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STRUCTURAL PROPERTIES OF $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ AND $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ CRYSTALS

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Electron probe microanalysis and X-ray diffraction studies have been performed on samples of ternary $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ ($0.05 \leq x \leq 0.09$) and quaternary $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ ($0.025 \leq x \leq 0.4$; $0.025 \leq y \leq 0.7$) alloys. The investigated samples were cut from 24 different ingots grown by Bridgman method. Microprobe examinations have revealed significant differences between actual and nominal content of Mg along the longitudinal direction for both ternary and quaternary ingots. In contrast to Mg, for most $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ samples the actual Mn content was within $\pm 5\%$ of nominal content. The lattice constants have been determined by X-ray powder diffraction method. Whereas $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ samples exhibit only zinc blende crystal structure for the entire region of x and y investigated, the $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ alloy has two different structures depending on Mg content; a zinc blende structure below $x = 0.5$ and a wurtzite structure above it. In both alloys the lattice constant decreases with increasing Mg content.

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1. Introduction

Quaternary II-VI compounds have recently gained increased interest due to the possibility of the additional control of their physical properties. In ternary diluted semiconductors (DMS), like for example $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, the band gap increases and lattice constant decreases with increasing Mn content. It means, for one given Mn concentration this pair of physical parameters as well as its magnetic properties remain fixed. However, in a quaternary DMS, the magnetic properties can be fixed while the band gap and lattice constant can be varied, by incorporating another non-magnetic element such as magnesium.

Optical properties of both $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ and $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ alloys have recently been reported [1], however, some inhomogeneities have been found. They

were evident from the photoluminescence and Raman measurements and were dependent upon the portion of the ingot from which the samples were taken.

In the following we report on crystal growth and structural examination of magnesium-based ternary and quaternary DMS motivated by the above findings.

2. Crystal growth

$\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ and $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ single crystals were grown by the Bridgman technique. In this method the growth ampoule is kept stationary while the resistive heating furnace, with a temperature gradient of $40^\circ\text{C}/\text{cm}$, is moved at a rate of 0.5–2.5 mm/hour. Decanting experiments demonstrated that a planar interface could be achieved with this temperature profile. Mixtures of CdTe, Mg, Mn and Te were melted together in a pretreated, 15 mm diameter by 10 cm long, fused quartz growth ampoule which contained 15–18 g of total charge. The starting materials Cd (99.9999%) and Te (99.9999%) were purified further by repeated sublimation in vacuum. The CdTe was prepared by fusing a stoichiometric mixture of purified Cd and Te. Both Mg and Mn are commercially available with a purity not better than 4N and they are heavily oxidized. Metallic manganese was effectively purified by triple sublimation at a temperature of 1180°C in high purity alumina tubes under dynamic vacuum. Metallic magnesium was distilled in vacuum at a temperature of 590°C . An adequate purity metal was obtained after triple distillation as confirmed by emission spectroscopy.

The charge was initially reacted at 600°C for about 5 h and then slowly raised to 900°C , where it was held for 12 h to drive the reaction to completion. Finally, the temperature of the charge was slowly increased to 1150 – 1180°C depending on Mg content in the alloy. The charge was then allowed to mix in the molten state for 24 h. During this stage of the heating period the ampoule was subjected to vibrations. The growth process was started by lowering the charge in the furnace. The temperature profile of the furnace allowed the crystallized alloy to be annealed for about 36 h at a temperature 150°C below its melting point. In this manner, the quality of the boules was found to be significantly improved.

3. Measurements

The investigations of actual chemical composition were carried out by means of JEOL JXA-50A scanning electron microscope equipped with an automated LINK system for energy dispersive microanalysis (ED EPMA). The surface of samples was first lapped and then manually polished under methanol. The measurements were done every two or three millimeters along the diameter of 24 samples cut from various ingots. The lattice parameter has been determined by X-ray powder diffraction using an automated DRON diffractometer and interpreted using DIIN-PDS and SCANIX packages.

4. Results and discussion

The results of ED EPMA measurements for all samples are given in Table. It can be seen that the actual Mg content differs from its nominal value in both

Cd_{1-x-y}Mg_xMn_yTe and Cd_{1-x}Mg_xTe alloys. However, the actual Mg content in quaternary alloy is much closer to the nominal one than in the ternary alloy. Such behavior was expected because the solidus and liquidus lines on the CdTe–MnTe pseudo-binary phase diagram coincide well as reported by Triboulet et al. [2].

TABLE
Lattice constants of ternary and quaternary CdTe–MgTe–MnTe systems.

Composition				Lattice constant
nominal		actual		
Mg [x]	Mn [y]	Mg [x]	Mn [y]	a[Å]
pure CdTe				6.481
0.05	0	0.026	0	6.479
0.20	0	0.114	0	6.474
0.30	0	0.199	0	6.468
0.30	0	0.228	0	6.467
0.45	0	0.260	0	6.462
0.40	0	0.379	0	6.455
0.50	0	0.381	0	6.454
0.45	0	0.399	0	6.453
0.60	0	0.480	0	6.447
0.60	0	0.497	0	6.446
0.025	0.025	0.015	0.023	6.4750
0.05	0.05	0.016	0.046	6.4718
0.10	0.10	0.031	0.097	6.4621
0.30	0.10	0.200	0.090	6.4517
0.15	0.15	0.076	0.150	6.4507
0.40	0.10	0.236	0.117	6.4439
0.20	0.20	0.100	0.197	6.4428
0.20	0.20	0.060	0.230	6.4381
0.10	0.30	0.098	0.280	6.4275
0.30	0.30	0.230	0.280	6.4200
0.10	0.50	0.082	0.447	6.4071
0.40	0.40	0.270	0.410	6.3983
0.10	0.70	0.068	0.578	6.3908
0.10	0.60	0.079	0.593	6.3900

The distribution of magnesium along Cd_{0.7}Mg_{0.3}Te crystal is presented in Fig. 1. It is seen that Mg content remains nearly constant from the bottom up

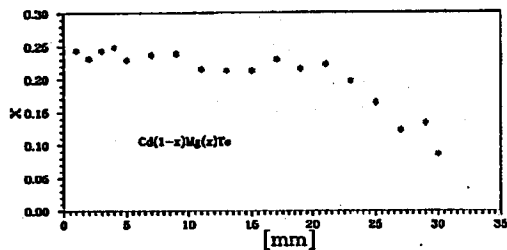


Fig. 1. Magnesium content x as a function of a distance along $\text{Cd}_{0.70}\text{Mg}_{0.30}\text{Te}$ ingot. The zero value of the scale corresponds to the bottom of ingot.

to 2/3 of the length of the ingot and then slightly decreases up to its top. In this particular crystal, the Mg content changes from 0.25 at the bottom to 0.09 at the top. To our knowledge, the phase diagram for CdTe-MgTe system is still unknown. Our results, however, seem to indicate that considerable segregation of Mg may occur as already reported for ZnTe-MgTe system [3].

Lattice constant values of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ determined by the X-ray powder diffraction are given in Table. These measurements showed that the $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ alloy crystallizes in the zinc blende structure when the actual Mg content is below about 50 at.% and in the wurtzite structure when it exceeds that value. We have obtained the same critical value of x for zinc blende phase existence for two various crystals with the nominal Mg content of 60 at.%. It leads us to the conclusion that the $x = 0.6$ value reported by Itoh [4] is too high, and it represents the Mg content of the charge rather than the actual value after the crystal growing process. In addition, we have also found that a sample with actual Mg content of 55 at.% crystallized in the wurtzite structure with $a = 4.554 \text{ \AA}$ and $c = 7.438 \text{ \AA}$ as already reported [5].

We have plotted in Fig. 2 the lattice constant versus both the nominal and actual Mg content for the ternary $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ system. Our dependence of the lattice constant versus actual Mg content can be described by the following equation:

$$a = 6.481 - 0.071x. \quad (1)$$

The zinc blende lattice constant of MgTe was found to be 6.41 \AA by extrapolation of the above equation, which is lower than that reported by Waag et al. (6.435 \AA) for MBE (molecular beam epitaxy) grown thin films [6]. As it is seen in Fig. 2, X-ray diffractions results for $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ thin films fit better to our nominal Mg content dependence, at least for lower x values. One can explain this somewhat surprising coincidence, since Waag et al. determined the x values for their thin films using the calibration curve for bulk $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ taken from the literature available so far [7].

Figure 3 also shows the dependence of the lattice constant versus the actual Mn content for $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ samples. The best fit can be described by the equation

$$a = 6.480 - 0.151y, \quad (2)$$

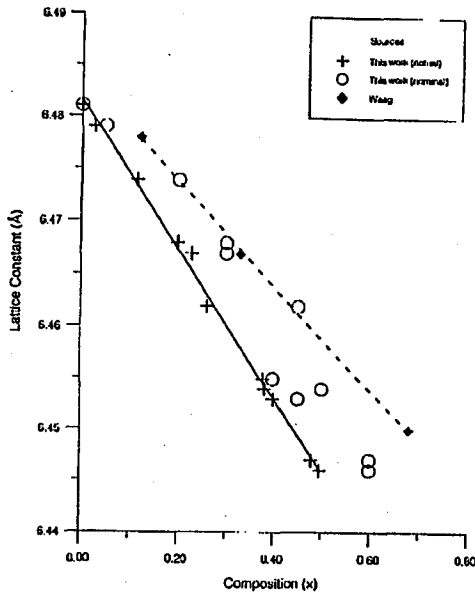


Fig. 2. Lattice constant as a function of Mg content for $Cd_{1-x}Mg_xTe$ alloy.

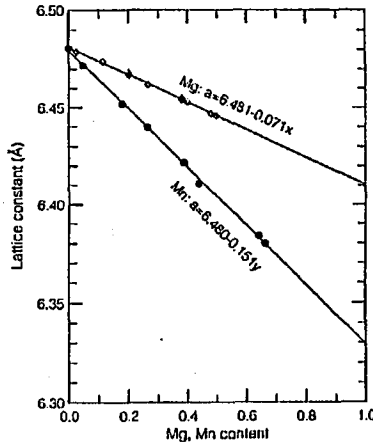


Fig. 3. Lattice constant as a function of Mg and Mn content for ternary $Cd_{1-x}Mg_xTe$ and $Cd_{1-y}Mn_yTe$ alloys.

which differs slightly from the results reported by Bottka et al. [8]. By extrapolating, the value of 6.329 Å for the zinc blende phase of MnTe was found, which is close to 6.334 Å reported by Furdyna et al. [9].

The analysis of the actual content of Mg and Mn, given in Table indicates that the incorporation of Mg atoms into $Cd_{1-x-y}Mg_xMn_yTe$ crystals is facilitated by the presence of large quantities of Mn. This was observed for five different

crystals with a constant Mg content of 10 at.% and Mn content which varied between 10 and 70 at.%. The higher values of the actual Mg content were found in those crystals in which the Mn content exceeded 30 at.%.

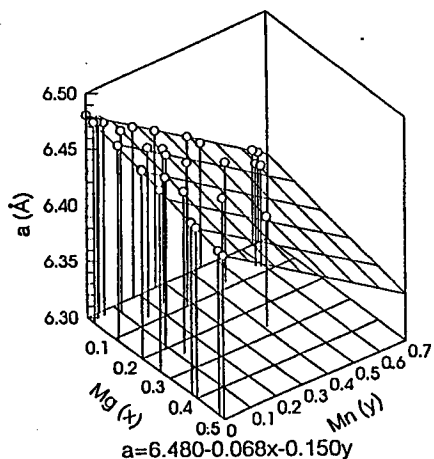


Fig. 4. Lattice constant as a function of Mg and Mn content for quaternary $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ alloy.

The $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ quaternary alloy crystallizes in the sphalerite structure for the entire investigated composition range ($0.015 \leq x \leq 0.27$; $0.023 \leq y \leq 0.593$). The lattice constant changes from 6.390 ± 0.001 Å (for $x = 0.079$, $y = 0.593$) to 6.4750 ± 0.0006 Å (for $x = 0.015$, $y = 0.023$). The results of the measurements are given in Table and are also plotted in Fig. 4. Changes of the $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ lattice constant are represented by the plane defined by the two lines describing both $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ and $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ ternary compounds. The best fit for all quaternary and ternary samples taken together was found to be

$$a = 6.480 - 0.068x - 0.150y. \quad (3)$$

The coefficients slightly differ from Eqs. (1) and (2) obtained for ternary samples alone.

5. Conclusions

Investigation of the structural properties of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ and $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ crystals have shown that the lattice constant in both alloys decreases linearly as the Mg and Mn contents increases. The $\text{Cd}_{1-x-y}\text{Mg}_x\text{Mn}_y\text{Te}$ samples exhibit only one crystal structure of zinc blende type in the entire region of x and y investigated, while $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ alloy has two different structures; a zinc blende structure below $x = 0.5$ and a wurtzite structure above it. An investigation of the actual composition of crystals revealed differences between the actual and nominal content of Mg in both ternary and quaternary ingots. The segregation of

Mg atoms was observed along the ingots. The Mg content decreases as the distance from the bottom of the ingot increases. It was also found that the incorporation of Mg atoms into the quaternary alloy is facilitated by large amounts of Mn.

Acknowledgments

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