

# Temperature dependences of optical and piezoelectric characteristics of ZnMgSe single crystals

*Yu.A.Zagoruiko, N.O.Kovalenko, V.M.Puzikov, O.A.Fedorenko*

Institute for Single Crystals, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv,  
Ukraine

*Received September 30, 2009*

The temperature dependences of the light refraction index for single crystals of  $Zn_{1-x}Mg_xSe$  solid solutions grown by the Bridgman method have been measured. It is established that within 300–583 K temperature interval, the  $dn/dT$  value for  $Zn_{0.52}Mg_{0.48}Se$  crystals is  $9.31 \cdot 10^{-5}$  at  $\lambda = 0.63 \mu m$  and  $5.29 \cdot 10^{-5}$  at  $\lambda = 10.6 \mu m$ . Studied have been the temperature dependences of the piezoelectric properties of  $Zn_{1-x}Mg_xSe$  single crystals. It is found that at  $0.34 \leq x \leq 0.48$ , the electromechanical bond coefficient  $k_t$  amounts  $(11 \pm 1) \%$ , and this value remains unchanged at temperatures ranging between 295 and 495 K.

Измерены температурные зависимости показателя преломления света для монокристаллов твердых растворов  $Zn_{1-x}Mg_xSe$  выращенных методом Бриджмена. Установлено, что в интервале температур 300–583 К величина  $dn/dT$  кристаллов  $Zn_{0.52}Mg_{0.48}Se$  составляет  $9,31 \cdot 10^{-5}$  при  $\lambda = 0,63 \mu m$  и  $5,29 \cdot 10^{-5}$  при  $\lambda = 10,6 \mu m$ . Исследованы температурные зависимости пьезоэлектрических свойств монокристаллов  $Zn_{1-x}Mg_xSe$ . Установлено, что при  $0,34 \leq x \leq 0,48$  величина коэффициента электромеханической связи  $k_t$  составляет  $(11 \pm 1) \%$  и сохраняет свое значение в диапазоне температур 295–495 К.

## 1. Introduction

In [1–6], the structure and lattice parameters of  $Zn_{1-x}Mg_xSe$  single crystals depending on the Mg concentration were measured; the behavior of the mechanical, electrooptical, photoelectric, and dielectric properties of these crystals was studied within a wide temperature range in the samples of different chemical composition. However, till quite recently, the temperature dependences of the refractive index for  $Zn_{1-x}Mg_xSe$  single crystals and their piezoelectric properties have not been established. It should be noted that the available literature data on the temperature dependences of the refractive index differ essentially even for the well-known classic crystals such as ZnSe or CdS, and in some cases are of estimative character. This is ex-

plained by the fact that the  $dn/dT$  values were determined by different experimental methods, and the investigated samples of semiconductor materials were grown by different techniques and had different doping levels [7].

## 2. Experimental methods

In this study, the temperature dependences of the refractive index  $dn/dT$  (thermooptical coefficient) were measured for  $Zn_{0.52}Mg_{0.48}Se$  samples at different wavelengths (0.63  $\mu m$  and 10.6  $\mu m$ ) within the temperature interval from 300 to 583 K. At the mentioned magnesium concentrations, the single-crystal substitution solid solution  $Zn_{1-x}Mg_xSe$  has the structure of wurtzite, and is a uniaxial crystal [3]. For comparison, there the thermooptical coefficients for

ZnSe crystals were also measured. The investigated ZnSe, CdS, and ZnMgSe single crystals were grown by the vertical Bridgman method. The measurements were carried out using an experimental unit which operation was based on the refractive property of a prism.

The error of the refractive index measurements was  $\pm 1.5 \cdot 10^{-3}$  [6], the relative error for the thermo-optical coefficient determination did not exceed  $\pm 7\%$ . The reproducibility of the measurement results lay within limits of calculated error and agreed well with the available literature data.

In this work, the piezoelectric properties of  $Zn_{1-x}Mg_xSe$  single crystals and the temperature dependences of these properties were investigated for the first time. The electromechanical bond coefficient  $k_t$  was determined from the measurements of the resonance and antiresonance frequencies for thin plane-parallel crystal samples with the planes oriented perpendicular to the [0001] direction. The measurements were realized at temperatures ranging between 295 and 495 K.

### 3. Results

Table 1 and Fig. 1 present the results of our  $dn/dT$  measurements for ZnSe, CdS,

and ZnMgSe single crystals as well as the data obtained by other authors [7–10]. The agreement of our results with the literature data within limits of experimental error testifies that the results of this research are reliable. The data reported in our previous study [11] and those obtained in this work show that hexagonal  $Zn_{1-x}Mg_xSe$  single crystals ( $0.14 \leq x \leq 0.55$ ) are highly thermally stable, operable within a wide range of working temperatures and highly radiation resistant (Table 2). In particular, at  $\lambda = 10.6 \mu m$ , the laser damage threshold of  $Zn_{0.52}Mg_{0.48}Se$  samples is twice as high in comparison with that of CdS single crystal samples. Due to this fact, we have produced thermally stable half- and quarter-wave phase plates intended to work with high-intensity CO- and CO<sub>2</sub>-laser radiation as an example of the use of hexagonal  $Zn_{1-x}Mg_xSe$  single crystals ( $x \sim 0.2$ ) in practice. The strong thermally stable antireflection oxide coatings of these plates have been obtained by the photo-thermal oxidation [12].

We have measured the piezoelectric properties of  $Zn_{1-x}Mg_xSe$  single crystals and determined the temperature dependences of the electromechanical bond coefficient ( $dk_t/dT$ ) for this material (Fig. 2). The hexagonal  $Zn_{1-x}Mg_xSe$  single crystals were found to show a rather high electromechanical

Table 1. Thermo-optical coefficients of single crystalline A<sup>II</sup>B<sup>VI</sup> samples

Material	$dn/dT, K^{-1}$ the present study		$dn/dT, K^{-1}$ data [7–10]	
	$\lambda = 0.63 \mu m$	$\lambda = 10.6 \mu m$	$\lambda = 0.63 \mu m$	$\lambda = 10.6 \mu m$
CdS	$1.7 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	$(2.1 \dots 2.4) \cdot 10^{-4}$	$1.09 \cdot 10^{-4}$
$Zn_{0.52}Mg_{0.48}Se$	$9.31 \cdot 10^{-5}$	$5.29 \cdot 10^{-5}$	–	–
ZnSe	$1.13 \cdot 10^{-4}$	$4.95 \cdot 10^{-5}$	–	–

Table 2. Comparative characteristics of single-crystalline A<sup>II</sup>B<sup>VI</sup> compounds meant for IR optics

Material	ZnSe	$Zn_{1-x}Mg_xSe$ ( $0.4 \leq x \leq 0.5$ )	CdS
Structure	cubic	hexagonal	hexagonal
$\Delta E, eV$	2.7	3.0	2.4
$\rho_{max}, \Omega \cdot cm$	$\sim 10^{13}$	$10^{13}$	$10^{12}$
$\beta, cm^{-1}$ at $\lambda = 10.6 \mu m$	$< 5 \cdot 10^{-3}$	$< 7 \cdot 10^{-3}$	$3 \cdot 10^{-2}$
Radiation resistance in spot $\varnothing 1.0 mm$ at $\lambda = 10.6 \mu m, kW/cm^2$	$> 60$	$> 50$	$\cong 25$
$dn/dT$ at $\lambda = 10.6 \mu m, K^{-1}$	$5.0 \cdot 10^{-5}$	$5.29 \cdot 10^{-5}$	$10.1 \cdot 10^{-5}$
$T_{oper.max}, K$	423	423	343

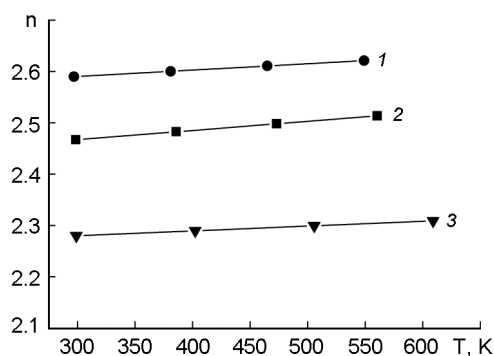


Fig. 1. Temperature dependences of refractive index for single-crystal  $A^{II}B^{VI}$  compounds: 1, ZnSe; 2, CdS; 3,  $Zn_{0.52}Mg_{0.48}Se$ .

bond coefficient: at  $0.34 \leq x \leq 0.48$ ,  $k_t = (11 \pm 1) \%$ , which is close to the values typical of well-known hexagonal  $A^{II}B^{VI}$  compounds and the solid solutions based thereon [13]. The frequency variation coefficient for a resonator made from  $Zn_{0.52}Mg_{0.48}Se$  single crystal was equal to  $4.3 \cdot 10^{-5} K^{-1}$ , i.e. lower than that of CdS resonator ( $6.7 \cdot 10^{-5} K^{-1}$ ). Moreover, it was established experimentally that the  $Q$ -factor of  $Zn_{1-x}Mg_xSe$  resonators was almost twice as high in comparison with that of the piezoelectric resonators made from hexagonal CdS single crystals.

#### 4. Conclusions

The temperature dependences of the refractive index of  $Zn_{1-x}Mg_xSe$  single crystals were measured within the temperature range from 300 to 583 K. It is shown that for  $Zn_{0.52}Mg_{0.48}Se$  single crystals grown by the vertical Bridgman method, the  $dn/dT$  value is  $9.31 \cdot 10^{-5} K^{-1}$  (at  $\lambda = 0.63 \mu m$ ) and  $5.29 \cdot 10^{-5} K^{-1}$  (at  $\lambda = 10.6 \mu m$ ). The measured  $dn/dT$  values for hexagonal  $Zn_{0.52}Mg_{0.48}Se$  single crystals differ slightly from those for cubic ZnSe single crystals and are essentially lower than the corresponding values for hexagonal CdS crystals grown by the same method. For the first time has been measured the electromechanical bond coefficient  $k_t$  for  $Zn_{1-x}Mg_xSe$  single crystals. It is established that hexagonal  $Zn_{1-x}Mg_xSe$  single crystals have rather high electromechanical bond coefficient  $k_t = (11 \pm 1) \%$  which value slightly changes

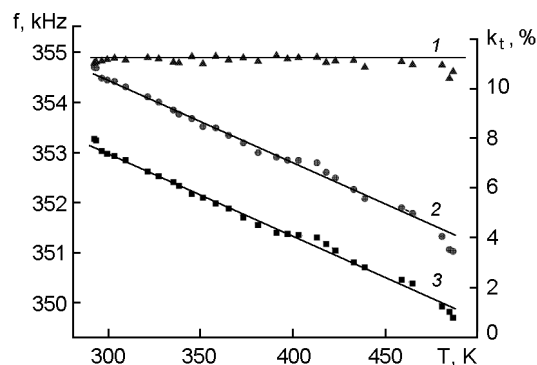


Fig. 2. Temperature dependences of piezoelectric properties for single crystals of  $Zn_{0.62}Mg_{0.38}Se$  substitution solid solution: 1, electromechanical bond coefficient; 2, anti-resonance frequency; 3, resonance frequency.

within 295–495 K temperature interval and is close to the values typical of those for the known hexagonal  $A^{II}B^{VI}$  crystals.

#### References

1. M.P.Kulakov, A.V.Fadeev, *Neorg. Mater.*, **22**, 392 (1986).
2. Yu.A.Zagoruiko, O.A.Fedorenko, N.O.Kovalenko et al., *SPIE Proc.*, **3794**, 96 (1999).
3. Yu.A.Zagoruiko, O.A.Fedorenko, N.O.Kovalenko et al., *Semiconductor Physics, Quantum & Optoelectronics*, **3**, 165 (2000).
4. V.M.Puzikov, Yu.A.Zagoruiko, O.A.Fedorenko et al., *Kristallografia*, **49**, 266 (2004).
5. W.Paszkwicz, P.Dluzewski, Z.M.Spolnik et al., *J. Alloys and Compounds*, **286**, 224 (1999).
6. Yu.A.Zagoruiko, N.O.Kovalenko, O.A.Fedorenko, *Functional Materials*, **12**, 731 (2005).
7. V.B.Bogdanov, A.N.Pikhtin, V.T.Prokopenko, A.D.Yas'kov, *Zh. Prikl. Spektrosk.*, **51**, 654 (1989).
8. V.I.Gavrilenko, A.M.Grekhov, D.V.Korbutyak, V.G.Litovchenko, *Optical Properties of Semiconductors*, Naukova Dumka, Kiev (1987) [in Russian].
9. G.A.Abil'siitov, V.S.Golubev, V.G.Gontar', *Technological Lasers*, Mashinostroenie, Moscow (1991) [in Russian].
10. M.P.Shaskol'skaya, A.A.Blistanov, V.S.Bondarenko, V.N.Perelomova, *Acoustic Crystals*, Nauka, Moscow (1982) [in Russian].
11. Patent of Ukraine 46429A, (2002).
12. Patent of Russian Federation 1349543, (1993).
13. N.F.Obukhova, L.V.Atroshchenko, A.I.Kolodyazhnyi, *Izv. AN SSSR. Neorg. Mater.*, **13**, 1390 (1977).

## **Температурні залежності оптичних та п'єзоелектричних характеристик монокристалів ZnMgSe**

***Ю.А.Загоруйко, Н.О.Коваленко, В.М.Пузіков, О.О.Федоренко***

Досліджено температурні залежності коефіцієнта заломлення світла у монокристалах твердих розчинів  $Zn_{1-x}Mg_xSe$ , отриманих за методом Бриджмена. Встановлено, що у діапазоні температур 300–583 К величина  $dn/dT$  кристалів  $Zn_{0,52}Mg_{0,48}Se$  складає  $9,31 \cdot 10^{-5} \text{ K}^{-1}$  при  $\lambda = 0,63 \text{ }\mu\text{m}$  та  $5,29 \cdot 10^{-5} \text{ K}^{-1}$  при  $\lambda = 10,6 \text{ }\mu\text{m}$ . Досліджено температурні залежності п'єзоелектричних властивостей монокристалів  $Zn_{1-x}Mg_xSe$ . Встановлено, що при  $0,34 \leq x \leq 0,48$  величина коефіцієнта електромеханічного зв'язку  $k_t$  складає  $(11 \pm 1) \%$  та зберігає своє значення у діапазоні температур 295–495 К.