samples were annealed at 1170 °K for 40 h in liquid zinc or zinc vapor.

The composition was measured by the electron microprobe analysis (EPMA) in the wavelength dispersion mode (WDS) using the instrument JEOL-JXA-50A. The accuracy of the composition determination, $\Delta c$, is estimated to be 0.02. For selected samples, the composition was additionally controlled with the help of spectral analysis of solutions in argon plasma (ICP) using the plasma spectrometer SPECTROFLAME.

X-ray diffraction measurements were performed using an automated Bragg-Brentano diffractometer working in the step-scanning mode, using Ni-filtered CuK$\alpha$ radiation. The angular range studied was 4-160° (2θ). To minimize the effect of preferred orientation on peak intensities the samples were prepared by dusting finely ground crystal on a thin layer of vaseline.

Photoluminescence spectra were measured at $T=40$ °K using the SPECTRIM closed-cycle helium cryostat, an SPM-2 monochromator and He-Cd laser (326 nm radiation) as the excitation source.

RESULTS AND DISCUSSION

Samples with dominating Mg contribution ($x > 0.5$) are found to be instable in air. For this reason, the results obtained for the sample of the highest $x=0.615$ are thought to be less reliable, and, consequently, no attempts were made to prepare crystals of still higher $x$. (Thin layers have been reported to be hygroscopic over $x \approx 0.7$ [5]). The instability manifests itself by darkening of the sample surface and, after many days, by fragmentation into smaller pieces. Those of $x < 0.5$ remain transparent light yellow crystals during months of storage in air without any visible contamination. EPMA analysis shows that a gradient of Mg content occurs, with $x$ increasing by about or less than 0.1 along each crystal in the direction of its top. For low $x$, the bulk Zn$_{1-x}$Mg$_x$Se forms a sphalerite-type solid solution. For high $x$, it crystallizes in the wurtzite-type structure. The transition point lies between $x = 0.15$ and $x = 0.20$. This behaviour is different than that for thin layers deposited on GaAs and InAs where the sphalerite structure type has been observed in full investigated composition range and the transition to wurtzite has not been reported [3-6]. The only transition reported for thin layers was that to the NaCl type found for some samples with $x > 0.5$ in [4] and for $x = 1$ in [6]. For some samples of $x$ close to the phase transition, the presence of at least one polytype (usually 4H, in one case - 8H) as a main or secondary phase was observed. Annealing of 4H sample zinc vapour at $T=1250$ °K for 48 hours followed by rapid cooling resulted in wurtzite-type final structure. X-ray diffraction shows that small amounts of polytypes (probably mainly 4H) were formed in other unannealed and annealed crystals with $0 < x < 0.25$. X-ray and electron diffraction studies of polytypism in Zn$_{1-x}$Mg$_x$Se are in preparation and will be published elsewhere. Analogous formation of 4H and 8H polytypes has been reported, e.g., for Zn$_{1-x}$Mn$_x$Se [15] solid solutions.

Lattice constants for the sphalerite type Zn$_{1-x}$Mg$_x$Se match well with the linear approximation based on results of [3] (see Fig. 1). Also those of the wurtzite type can be approximated by linear dependences (Vegard's rule) on $x$ (see Fig. 2). Their values (in Å units) are described by the following equations with coefficients obtained by least-squares fitting:
Fig. 1. Lattice constant of the sphalerite-type Zn$_{1-x}$Mg$_x$Se as a function of magnesium content, $x$. Squares refer to bulk crystals, this work (the value for $x=0$, $a=5.6675$ Å is taken from [16]), open triangles refer to thin films from [3], open diamond to the thin film from [17].

\[ a = 4.0010 + 0.1878x \]  
\[ c = 6.5717 + 0.1930x \]  

The values for ZnSe ($a=4.0010$ Å, $c=6.5717$ Å) derived from eq. (1) and eq. (2) are slightly higher than those reported for wurtzite-type ZnSe ($a=3.996$ Å, $c=6.550$ Å [18]). Similar result can be obtained by extrapolation of Zn$_{1-x}$Mn$_x$Se data published in [16]. The extrapolated $a$ and $c$ values of the wurtzite-type polymorph of MgSe, $a=4.1888$ Å, $c=6.7647$ Å are by about 1% higher than those experimentally found in an early paper [19] ($a=4.145$ Å, $c=6.723$ Å). The present result is related to that for thin Zn$_{1-x}$Mg$_x$Se layers [6] giving a higher cation-cation distance: our result is 4.1888 Å, that derived from $a=5.91$ Å given in [6] is 4.186 Å, compared to the earlier data of [3] giving 4.165 Å. Despite of the minor problems with extrapolation of wurtzite data to ZnSe and MgSe, the lattice-constant dependence on $x$ for both, sphalerite and wurtzite, types of bulk crystals provides a way of determining $x$ value from X-ray diffraction experiments with a higher accuracy than the EPMA results.

Also the exciton transition energy, $E_{gw}$ (which is lower than the energy gap by the exciton binding energy, i.e. by a few tens of meV) at 40 K shows approximately linear dependence on $x$ for the given structure type (see Fig. 3). Its value expressed in eV is given by fitted lines:

\[ E_{gw} \text{ (sphalerite)} = 2.801 + 0.998x \]  
\[ E_{gw} \text{ (wurtzite)} = 2.854 + 1.035x \]
A nonlinearity in the band-gap dependence of composition was found for thin $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ layers in [6]. However, the deviation from linearity occurs there at Mg-rich layers: values reported for MgSe are 4.05 eV [17] and 4.0 eV [6] which are higher than:

a) the value 3.60 eV extrapolated from the Zn-rich samples of thin layers [3],

b) the value 3.799 eV obtained from eq. (3) for bulk sphalerite-type crystals

c) the value 3.889 eV obtained from eq. (4) for bulk wurtzite-type crystals.

Therefore, the behaviour of the energy gap for the Zn-rich alloys (up to $x$ about 0.6-0.7) may be concluded to be approximately linear whatever is either the structure type or the crystal form (bulk or layer).

Investigation of luminescence of two phase samples shows that the known small difference (of the order of 60 meV) in exciton transition energy between the sphalerite and wurtzite forms of ZnSe extends to $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ alloys and that the $E_g$ value for 4H polytype is located between those for sphalerite and wurtzite.
Fig. 3. The exciton transition energy of Zn_{1-x}Mg_xSe at 40 °K as a function of magnesium content, x. Solid circles and linear fit indicated by the dashed line refer to the wurtzite type, solid squares and the linear fit indicated by the solid line refer to the sphalerite type. Values for x=0 included in both these fits refer to the exciton line for sphalerite type $E_g \approx 2.802$ eV at $T \approx 4$ °K, for the wurtzite type $E_g \approx 2.860$ eV at $T < 15$ °K, both taken from [20]. Comparison with data reported for: thin layers at 77 °K - open diamonds and dotted line [3], thin layers at 4.2 °K - open squares [21], guided by dash dot line, and with data for bulk Zn_{1-x}Mn_xSe at $T=77$ °K [16] - crosses.

The difference between sphalerite and wurtzite is seen in Fig. 3 despite some scatter of experimental points caused by low accuracy ($\Delta x=0.02$) of the EPMA composition. The $E_g$ values are markedly higher than those reported in [3,6,21] for thin Zn_{1-x}Mg_xSe layers on GaAs and than $E_{gd}$ of Zn_{1-x}Mn_xSe bulk alloys reported in [16]. The luminescence in the blue wavelength range was observed for all our samples during EPMA measurements: the electron bombardement of the crystals caused very bright blue luminosity.

There is a remarkable similarity between (A,X)$_{II}^{IV}$ systems with X=Mg and Mn. The sphalerite-wurtzite transition, lattice constants, energy gaps, Mg and Mn solubility and even the polytypism are usually similar in such systems differing by the X element. Zn$_{1-x}$Mg$_x$Se and Zn$_{1-x}$Mn$_x$Se differ negligibly by lattice constants, the same 4H and 8H politypes were found in both systems at the region of sphalerite-wurtzite transition (the transition occurring for slightly differing x values). These similarities are due to the same valency and very close ionic radii of Mn and Mg. The energy gap increases with x for both systems, but the increase for Zn$_{1-x}$Mg$_x$Se is more pronounced.
CONCLUSIONS

Structural properties of Zn$_{1-x}$Mg$_x$Se solid solutions grown by the high-pressure Bridgman method were determined using the X-ray diffraction and EPMA. Just below $x=0.2$ there is a phase transition from sphalerite to wurtzite structure type. The dependence of lattice constants and energy gap on magnesium content is found to be approximately linear for the given structure type. In the region of sphalerite-wurtzite phase transition ($x$ between 0.15 and 0.20) formation of 4H and 8H polytypes is observed. The energy gap of Zn$_{1-x}$Mg$_x$Se bulk crystals estimated from measurements of photoluminescence and reflection spectra at 40 K is higher than that reported for thin Zn$_{1-x}$Mg$_x$Se layers on GaAs substrate.

REFERENCES

18. I.V.Korneeva, Sov. Kristallogr. 6 (1962) 505
20. Landolt-Börnstein Tables, vol. 17b, p.139-140