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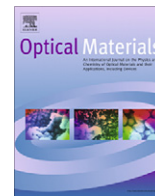
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## Refractometric studies of chalcogenide glasses in Ag–As–S system

O.I. Shpak, M.M. Pop, I.I. Shpak, I.P. Studenyak\*

Uzhhorod National University, 46 Pidhirna St., Uzhhorod 88000, Ukraine

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### ABSTRACT

Compositional behavior of refractometric parameters and refractive index dispersion for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys in Ag–As–S system were studied. Nonlinear compositional dependences of density and refractive index were revealed. Chemical bond ionicity as well as average coordination number and molar refraction versus silver content variation in the glassy alloys were estimated.

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### 1. Introduction

Chalcogenide glassy semiconductors which contain silver are applied as ion selective membranes, sensors and solid-state power sources [1–8]. They are characterized by high transparency, the possibility of synthesis of materials with a broad range of physical, chemical and optical parameters by variation of type and proportion of anionic and cationic components in the alloys. The increase of silver content in silver-containing glassy semiconductors of Ag–As–S system leads to significant changes in their properties that cause the interest towards the studies of compositional behavior of the parameters of these glasses. Structural, electrical, and dielectric parameters of  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys change most rapidly at  $x \sim 5\text{--}7$  mol%, while at  $x > 8\text{--}10$  mol% the alloys are characterized by high ionic conductivity [3–6].

Accordingly, the main attention in previous papers was focused on the measurements of electric characteristics, while the optical properties have been investigated insufficiently.

In this paper, compositional behavior of density, refractive index as well as molar refraction of  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys for  $x = 0\text{--}20$  mol% was studied.

### 2. Experimental

Glasses in  $\text{Ag}_2\text{S}\text{--}\text{As}_2\text{S}_3$  system were prepared by direct synthesis of extra pure elemental components in evacuated ( $\sim 1.5 \times 10^{-3}$  Pa) quartz ampoules. The ampoules with initial substances were heated up to 600 °C at 30–40°/h rate and kept at this temperature

for 8 h. Then the temperature was increased to 950 °C, the ampoules were kept at this temperature for 2–2.5 h and then cooled down to 600 °C at 100°/h rate with subsequent sample quenching in air.

The glass samples were obtained in ampoules in the shape of 1 cm high cylinders, 1 cm in diameter, their mass being 3–3.5 g. A characteristic conchoidal fracture was the visual evidence for the glass nature of the samples obtained.

The obtained  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glasses with  $\text{Ag}_2\text{S}$  content up to  $x = 20$  mol% appeared to be optically transparent in the visible spectral range. The homogeneous structure of the samples was confirmed by X-ray and microstructural studies. The density of the glasses was determined by hydrostatic weighing in toluene with the relative error of 0.5%.

Spectrometric studies of transmission spectra were carried out using a LOMO MDR-3 grating monochromator. The refractive index dispersion was measured by prism technique in the spectral range 0.6–12 μm. From 0.6 to 0.84 μm a LOMO MDR-3 monochromator was used while in the infrared range an IKS-21 spectrometer was used [9]. The refractive index in the spectral range under investigation was determined within the error of  $\pm 1 \times 10^{-3}$ .

### 3. Results

Fig. 1 shows the transmission spectra of  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys with  $x = 0, 5, 10, 15$  mol% measured at room temperature. It is seen that with  $\text{Ag}_2\text{S}$  content increase the transmission spectra shift towards longer wavelengths, the slope of the spectra in the range of the optical absorption edge becomes less steep and the transmittance value in the transparency range decreases.

\* Corresponding author. Tel.: +380 312 235 044; fax: +380 312 233 341.

E-mail address: [studenyak@dr.com](mailto:studenyak@dr.com) (I.P. Studenyak).

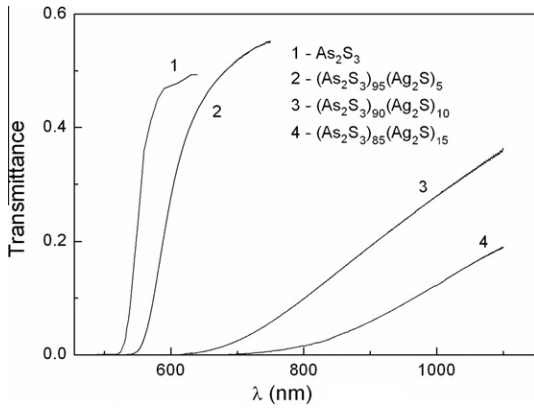


Fig. 1. Transmission spectra of  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys.

The refractive index dispersion for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys with  $x = 0, 3, 5, 10, 15, 20$  mol% is presented in Fig. 2. It should be noted that the refractive indices were calculated using a well known formula.

$$n = \frac{\sin(\varphi + \delta)}{\sin \varphi} \quad (1)$$

where  $\varphi$  is the refractive angle of the prism,  $\delta$  is the deflection angle of the beam while passing through the prism. In the spectral range under investigation the refractive index dispersion is observed which slightly varies in the infrared spectral range and essentially increases with the approach to the optical absorption edge of the glasses (Fig. 2).

Compositional dependences of the refractive index and density for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys with  $0 \leq x \leq 20$  are shown in Fig. 3. It is seen that with the increase of  $\text{Ag}_2\text{S}$  content both the refractive index and the density nonlinearly increase with upward bowing. The molar refraction  $R_{\text{exp}}(x)$  was determined using the values  $n$  and  $\rho$  (Fig. 3) according to the formula

$$R_{\text{exp}}(x) = \frac{\mu(x)}{\rho(x)} \times \frac{n^2(x) - 1}{n^2(x) + 2} \quad (2)$$

where  $\mu$  is molar mass. The compositional dependence of the molar refraction  $R_{\text{exp}}(x)$  are shown in Fig. 4. Refraction is caused by a purely electronic process and its variation with composition reflects the change of the effective size of the electron shells of the alloy atoms. Therefore, incorporation of small Ag atoms in the alloys structural network leads to the refraction decrease (Fig. 4).

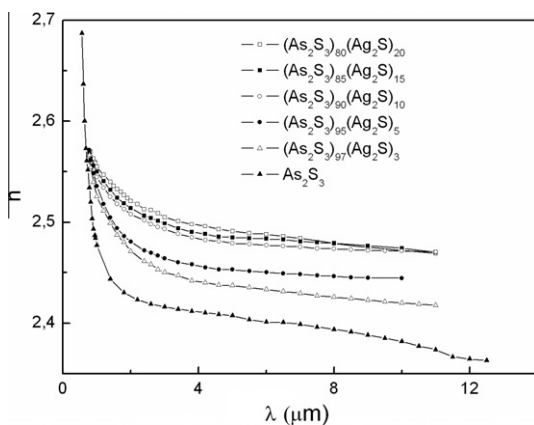


Fig. 2. Dispersion of the refractive index for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys.

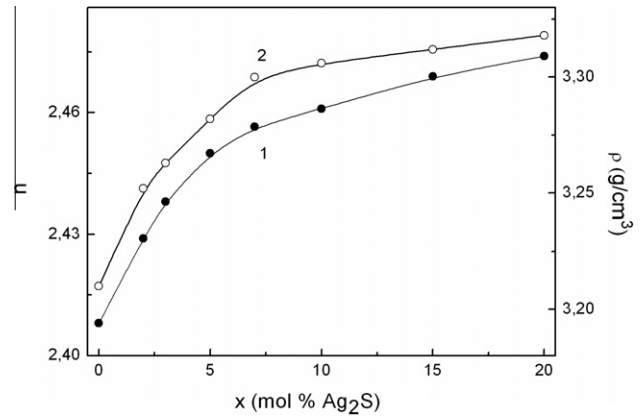


Fig. 3. Dependences of the refractive index at  $\lambda = 5 \mu\text{m}$  (1) and density (2) on  $\text{Ag}_2\text{S}$  content in  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys.

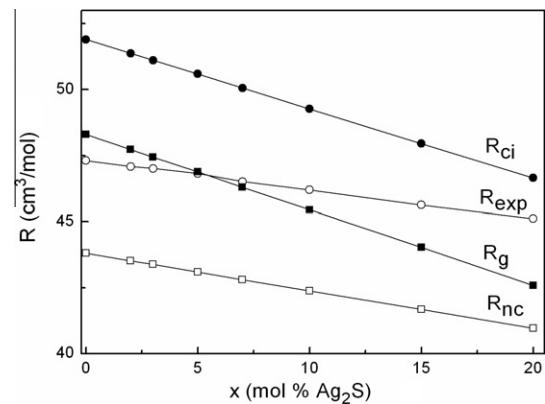


Fig. 4. Compositional dependences of molar refraction in  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys: crystalline ionic refraction  $R_{\text{ci}}$ , "glassy" refraction  $R_{\text{g}}$ , normal covalent refraction  $R_{\text{nc}}$ , and experimental refraction  $R_{\text{exp}}$ .

#### 4. Discussion

According to the dispersion theory, the spectral dependence of the refractive index  $n(\lambda)$  can be expressed as follows [10]:

$$n^2(\lambda) - 1 = \sum S_i \lambda_i^2 \left[ 1 - (\lambda_i/\lambda)^2 \right] \quad (3)$$

where  $S_i$  and  $\lambda_i$  are the strength and the wavelength of the oscillator, respectively. If the electronic subsystem is replaced by the equivalent number of identical independent oscillators, Eq. (3) can be written as [11]

$$n^2(\lambda) - 1 = S_0 \lambda_0^2 \left[ 1 - (\lambda_0/\lambda)^2 \right] \quad (4)$$

where  $S_0$  and  $\lambda_0$  are the average values of the oscillator strength and wavelength, respectively. Using the Kramers–Kronig relations, it was shown that  $S_0$  can be replaced by a product of two parameters [12]

$$S_0 \equiv E_d E_0 = (hc/e^2) \quad (5)$$

where  $E_0 = hc/e\lambda_0$  ( $h$  is the Planck's constant,  $c$  is the speed of light in vacuum,  $e$  is the electron charge),  $E_d$  is the dispersion energy of the refractive index.

Taking into account Eqs. (4) and (5), Wemple and Di Domenico obtained an expression to describe the dispersion of the refractive index:

$$n^2 - 1 = \frac{E_0 \cdot E_d}{E_0^2 - E^2} \quad (6)$$

The oscillator energy  $E_0$  roughly corresponds to the maximum of the imaginary part of the dielectric constant and can be identified with an average energy transition from the valence band to the conduction band. The dispersion energy  $E_d$  determines the dielectric constant dispersion in nonmetallic nonmagnetic solids and is related by a simple expression to the cation coordination number  $N_c$ , anion valence  $Z_a$  and the number of effective valence electrons  $N_v$  per anion

$$E_d = \beta N_c N_v Z_a \quad (7)$$

where  $\beta$  is a parameter depending on the bond ionicity degree:  $\beta = (0.26 \pm 0.04)$  eV for ionic compounds and  $\beta = (0.37 \pm 0.04)$  eV for covalent materials. Using the relation between  $E_d$  and the ionicity degree  $f_i$  [12]

$$E_d \approx 60[\xi(1 - f_i)]^{1/2} \quad (8)$$

where  $\xi = 1/2$ , one can determine the  $f_i$  value. The ionicity degree, evaluated according to Eq. (8) and Phillips relation [13] as

$$f_i^F = (\varepsilon - n^2)/(\varepsilon - 1) \quad (9)$$

where  $\varepsilon$  is dielectric permittivity, is the evidence for mixed (covalent and ionic) nature of chemical bonds of the alloys under investigation (Table 1). The values of  $f_i$  determined by different procedures are quite close to each other and show the increase of ionicity with the silver content increase in the alloys. Taking into account the mixed covalent-and-ionic nature of the chemical binding, we used the equation

$$\beta = 0.26f_i + 0.37(1 - f_i) \quad (10)$$

to determine the parameter  $\beta$ . Based on Eqs. (7) and (10), the parameter  $N_c$  was calculated which is quoted in Table 1. The dispersion parameters  $E_0$  and  $E_d$  were determined by linearization in the coordinates  $n^2(\lambda) - 1 = f(\lambda^2)$

It should be noted that glasses in the  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  system represent a combination of polar and nonpolar trigonal structural units of  $\text{AsS}_{3/2}$  and  $\text{Ag}^+\text{S}^-\text{AsS}_{3/2}$  type and this causes the variation of  $f_i$  and  $N_c$ . Silver ions crosslink the groups of pyramids in double layers, the chemical binding within the layers is ionic-and-covalent while the chemical binding between the layers is of Van-der-Waals type, forming dipoles and quadrupoles:  $\text{S}_{3/2}\text{AsS}^-\text{Ag}^+$ ,  $\text{S}_{2/2}\text{AsS}^-\text{Ag}^+$  and  $\text{Ag}^+\text{S}^-\text{AsS}_{3/2}$  [2,3]. Incorporation of silver in the mainly covalent-bound structural network of the initial glass leads to the formation of structural fragments (clusters containing  $\text{Ag}^+\text{S}^-$  ion bond or complexes containing Ag impurity atoms and the matrix atoms and that are apparently formed on surfaces within the structural fragments or in the intermolecular space) [1,4]. The increase of  $\text{Ag}_2\text{S}$  content leads to the reduction of the total area of the boundary surfaces and to an intense “matching” of the structural fragments, i.e. the process of their accumulation and consolidation takes place resulting in an decrease of the average coordination number and in an increase of the bond ionicity degree.

The comparative analysis of the compositional dependences of the experimental refraction  $R_{\text{exp}}(x)$  and the calculated refraction for different schemes of chemical binding using the crystalline covalent refraction  $R_{\text{cc}}$ , normal covalent refraction  $R_{\text{nc}}$ , crystalline ionic refraction  $R_{\text{ci}}$ , atomic refraction  $R_a$  as well as “glassy” refraction  $R_g$  [13,14] enables one to conclude on the prevailing type of chemical binding in the materials under investigation. The most

**Table 1**

Dispersion parameters  $E_0$  and  $E_d$ , degree of bond ionicity  $f_i$ , average coordination number  $N_c$ , and  $\beta$  parameter for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys.

Glass	$E_0$ (eV)	$E_d$ (eV)	$\beta$	$f_i$ (%)	$N_c$
$\text{As}_2\text{S}_3$	4.87	23.43	0.30	0.41	4.21
$(\text{Ag}_2\text{S})_3(\text{As}_2\text{S}_3)_{97}$	4.83	23.38	0.31	0.43	4.03
$(\text{Ag}_2\text{S})_5(\text{As}_2\text{S}_3)_{95}$	4.75	23.12	0.31	0.45	4.01
$(\text{Ag}_2\text{S})_{10}(\text{As}_2\text{S}_3)_{90}$	4.05	22.52	0.31	0.48	3.91
$(\text{Ag}_2\text{S})_{15}(\text{As}_2\text{S}_3)_{85}$	3.51	21.94	0.32	0.51	3.70
$(\text{Ag}_2\text{S})_{20}(\text{As}_2\text{S}_3)_{80}$	2.94	21.32	0.32	0.54	3.61

realistic schemes of the chemical binding, taking into account the experimental data on the chemical structure of the alloys under investigation (e.g. [15]), were systems with refraction  $R_{\text{ci}}$ ,  $R_{\text{nc}}$ , and  $R_g$ . However, taking into account the mixed ionic-and-covalent binding type, we proposed a combined scheme for the compositional behavior of  $R_{\text{exp}}(x)$  where the “glassy” refraction is chosen for As and S atoms and crystalline ionic refraction is taken for Ag atoms with the account of the change of the ionicity degree with the concentration of the latter. Thus, based on this scheme, using optimal polynomial method [14] and considering linear behavior of the experimental molar refraction  $R_{\text{exp}}(x)$ , we obtained the additive values of atomic refractions for Ag (14.7 cm<sup>3</sup>/mol), As (12.5 cm<sup>3</sup>/mol) and S (7.1 cm<sup>3</sup>/mol) that according to the additive principle enable the refraction value for any composition of this system to be calculated.

## 5. Conclusions

Glasses in  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  system were obtained and their structural properties were studied. The refractive index dispersion of  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys with  $x = 3, 5, 10, 15, 20$  mol% was measured in the spectral range 0.6–12  $\mu\text{m}$ . The spectral dependences of refractive indices are well described in the framework of Wemple and Di Domenico model. The dispersion parameters, the degree of bond ionicity, and the average coordination number for  $(\text{Ag}_2\text{S})_x(\text{As}_2\text{S}_3)_{100-x}$  glassy alloys were calculated. Based on the compositional dependences of the density, the refractive index, and the molar refraction, the values of additive refraction for the atoms being contained in the alloy composition were obtained.

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