

PACS: 78.20.Fm, 61.10.-i, 62.20.Qp

Physical properties of ZnSe-MgSe, ZnSe-CdS solid solutions and possibilities of their application in IR engineering

Yu.A. Zagoruiko, O.A. Fedorenko, N.O. Kovalenko, M.A. Rom, P.V. Mateychenko

*Department of Optical and Constructional Crystals
of Scientific & Technological Concern "Institute for Single Crystals"
60 Lenin Ave., Kharkov, 310001, Ukraine*

Abstract. The vertical Bridgman method is used to obtain crystals of $Zn_{1-x}Mg_xSe$ and ZnSe-CdS solid solutions (with $0.03 \leq x \leq 0.55$ and Cd concentrations varying from 0.3 to 35 at.%, respectively). The composition of the samples is determined by means of electron-probe microanalysis. The methods of optical microscopy and X-ray analysis are used to investigate the structure of the crystals and to determine their lattice parameters. Investigated are the microhardness and microbrittleness of the grown ZnMgSe crystals, as well as their polarizational, optical, photoelectric and dielectric properties depending on Mg concentration. The obtained crystals are found to possess anisotropy of physical properties. The largest anisotropy of their mechanical, polarizational and optical properties is observed in the crystals containing 5-6 at.% of Mg. The samples with such a concentration of Mg are applicable as a base for making thermostable multifunctional IR optical elements which can operate within a wide spectral region.

Keywords: ZnMgSe crystals, anisotropy of physical properties, microhardness, birefringence

Paper received 04.10.99; revised manuscript received 18.12.99; accepted for publication 14.03.00.

1. Introduction

From the viewpoint of basic operational characteristics, crystalline ZnSe is considered to be the best material for passive IR optical elements. However, such purposely undoped crystals have the cubic structure of sphalerite with an insignificant concentration ($0 \div 2\%$) of the hexagonal phase. The isotropy of properties characteristic of crystals with cubic structure limits the use of ZnSe as a base for controlling optical elements. As is known, by doping ZnSe with certain impurities in the process of growth, its crystal structure may be changed. Thus, the crystals with an elevated concentration of hexagonal phase or those with hexagonal structure, may be obtained [1-3]. These crystals should have an essential anisotropy of physical properties, and this will allow to use them for making thermostable multifunctional optical devices which can operate both as passive and controlling optical elements. With a view of obtaining an optical anisotropic material on the base of A^{II}B^{VI}-type compounds, the growth of ZnMgSe and ZnSe-CdS single crystals was performed, and their structure, composition and physical properties were studied.

2. Experimental procedure

ZnMgSe and ZnSe-CdS crystals were grown from the melt under the pressure of inert gas (argon). The composition of the grown crystals was investigated by the method of electron-probe microanalysis on a scanning microscope of JSM-820 type.

The structure perfection and phase composition of the crystals were studied by X-ray methods. Diffraction reflection curves (DRC) were obtained in Cu $K\alpha_1$ radiation. The crystal lattice periods α were determined by the Bond method. Phase analysis was performed on the base of powder diffraction patterns obtained with Cu $K\alpha$ radiation.

The value of microhardness was measured using a PMT-3 device according to the standard procedure. As an indenter, tetrahedral Vickers diamond pyramid was used. Microbrittleness was investigated from the patterns of the formation of cracks around the indentation. The cracks were studied by the method of optical microscopy. To precisely determine the tip of a crack, the surface was subjected to chemical etching.

3. Results

3.1. Composition of the grown crystals

The data obtained by the method of electron-probe microanalysis show that the grown crystals are $Zn_{1-x}Mg_xSe$ solid solutions of substitution (where $0.03 \leq x \leq 0.55$). The results of microanalysis performed on ZnSe-CdS crystals point to the fact that these crystals are solid solutions of substitution with a varying composition, the content of Cd in the samples running into 0.3-35 at.%.

3.2. Structure of ZnMgSe single crystals

As seen from Table 1, the dependence of $\beta_{1/2}$ (DRC half-width) on the crystal rotation angle φ is characterized by an essential anisotropy testifying to a noticeable influence of the dopant on the structure perfection. The Debye pattern of Sample 1 shows the presence of only the sphalerite modification of the compound. Sample 2 is characterized by the presence of 3...4% of the wurtzite modification. The broadening of the reflexes (111) points to the increase of packing defects concentration. The DRC of Sample 2 reveals a developed mosaic structure with 0.05-0.07° disorientation angles. At the concentrations of Mg higher than 7 at. % the crystals have the structure of wurtzite (Table 2).

3.3. Microhardness of ZnMgSe single crystals

Spalling plane

On the spalling planes the indentation was obtained in such a manner that one of the diagonals denoted as d_c was located along the line of intersection of two spallings (for the sphalerite and wurtzite structures these directions are [111] and [0001], respectively); the other diagonal is denoted as d_a . Microhardness measurements show that the indentation is rhombic in shape, and $d_a > d_c$. The indentation distortion is caused by heaps of the substance pressed out at the angles connected by the diagonal d_a . Fig. 1 and 2 present the dependences of the coefficient of type I microhardness anisotropy ($K_I = d_c/d_a$) and of the indentation diagonals on the concentration of Mg.

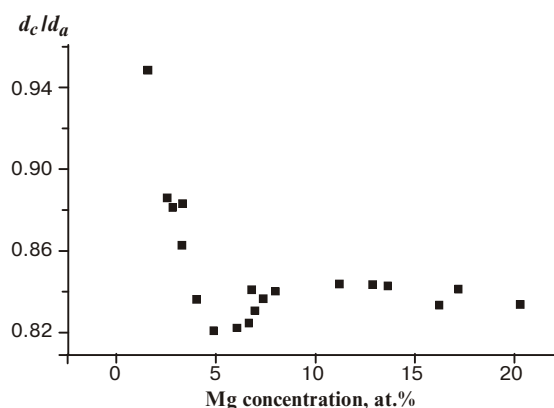


Fig. 1. Degree of indentation distortion depending on Mg concentration on spalling surface of ZnMgSe crystals.

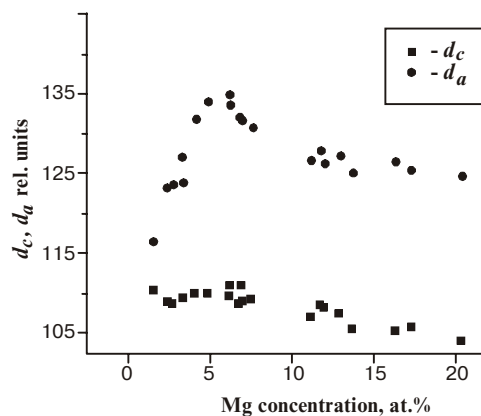


Fig. 2. Dependence of indentation diagonal length on Mg concentration in ZnMgSe crystals.

Closely packed face

The results of microhardness measurements on the closely packed face show that the indentation is square in shape; the value of microhardness for the crystals with 1.5-7 at.% Mg concentrations increases from 187 kg/mm² to 253 kg/mm². The coefficient of type II microhardness anisotropy K_{II} (the ratio of the value of microhardness on the closely packed face to that on the spalling plane) increases from

Table 1. Data of X-ray structure analysis of ZnMgSe samples

Sample	a , E	$\beta_{1/2min}(220)$, grad	$\beta_{1/2max}(220)$, grad	Concentration of Mg, at.%	$\beta_{1/2}(111)$, grad	Concentration of twins
№ 1	5.6878	0.02	0.07	2,5	0.05	0.5/0.5
№ 2	5.6987	0.005	0.016	6,5	0.3-0.55	0.5/0.5
primary standard	5.6687	0.005	0.005	undoped ZnSe	0.025	—

Table 2. Lattice parameters of hexagonal ZnMgSe single crystals

a , Å	c , Å	Concentration of Mg, at. %
4.0435	6.6078	7.5
4.059	6.6323	10-11.8
4.0657	6.640	13.5-14
4.0694	6.6451	16.8-17.6
4.0773	6.6580	19.6-20.7

1.38 up to 1.99. For ZnMgSe crystals with the structure of wurtzite, the values of microhardness and K_{II} decreases to some extent while increasing the concentration of Mg (for instance, at 12at.% concentration the mentioned values are equal to 244 kg/mm² and 1.7, respectively).

3.4. Microbrittleness of ZnMgSe single crystals

Closely packed face

In ZnMgSe crystals “rosettes of brittleness” have 6 radial rays corresponding to the traces of the perpendicular cleavage planes on the closely packed face. The symmetry of the rosette is hexagonal (even in the crystals with the concentration of Mg lower than 7 at. %); after chemical etch-

Table 3. Microhardness on spalling surface and ZnSe-CdS solid solution structure

Cd concentration in at. %	d_a/d_c	Microhardness, kg/mm ²	Crystal structure
3	0.93	186.7	sphalerite+ wurtzite
4	0.92	182.1	sphalerite+ wurtzite
19.5	0.84	173.1	wurtzite
25	0.84	167.8	wurtzite

ing of the crystal surface the end of a radial crack corresponds to a hexagonal etching pit. Besides radial cracks, separate lateral ones are often observed. The probability of the formation of lateral cracks in ZnMgSe crystals increases with the growth of Mg concentration. The formation of lateral cracks and the “rosette of brittleness” of hexagonal symmetry is characteristic of the closely packed faces of hexagonal A²B⁶ crystals [4,5].

Spalling plane

Investigation of the brittle failure patterns showed that at low Mg concentrations cracks are formed along the closely packed faces. The obtained pattern resembles the “rosette of brittleness” observed on the spalling planes of hexagonal CdS and CdSe single crystals [5]. With the growth of Mg concentration the brittleness of ZnMgSe crystals increases: besides cracks on the closely packed faces, those on inclined cleavage planes, as well as lateral cracks are observed (Fig. 3). The cracks are classified in accordance with [6].

3.5. Stress patterns

On the spalling plane of ZnMgSe single crystal, a pattern of stresses formed around the indentation was obtained in polarized light. Investigations show that the introduction of Mg leads to certain changes in the stress pattern as against undoped ZnSe. Even at low Mg concentrations this pattern resembles the one characteristic of the hexagonal crystals. Fig. 4 presents the stress patterns obtained on the spalling planes of undoped ZnSe crystals with the structure of sphalerite (a), twinned sphalerite (b), ZnMgSe (c) and hexagonal CdS (d).

3.6. Microhardness of ZnSe –CdS crystals

Microhardness was investigated on the spalling planes. On all samples the indentation was shaped as rhomb. The degree of indentation distortion ($d_a > d_c$) depended on the concentration of Cd in the sample. With the growth of Cd concentration type I microhardness anisotropy increased, the value of microhardness lowered. At high contents of Cd the samples had hexagonal structure. The

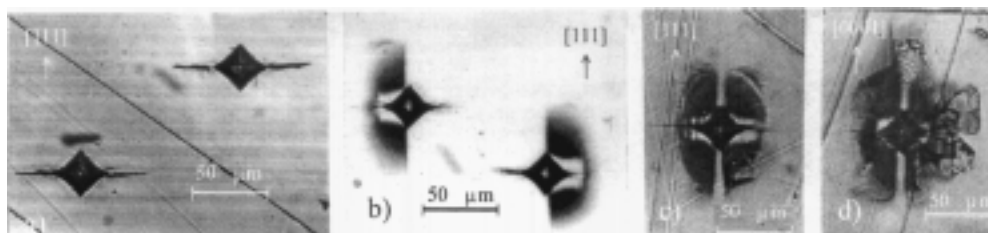


Fig. 3. Patterns of cracking on the spalling plane of ZnMgSe single crystals with different content of Mg (transmitted light): a) Zn_{0.97}Mg_{0.03}Se; b) Zn_{0.93}Mg_{0.07}Se; c) Zn_{0.9}Mg_{0.1}Se; d) Zn_{0.76}Mg_{0.24}Se.

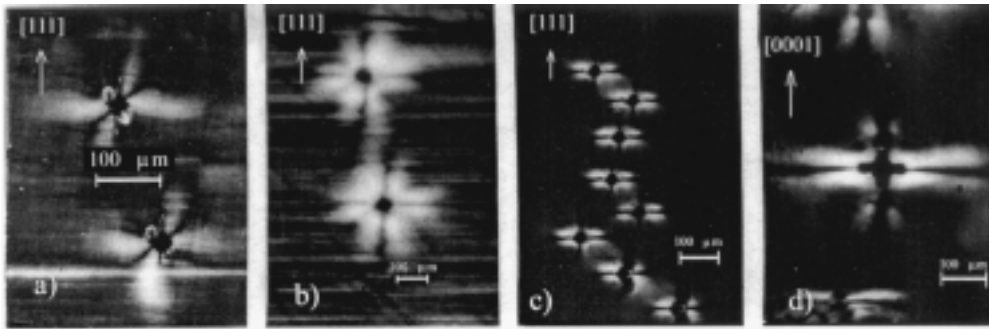


Fig. 4. Patterns of stresses around indentation on spalling plane of crystals $A^{II}B^{VI}$:
 a) ZnSe, sphalerite, $P = 100$ g; b) ZnSe, twinned sphalerite, $P = 200$ g; c) $Zn_{0.96}Mg_{0.04}Se$, $P = 100$ g; d) CdS, $P = 200$ g.

obtained results are presented in Table 3. So, it is to be emphasized that in ZnSe-CdS the value of microhardness is noticeably higher as against undoped ZnSe and CdS components. For instance, in the sample with 3 at.% Cd concentration microhardness is by 3.7 and 1.6 times higher in comparison with CdS and ZnSe, respectively.

The solid solutions are characterized by a lower cracking resistance than ZnSe and CdS. This is confirmed by both the presence of a developed system of cracks around indentations and by microcracks in ZnSe-CdS boules.

3.7. Birefringence in ZnMgSe crystals

The value of birefringence was determined in a sample with a thickness of 3.7 mm and a length of about 30 mm extended along the direction [111]. The concentration of Mg varied from 3 to 7 at.% along the crystal axis. The cleavage planes (110) were used as the working ones. In the performed experiments, the value of transmitted power was determined depending on the angle of the analyzer rotation about the polarizer. The relation between the values of transmitted radiation power at the parallel and perpendicular arrangement of the analyzer and polarizer was used to calculate the difference between the phases of the ordinary and extraordinary waves ($\Delta\phi$). The obtained results are presented in Fig. 5. The phase difference was used to determine the value of $n_e - n_o$ (Fig. 6). The phase difference extremum was observed in that region of the crystal where Mg concentration was 5.5-6 at. %. In the said region it was impossible to determine Δn .

3.8. Photoelectric properties of ZnMgSe single crystals

The value of photosensitivity at an illuminance varying from 0 to 10000 lux was measured in the samples with different Mg concentrations. As seen from these dependences, the samples' photosensitivity weakly depends on Mg concentration. This is another proof of the fact that the grown ZnMgSe crystals are the solid solutions of substitution. The photoelectric properties of ZnMgSe crys-

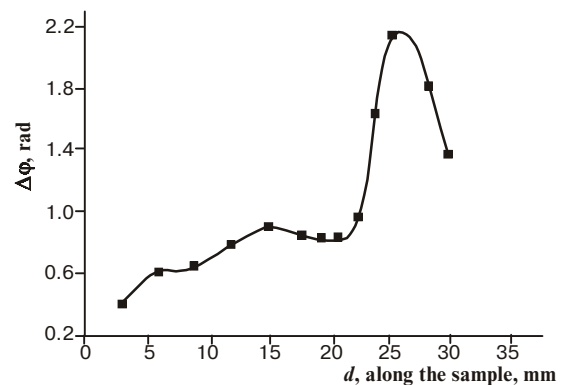


Fig. 5. Difference between the phases of ordinary and extraordinary waves along the sample.

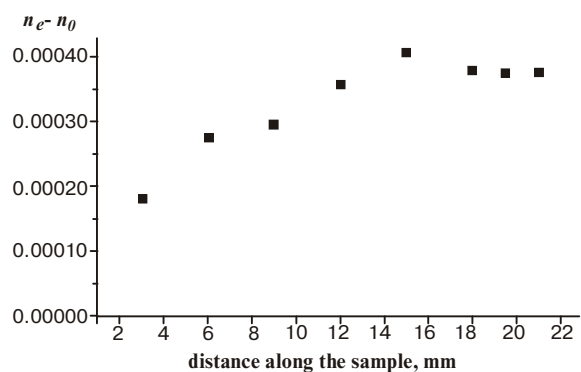


Fig. 6. Difference between the refractive coefficients along the sample.

tals essentially differ from those of undoped ZnSe crystals. In particular, for the photosensitivity spectra of ZnMgSe measured in varying electric field within 18...140 °C temperature range, the presence of a pronounced maximum was observed in the region of 1.05 μm. The relative height and half-width of such a maximum are stable enough at temperatures not higher than 90°C. The appearance of the said maximum seems to be bound up with mechanical stresses caused by the doping.

Conclusions

Single crystals of the solid solutions $Zn_{1-x}Mg_xSe$ ($0.03 \leq x \leq 0.55$) and ZnSe-CdS (with Cd content varying from 0.3 to 35 at.%) are grown. The introduction of Mg impurity leads to a change in the crystal structure of magnesium selenide: first of all, the concentration of the hexagonal phase increases, and then the structure is transformed into the hexagonal one of wurtzite. $Zn_{1-x}Mg_xSe$ and ZnSe-CdS crystals are characterized by anisotropy of physical properties. The largest anisotropy of their mechanical, polarizational and optical properties is observed in the samples with 5-6 at. % concentration of Mg.

The presence of Mg in ZnMgSe crystals leads to the appearance of birefringence which makes the crystals applicable for the manufacture of quarter- and half-wave plates for the IR range of the spectrum, in particular, for working with CO- and CO₂- laser radiation.

Acknowledgments

This work is supported in part by Science and Technology Center in Ukraine (STSU), Project # 380.

References

1. N.F. Obukhova, L.V. Atroshchenko, A.I. Kolodyazhniy, Obtaining and investigation of single crystals of ZnS-MgS solid solutions with wurtzite structure // *Izv. AN SSSR, Neorganicheskie materialy*, **13**(8), pp. 1390-1393 (1977).
2. M.P. Kulakov, A.V. Fadeev, Growth of zinc selenide single crystals doped with magnesium // *Izv. AN SSSR, Neorganicheskie materialy*, **22**(3), pp. 392-394 (1986).
3. U.Debska, W.Giriat, H.R.Harrison, D.R.Yoder-Short, RF-heated Bridgman growth of $(ZnSe)_{1-x}(MnSe)_x$ in self-sealing graphite crucibles // *J.Cryst.Growth*, **70**, North Holland, Amsterdam, pp.399-402 (1984).
4. O.A.Fedorenko, L.V.Atroshchenko, Microplasticity and microfragility of $A^{II}B^{VI}$ single crystals at room temperature // *Single Crystals and Engineering*, collected volume, issue 7, pp.3-11, Kharkov (1972).
5. L.V.Atroshchenko, B.L.Timan, O.A.Fedorenko, Crack formation in A^2B^6 single crystals at indentation // *Crystalline materials*, collected volume, Institute for Single Crystals, №11, pp.7-11, Kharkov (1983).
6. A.G.Evans, Impact damage in ceramics // *Fracture Mechanics of Ceramics*, Ed. By Brandt R.C. e.a.-New York: Plenum Press, **3**, pp. 303-331 (1978).