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$Zn_{1-x}Mg_xSe$ single crystals as a functional material for optoelectronics

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Structure, mechanical, optical, and electro-physical properties of single crystals of $Zn_{1-x}Mg_xSe$ ($0.03 \le x \le 0.55$) solid solutions have been studied. The hexagonal $Zn_{1-x}Mg_xSe$ single crystals ($x \ge 0.12$) have been found to be suitable as a functional material for manufacturing of thermally stable polarizing, electro-optical, and multifunctional devices intended to be operated under intense irradiation in near and medium IR range.

Исследованы структурные, механические, оптические и электрофизические свойства монокристаллов твердых растворов $Zn_{1-x}Mg_xSe$ ($0,03 \le x \le 0,55$). Установлено, что монокристаллы гексагонального $Zn_{1-x}Mg_xSe$ ($x \ge 0,12$) пригодны в качестве функционального материала для изготовления на их основе термостабильных поляризационных, электрооптических и многофункциональных элементов, предназначенных для работы с интенсивным излучением ближнего и среднего ИК диапазонов.

The wide-band $A^{II}B^{VI}$ semiconductors are among the most important and promising materials for optoelectronics. So, hexagonal structure crystals (CdS, CdSe, and solid solutions thereof) are used in manufacturing of polarizing optical elements, in particular of phase rotating plates. Such elements, however, are unsuitable for work with high-intensity laser radiation due to low radiation resistance, thermal instability, and limited working temperature range. CdSe crystals are opaque in the visible spectral region, therefore, the polarizing optical elements made of that material are difficult to adjust. Zinc selenide crystals exceed the hexagonal $A^{II}B^{VI}$ crystals in all the above-mentioned characteristics. However, the use of undoped ZnSe for the phase plates is hindered by the real structure defects (twin interlayers).

It is known that the ZnSe structure can be modified by doping it in the course of growing with impurities that stabilize the wurtzite hexagonal structure, thus obtaining the twin-free crystals [1]. Mg and Mn are the most suitable dopants [1, 2]. Note that introduction of Mg impurity results in a considerable lowered phase transition temperature [3]. Physical properties of single crystals of $Zn_{1-x}Mg_xSe$ have been studied in [4-12]. In these works, the $Zn_{1-x}Mg_xSe$ single crystal physical properties are considered as well as the practical use thereof in optoelectronics, in particular, manufacturing of thermally stable polarizing optical elements for IR spectral range.

The $Zn_{1-x}Mg_xSe$ single crystals ($0.03 \le x \le 0.55$) up to 25 mm in diameter were grown using the vertical Bridgeman technique in graphite crucibles under positive argon pressure (20 atm) using a special raw charge. The magnesium distribution along the crystal ingot was examined by emission spectroscopy and electron probe microanalysis using a JSM-820 electron microscope and a Link AN 10/85S energy dispersion microanalyzer. Basing on the data obtained as well as on X-ray structure analysis and photoelectrical data, the crystals have been classified as substitutional solid solutions.

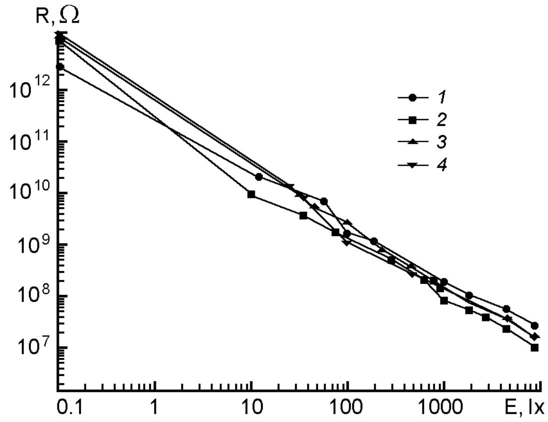

Fig. 1. Photosensitivity of $Zn_{1-x}Mg_xSe$ crystals at various Mg concentrations (at. %): 7.0 (*1*), 5.0 (*2*), 3.5 (*3*), 2.5 (*4*).

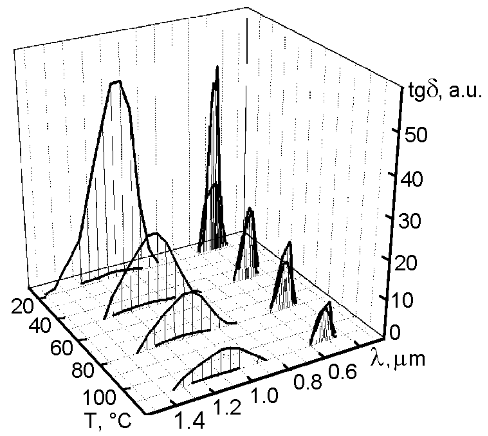

Fig. 2. Photosensitivity spectra of $Zn_{1-x}Mg_xSe$ (upper curves) and ZnSe (lower curves).

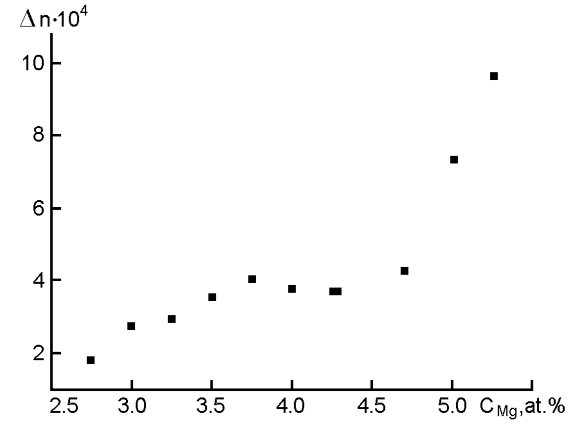

Fig. 3. Dependence of birefringence Δn on magnesium concentration in $Zn_{1-x}Mg_xSe$ crystals.

The structure characteristics of the crystals have been obtained by means of diffraction modeling using the developed calculation models and programs [9, 10]. The results obtained have shown that the $Zn_{1-x}Mg_xSe$ samples with minimum Mg content possess a 3C sphalerite structure containing twin boundaries. As Mg concentration increases, the twin boundaries become more and more ordered and their spacing diminishes. At Mg concentrations corresponding to $0.10 \le x \le 0.12$, a special hexagonal structure referred to as 4H polytype [9] is formed in $Zn_{1-x}Mg_xSe$ crystals. No variable birefringence bands are observed on cleavage surfaces of crystals having the above composition, thus offering a possibility to use that material to transmit the high-intensity IR laser radiation without distortions of the laser beam phase front. At that magnesium concentration, the crystals grow without residual stresses (internal cracks) and thus show a high mechanical strength [7]. Such $Zn_{1-x}Mg_xSe$ single crystals with the 4H structure are usable to manufacture polarizing optical elements, in particular, thermally stable quarter- and half-wave plates of IR range intended for operation with intense radiation of CO and CO_2 lasers.

The photosensitivity was measured for samples with different Mg concentrations under illumination varying from 0 to 10,000 lx. The photosensitivity dependences on illumination are plotted in Fig. 1. The photosensitivity is seen to depend only slightly on Mg concentrations, thus confirming additionally that the grown $Zn_{1-x}Mg_xSe$ crystals are isovalent substitutional solid solutions, since it is just such solid solutions where the doping effects are not appeared as an impurity is introduced (dissolved) [13].

The $Zn_{1-x}Mg_xSe$ crystals exceed considerably the undoped ZnSe in photosensitivity (Fig. 2). These experimental results confirm the theory by R.Bube [14] who has stated that the $A^{II}B^{VI}$ single crystals grown in the highest pure and perfect state provided by technology show much lower photosensitivity as compared with crystals containing the introduced imperfections. Note that the photosensitivity spectra of $Zn_{1-x}Mg_xSe$ crystals include a strong maximum around 1.05 μm in the 18 to 140°C temperature range (Fig. 2). The photosensitivity peak height and half-width remain stable enough at temperatures of ≤90°C. Its appearance seems to be associated with mechanical stresses resulting from the doping.

The birefringence was studied along the [111] direction, the cleavage planes (110) being the working surfaces. The phase difference maximum between the ordinary and

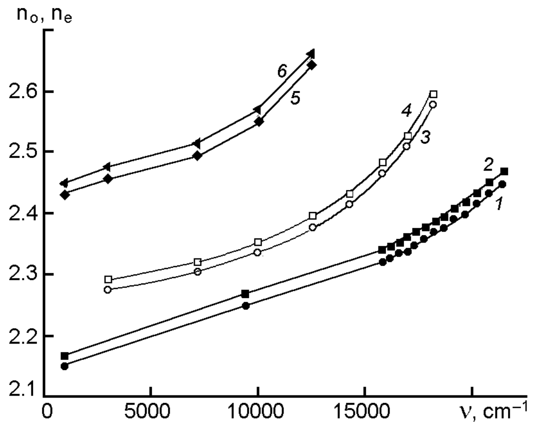

Fig. 4. Dispersion dependence of refractive indices for ordinary (*1*, *3*, *5*) and extraordinary (*2*, *4*, *6*) wave for single crystals of $Zn_{0.48}Mg_{0.52}Se$ (*1*, *2*), CdS (*3*, *4*) and CdSe (*5*, *6*).

extraordinary waves was observed in the crystal part where the Mg concentration was 5.0 to 6.0 at. %. From the phase difference, $\Delta n = n_e - n_o$ value was calculated as a function of Mg concentration (Fig. 3). The $Zn_{1-x}Mg_xSe$ has been stated to be a positive uniaxial crystal with a substantial refractive index difference between the ordinary and extraordinary waves (Fig. 4) exceeding that characteristic for CdS and comparable to that for CdSe. Thus, the material is suitable for polarizing and phase-rotating optical elements.

The optical transmission spectra of $Zn_{1-x}Mg_xSe$ solid solutions evidence a high transparency of the material in a wide spectral range, thus providing its use in visible, near and medium IR regions (Fig. 5a, b). The optical absorption of the material is as low as $7 \cdot 10^{-3}$ cm^{-1} at $\lambda = 10.6$ μm. As the magnesium concentration increases, the band gap of $Zn_{1-x}Mg_xSe$ crystals increases from 2.7 eV (at $x = 0.03$) to 3.0 eV (at $x = 0.44$). The temperature dependence of refractive index (dn/dT) is characterized by the value of $9 \cdot 10^{-5}$ K^{-1} (at $\lambda = 0.63$ μm).

Electro-optical characteristics of $Zn_{1-x}Mg_xSe$ solid solutions were not known until recently. At magnesium concentrations corresponding to $x > 0.12$, the solid solution has the wurtzite structure (symmetry class 6mm). The longitudinal electro-optical effect is impossible in materials of that symmetry class, therefore, the module of electro-optical coefficient difference $r_{13} - r_{33}$ was measured as described in [15]. At high Mg concentrations ($x > 0.35$), the $Zn_{1-x}Mg_xSe$ crystals show a high birefringence, the anisotropy of optical properties ($\Delta n = n_e - n_o$) is higher than that in CdS [16].

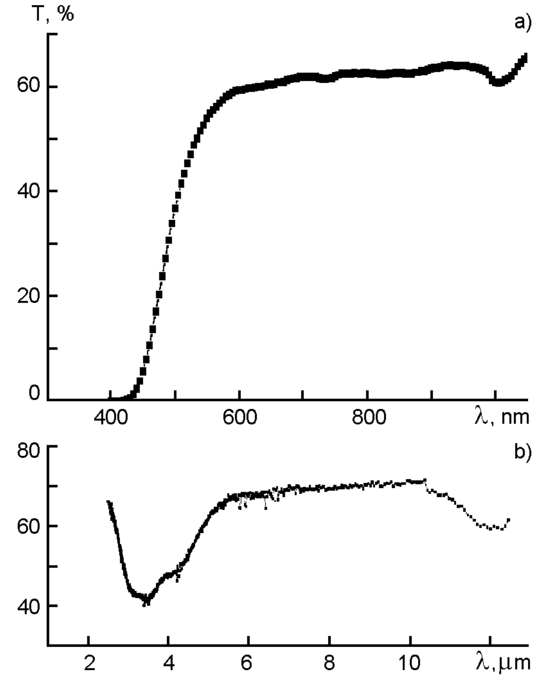

Fig. 5. Transmission spectra of $Zn_{1-x}Mg_xSe$ single crystals in visible (a), near IR and medium IR ranges (b).

As our measurements have shown, the average $r_{13} - r_{33}$ value is $(1.1 \pm 0.22) \cdot 10^{-12}$ m/V, that is comparable in the order of magnitude with the classical binary hexagonal $A^{II}B^{VI}$ compounds such as CdS and CdSe [16]. The high electro-optical parameters in combination with a high resistivity (10^{12} to 10^{13} Ω·cm at 300 K) evidence a possibility to use the $Zn_{1-x}Mg_xSe$ single crystals in manufacturing of electro-optical modulators intended for the wavelength range from visible to medium IR.

The IR radiation resistance (at $\lambda = 10.6$ μm) of the $Zn_{1-x}Mg_xSe$ solid solution single crystals exceeds more than twice that of CdS ones. This is due to the fact that the $Zn_{1-x}Mg_xSe$ crystals have a larger band gap and much lower (about one decimal order) optical absorption coefficient in the IR range as compared to CdS ones. Therefore, the IR range phase plates made of $Zn_{1-x}Mg_xSe$ (e.g., quarter- and half-wave plates for CO and CO_2 lasers) show a higher thermal stability and can be operated at higher optical radiation intensities and in wider temperature ranges as compared to the corresponding plates made of CdS single crystals [12, 17]. The optical material $Zn_{1-x}Mg_xSe$ is suitable for thermally stable multi-functional optical elements of through-pass type for a wide spectral region. Such devices combine the functions of the phase plates and the power sensors for continuous or modulated IR laser radiation [12, 17].

Thus, the structure, optical, electrical, and electro-optical properties of large-size $Zn_{1-x}Mg_xSe$ single crystals have been studied in a wide range of chemical composition thereof ($0.03 \le x \le 0.55$). Those crystals have been characterized as isovalent substitutional solid solutions. The zinc selenide crystal doping with magnesium has been shown to change its structure. In the Mg concentration range from 1.5 to 6 at. %, the twin boundaries are ordered and their spacing diminishes. At Mg concentrations of 5 to 6 at. %, the crystals show a specific hexagonal structure (polytype 4H) and from 7 at %. Mg on, $Zn_{1-x}Mg_xSe$ crystallizes in hexagonal wurtzite structure. No variable birefringence bands are observed on cleavage surfaces of the polytype 4H crystals, thus, no distortion of the laser beam phase front occurs. In such crystals, an extreme of the phase difference between the ordinary and extraordinary waves is observed. A pronounced anisotropy of optical properties is typical of those crystals and comparable to that of CdS and CdSe ones. The $Zn_{1-x}Mg_xSe$ crystals where $0.10 \le x \le 0.12$ grow without residual stresses (internal cracks) and thus show a high mechanical strength. An advantage of $Zn_{1-x}Mg_xSe$ consists in that IR range phase plates made of that material (e.g., quarter- and half-wave plates for CO and CO_2 lasers) show a higher thermal stability and can be operated at higher optical radiation intensities and in wider temperature ranges as compared to the corresponding plates made of CdS or CdSe.

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Монокристали $Zn_{1-x}Mg_xSe$ — функціональний матеріал для оптоелектроніки

Ю.А.Загоруйко, Н.О.Коваленко, О.О.Федоренко, О.Г.Федоров, П.В.Матейченко

Проведені комплексні дослідження структурних, механічних, оптичних та електрофізичних властивостей монокристалів твердого розчину $Zn_{1-x}Mg_xSe$ ($0,03 \le x \le 0,55$). Встановлено, що монокристали гексагонального $Zn_{1-x}Mg_xSe$ (при $x \ge 0,12$) придатні в якості функціонального материалу для виготовлення на їх основі термостабільних поляризаційних, електрооптичних та багатофункціональних елементів, призначених для роботи з інтенсивним випромінюванням ближнього та середнього ІЧ діапазонів.