

## COMPOSITIONAL VARIATION OF OPTICAL AND REFRACTOMETRIC PARAMETERS OF $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> MIXED CRYSTALS

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Refractive index dispersion in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals with  $x=0.1; 0.2; 0.3; 0.4$  in a broad spectral range is shown to be well described by optical-refractometric relation. The effect of In→Ga cationic substitution upon the refractive index dispersion and molar refraction in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals is studied.

(Received July 14, 2003; accepted August 21, 2003)

*Keywords:* Refractive index, Optical-refractometric relation, Compositional dependence

### 1. Introduction

Crystals of (Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> semiconducting solid solutions with  $0.02 < x < 0.55$  belong to the  $\gamma_1$ -phase of the Ga<sub>2</sub>Se<sub>3</sub>-In<sub>2</sub>Se<sub>3</sub> chalcogenide ternary compounds [1]. They crystallize in hexagonal structure with defect wurtzite symmetry (P6<sub>1</sub> or P6<sub>3</sub> space group). A typical feature of this structure is high concentration of vacancies due to the fact 1/3 of sites in the cation sublattice being empty; these vacancies are the intrinsic defects of the crystal lattice, capable of forming spirals along the *c* axis [1].  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals are characterized by low electronic conductivity ( $\sim 10^{-10} \Omega^{-1} \times \text{cm}^{-1}$ ). Photoconductivity in  $\gamma_1$ -phase is almost by three orders higher than in other phases [1]. The crystals possess high optical activity along the optical axis and are promising materials for acousto-optical modulators [2–5]. Some optical properties (Raman scattering, far-infrared reflection spectra, fundamental absorption edge spectra) were presented in [2,6–11]. Refractive index dispersion for both ordinary  $n_o$  and extraordinary  $n_e$  rays in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals were studied at room temperature by prism technique [2].

Here we report the description of the refractive index dispersion by optical-refractometric (OR) relation and the analysis of the compositional behaviour of some optical and refractometric parameters for  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> mixed crystals with  $x=0.1; 0.2; 0.3; 0.4$ .

### 2. Theory

It was shown [2] that the experimental values of the refractive indices of  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals in a broad spectral range  $0.57 \div 5 \mu\text{m}$  are in a good agreement with those calculated using a well known one-term Sellmeier relation. However, deeper physical treatment of the dispersion dependences of the refractive indices can be obtained based on the relationship between the refractive index and the energy gap. A number of empirical and semiempirical relations of such kind are known from the

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literature [12–18]. Among them one should first of all mention the well known empirical Moss ( $n_{\infty}^4 E_g = 95$  eV [12] or  $n_{\infty}^4 E_g = 107$  eV [13]) and Penn [14] relations,

$$n_{\infty}^2 - 1 = E_{pv}^2 / E_g^2, \quad (1)$$

where  $n_{\infty}$  is the refractive index in the long-wavelength spectral range,  $E_g$  is the energy gap,  $E_{pv}$  is the energy of plasma vibrations of valence electrons. Wemple and DiDomenico [15,16] made an attempt to find theoretically a correlation between the refractive index and the energy gap and obtained the relation

$$(n_{\infty}^2 - 1)E_t \approx \frac{2}{3} \beta N_c Z_a N_e, \quad (2)$$

where  $E_t \approx E_g$ ;  $N_c$  is the coordination number;  $Z_a$  is the formal chemical valence of the anion;  $N_e$  is the total number of valence electrons per anion;  $\beta$  is a constant, equal to  $0.37 \pm 0.04$  eV for covalent and  $0.26 \pm 0.04$  eV for ionic crystals. Later, Ravindra et al. [17,18] supposed another empirical relationship

$$n_{\infty} = 4.084 - 0.62E_g. \quad (3)$$

The above relations describe exactly enough the relationship between  $E_g$  and  $n$  for different classes of semiconductor materials. However, they do not permit to describe the dispersion dependence of the refractive index. OR relation, proposed in [19], lacks this shortcoming.

### 3. Results and discussion

OR relation enables to describe the dependence of the refractive index on dispersion on the basis of its relationship to the optical pseudogap  $E_g^*$  and the energy of plasma vibrations of valence electrons  $E_{pv}$  as

$$\frac{1}{3} \frac{n^2(h\nu) + 2}{n^2(h\nu) - 1} = \left( \frac{\eta_s}{2} \right)^s \left( 1 + \frac{E_g^*}{E_{pv}} \right)^s - \left( \frac{h\nu}{E_s} \right)^s, \quad (4)$$

where  $E_{pv} = 28.82 \sqrt{n_v \rho / \mu}$ ,  $n_v$  is the number of valence electrons per formula unit,  $\rho$  is density,  $\mu$  is molecular mass;  $\eta_s$  and  $E_s$  are adjustment parameters;  $s=2$  for the medium-energy and  $s=3$  for the high-energy parts of the transparency range. The optical pseudogap  $E_g^*$  is the energy position of the absorption edge in semiconductors where direct allowed transitions are masked by exponential absorption tails caused by various types of disordering [20].

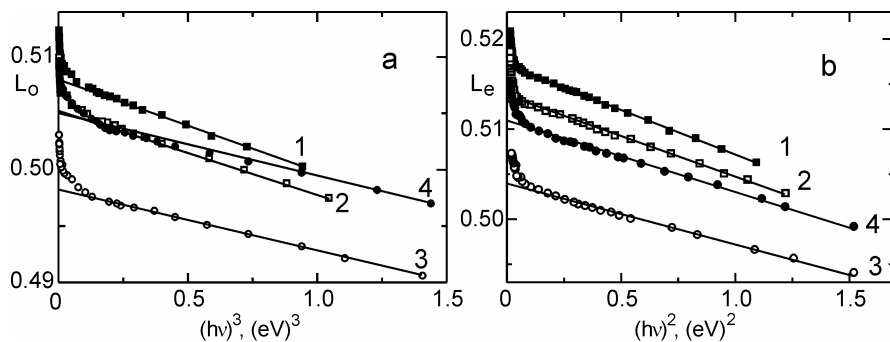


Fig.1. Dependences  $L_o=f[(h\nu)^3]$  (a) for the refractive index of the ordinary ray and  $L_e=f[(h\nu)^2]$  (b) for the refractive index of the extraordinary ray for  $\gamma_1-(\text{Ga}_x\text{In}_{1-x})_2\text{Se}_3$  crystals with various values of  $x$ : 1 – 0.1; 2 – 0.2; 3 – 0.3; 4 – 0.4.

It should be noted that the reliability of the OR relation has been shown for over 150 different non-metallic substances [19]. Hence, Eq. (4) was used to describe the experimental dispersion of the refractive indices of  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals, i. e. the linear dependences  $L=f[(h\nu)^s]$  (Fig.1) where  $L(h\nu) \equiv \frac{1}{3} \frac{n^2(h\nu) + 2}{n^2(h\nu) - 1}$  being the evidence for the successful description. The dependences  $L=f[(h\nu)^3]$  are given for the ordinary ray refractive index, and  $L=f[(h\nu)^2]$  – for the extraordinary one. The values of the adjustment parameters  $\eta_s$  and  $E_s$  resulting in the best fit between the calculated and experimental dependences  $n_o(h\nu)$  and  $n_e(h\nu)$ , are listed in Table 1.

Table 1. The main optical and refractometric parameters of  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals at room temperature.

Crystal		$\rho$ , g/cm <sup>3</sup>	$E_{pv}$ , eV	$E_g^*$ , eV	$E_2$ , eV	$E_3$ , eV	$\eta_2$	$\eta_3$
(Ga <sub>0.1</sub> In <sub>0.9</sub> ) <sub>2</sub> Se <sub>3</sub>	o	5.22	15.08	1.982	9.89	5.59	1.263	1.409
	e			1.950	9.66	5.53	1.274	1.418
(Ga <sub>0.2</sub> In <sub>0.8</sub> ) <sub>2</sub> Se <sub>3</sub>	o	5.37	15.45	2.044	10.37	5.62	1.258	1.406
	e			2.012	10.59	6.05	1.268	1.413
(Ga <sub>0.3</sub> In <sub>0.7</sub> ) <sub>2</sub> Se <sub>3</sub>	o	5.41	15.67	2.088	11.02	5.42	1.247	1.399
	e			2.074	11.17	5.48	1.254	1.404
(Ga <sub>0.4</sub> In <sub>0.6</sub> ) <sub>2</sub> Se <sub>3</sub>	o	5.50	15.96	2.188	10.07	5.59	1.253	1.400
	e			2.164	9.46	5.38	1.260	1.405

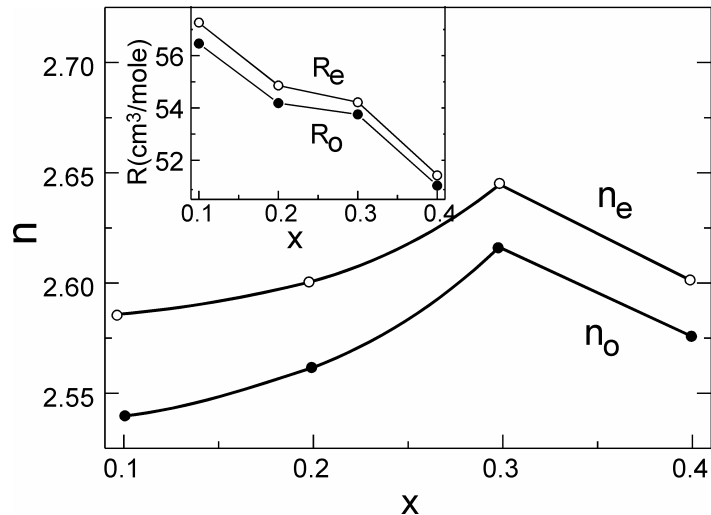


Fig. 2. Compositional dependences of the refractive indices  $n_o$  and  $n_e$  at room temperature and  $\lambda=5 \mu\text{m}$  for  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals. The inset shows the compositional dependences of molar refractions  $R_o$  and  $R_e$ .

All the crystals are optically positive, since for all of them  $\Delta n = n_e - n_o > 0$ . Fig. 2 presents the compositional dependences of the refractive indices  $n_o$  and  $n_e$  for  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals at room temperature and  $\lambda=5 \mu\text{m}$ . With the increase of gallium content the refractive indices increase, reaching maximum at  $x=0.3$ , and then decrease. Knowing the compositional dependences of density  $\rho(x)$ ,  $n_o(x)$  and  $n_e(x)$ , the compositional dependences of molar refraction  $R_{o,e}(x)$  were calculated (See the inset to Fig. 2) using the known formula

$$R_{o,e}(x) = \frac{\mu(x)}{\rho(x)} \times \frac{n_{o,e}^2(x) - 1}{n_{o,e}^2(x) + 2}. \quad (5)$$

It is seen from the inset to Fig. 2 that the increase of gallium content in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals results in the decrease of the molar refraction (electronic polarizability), a feature in the  $R_{o,e}(x)$  dependences being observed at  $x=0.3$ . Thus, the anomalous compositional behaviour of the refractive indices in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> is determined by the nonlinear compositional behaviour of density (Table 1) and the anomalous variation of molar refraction (Fig. 2).

### 3. Conclusions

The dispersion dependences of the refractive indices for ordinary and extraordinary rays in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> crystals with  $x=0.1, 0.2, 0.3, 0.4$  in a broad spectral range are shown to be well described by the optical-refractometric relation linking the dispersion  $n(h\nu)$ , optical pseudogap  $E_g^*$  and the energy of plasma vibrations of the valence electrons  $E_{pv}$ . With the increase of Ga content the value of the refractive index increases, reaches a maximum at  $x=0.3$  and then decreases. The anomalous compositional behaviour of the refractive indices in  $\gamma_1$ -(Ga<sub>x</sub>In<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> is shown to be determined by the nonlinear compositional behaviour of density and the anomalous variation of molar refraction.

### References

- [1] S. Popović, B. Čelustka, Ž. Ružić-Toroš, D. Broz, *phys. stat. sol. (a)* **41**, 255 (1977).
- [2] M. Kranjčec, I. D. Desnica, B. Čelustka, A. N. Borets, Gy. Sh. Kovacs, Z. P. Hadmashy, L. M. Suslikov, I. P. Studenyak, *phys. stat. sol. (a)* **153**, 539 (1996).
- [3] J. Ye. T. Yoshida, Y. Nakamura, O. Nittono, *Appl. Phys. Lett.* **67**, 3066 (1995).
- [4] J. Ye. T. Yoshida, Y. Nakamura, O. Nittono, *Jpn. J. Appl. Phys.* **35**, 4395 (1996).
- [5] M. Kranjčec, I. D. Desnica, I. P. Studenyak, B. Čelustka, A. N. Borets, I. M. Yurkin, Gy. S. h. Kovacs, *Applied Optics* **36**, 490 (1997).
- [6] P. Dubček, B. Etlinger, K. Furić, M. Kranjčec, *phys. stat. sol. (a)* **122**, K87 (1990).
- [7] P. Dubček, B. Etlinger, B. Pivac, M. Kranjčec, *Solid State Communications* **81**, 735 (1992).
- [8] M. Kranjčec, B. Čelustka, B. Etlinger, D. Desnica, *phys. stat. sol. (a)* **109**, 329 (1988).
- [9] D. I. Desnica, M. Kranjčec, B. Čelustka, *J. Phys. Chem. Solids* **52**, 915 (1991).
- [10] M. Kranjčec, D. I. Desnica, B. Čelustka, Gy. Sh. Kovacs, *phys. stat. sol. (a)* **139**, 513 (1993).
- [11] M. Kranjčec, D. I. Desnica, B. Čelustka, Gy. Sh. Kovacs, I. P. Studenyak, *phys. stat. sol. (a)* **144**, 223 (1994).
- [12] T. S. Moss, *phys. stat. sol. (b)* **131**, 415 (1985).
- [13] N. M. Ravindra, V. K. Srivastava, *Infrared Phys* **19**, 603 (1979).
- [14] D. R. Penn, *Phys. Rev.* **128**, 2093 (1962).
- [15] S. H. Wemple, *Phys. Rev. B* **7**, 3767 (1973).
- [16] S. H. Wemple, M. Di Domenico, *Phys. Rev. B* **3**, 1338 (1971).
- [17] N. M. Ravindra, S. Auluck, V. K. Srivastava, *phys. stat. sol.(b)* **93**, K155 (1979).
- [18] V. P. Gupta, N. M. Ravindra, *phys. stat. sol.(b)* **100**, 715 (1980).
- [19] A. N. Borets, *Ukr. Fiz. Zhurn.* **28**, 1346 (1983).
- [20] I. P. Studenyak, M. Kranjčec, Gy. Sh. Kovacs, V. V. Panko, D. I. Desnica, A. G. Slivka, P. P. Guranich, *J. Phys. Chem. Solids* **60**, 1897 (1999).