
**COMPOSITION DEPENDENCE AND INTERRELATION
BETWEEN OPTICAL-REFRACTOMETRIC
AND THERMOOPTICAL PARAMETERS
OF VITREOUS ALLOYS $(As_2S_3)_{100-x}(As_2Se_3)_x$** **I.I. SHPAK, I.P. STUDENYAK, D.G. SEMAK, M. KRANJCEC¹,
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The influence of the compositional disordering in the vitreous alloys $(As_2S_3)_{100-x}(As_2Se_3)_x$ on their optical absorption edge and the dispersion of the refractive index has been studied. The additive values of As, S, and Se refractions in those alloys have been determined experimentally. The interrelations between the composition dependences of optical pseudogap, refractive index, and refractions of initial components have been observed.

Chalcogenide vitreous semiconductors (ChVSs) belonging to the As–S–Se system are used as active and passive elements in the optoelectronics of mid- and far-IR ranges (2–25 μm). They possess good chemical and radiation stability and high transparency and enable materials with a wide spectrum of physical, chemical, and optical parameters to be synthesized by varying the types of the cation and anion components of alloys, as well as their quantitative ratio. Today, the alloys of the As–S–Se system are mostly used in IR fiber optics and laser equipment [1–3], optical pyrometry and thermal imaging [4, 5], medical diagnostics and gas analysis [4–7]. They also serve as the basis for the fabrication of negative and positive photoresists with high resolution, diffraction gratings, and compact disks [8–10]. As a consequence, the main attention has been focused on the study of massive glasses and thin layers made up of $As_{40}S_{60-x}Se_x$ compound [8, 11–14]. However, the researches of $As_{40}S_{60-x}Se_x$ -

based inorganic resists have demonstrated that the materials concerned with an enhanced content of Se are characterized by a certain instability of optical parameters. The thermo-optical properties of those alloys remained practically unexplored. In this work, we report the results of complex researches of the intrinsic absorption edge, the dispersion of the refractive index, and the thermo-optical properties of vitreous alloys belonging to the $(As_2S_3)_{100-x}(As_2Se_3)_x$ section of the As–S–Se system, with the main attention being focused on compositions with low content of selenium ($x = 0 \div 20$ mol.%).

The alloys of the system under investigation were synthesized by fusing elementary components with ultra purity grades in evacuated quartz ampoules at a single temperature. The temperature of homogenization was selected for every composition individually, so that it did not exceed the melting one by more than 50 \div 100 K. The rate of alloy cooling was approximately 10 K/s. The vitreous state was monitored by X-ray phase and microstructural analyses. The glass density was determined with an error of 0.5% by hydrostatic weighing of specimens in toluene.

The dispersion of the refractive index, $n(\lambda)$, was studied in the spectral range 1 \div 10 μm by the prism

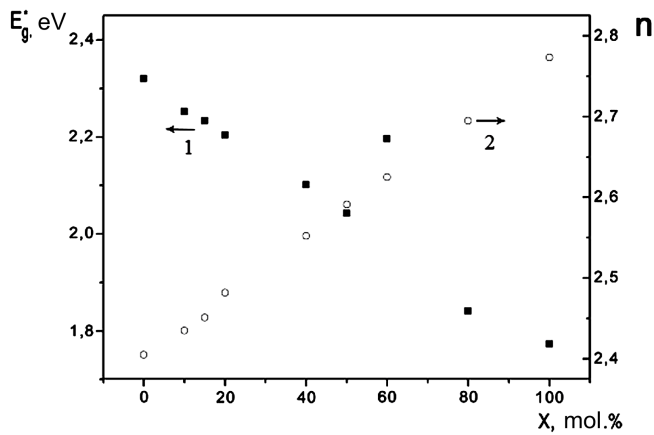


Fig. 1. Dependences of the optical pseudogap E_g^* (squares) and the refractive index n (circles) on the content x of vitreous alloy $(As_2S_3)_{100-x}(As_2Se_3)_x$

method, using specimens with refraction angles $\varphi = 11 \div 12^\circ$ and $5 \times 10\text{-mm}^2$ working surfaces polished to provide a surface finish of class 14. The deflection angles of the light beam were measured with the help of an attachment constructed on the basis of an ODG-10 optical dividing head, which allowed the deflection angles to be determined to within $10'$. The refraction angles of the prisms were determined by a GS-1.5 goniometer. The measurement error for n was 2×10^{-4} in the whole spectral range under consideration, the accuracy of temperature stabilization was ± 1 K. The spectral dependences of the absorption coefficient $\alpha(h\nu)$ were obtained on the basis of experimental researches of the transparency and the reflection power following the technique and using an installation described in work [15]. Specimens of various thicknesses $d = 40 \div 300 \mu\text{m}$ were used for studies. The relative error $\Delta\alpha/\alpha$ for the absorption coefficient was less than 10%, provided $0.2 \leq \alpha d \leq 3$.

Our researches showed that the temperature and spectral dependences of the absorption coefficient $\alpha(h\nu)$ in vitreous As–S–Se alloys along the $(As_2S_3)_{100-x}(As_2Se_3)_x$ section in the vicinity of the intrinsic absorption edge are characterized by the exponential behavior [16, 17]

$$\alpha(h\nu) = \alpha_0 \exp[(h\nu - E_g^*/W)], \quad (1)$$

where E_g^* is an optical pseudogap, which corresponds to the energy position of the absorption edge at a fixed absorption level $\alpha = 10^3 \text{ cm}^{-1}$; and $W(x, T)$ is the energy width of the exponential absorption edge, which is governed by the compositional and dynamic disorders. The composition dependences $E_g^*(x)$ and

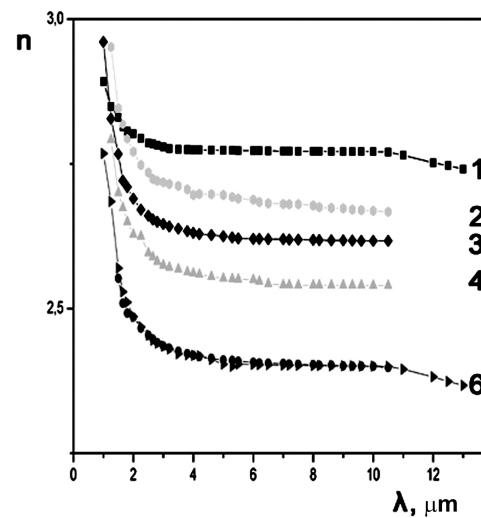


Fig. 2. Concentration dependences of the dispersion $n(\lambda)$ for the alloys of the system As–S–Se: $x = 100$ (1, As_2S_3), 80 (2), 60 (3), 40 (4), and 0 mol.% As_2S_3 (6). Points correspond to experimental data, solid curves to calculation ones

$n(x)$ are exhibited in Fig. 1. It is evident that those dependences are practically linear functions of the content x . Such a behavior of the optical pseudogap with respect to the solid solution composition enables one to consider vitreous alloys of the As–S–Se system as solid solutions of stoichiometric compounds As_2S_3 and As_2Se_3 [12, 17]. The change of the content ratio between them gives rise to a linear variation of the E_g^* magnitude: the latter grows from the value $E_g^* = 1.77$ eV, which corresponds to As_2Se_3 glass, to $E_g^* = 2.32$ eV for As_2S_3 one, i.e. it is determined by partial contributions of the initial compounds to a specific composition of the section concerned.

The results of researches of the dispersion $n(\lambda)$ are presented in Fig. 2. The normal behavior of the dispersion in the transparency range evidences for the absence of absorption bands in this spectral interval. The dispersion growth in the short-wave region is connected with the approach to the intrinsic absorption edge, while the shift of dispersion curves correlates with the variation of E_g^* which accompanies the content change. At a fixed wavelength $\lambda = 5 \mu\text{m}$, the quantity n linearly increases from the value of 2.410, which corresponds to the content As_2S_3 , to the value of 2.773, which is inherent to As_2Se_3 glass. For an annealed specimen with the content $x = 10$, the value of n is somewhat higher than that for an unannealed one, which is associated with a more arranged (less defective) structure of the former specimen. The temperature coefficient of the refractive index (TCRI) $\partial n/\partial T$ at the wavelength

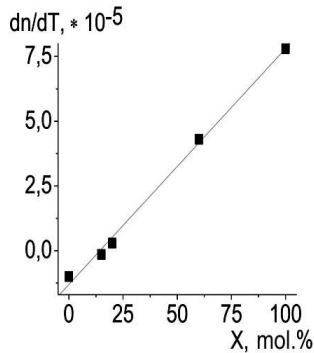


Fig. 3. Dependence of the temperature derivative $\partial n/\partial T$ of the refractive index on the vitreous alloy content along the section $(\text{As}_2\text{S}_3)_{100-x}(\text{As}_2\text{Se}_3)_x$

$\lambda = 3 \mu\text{m}$ amounts to $3.2 \times 10^{-5} \text{ K}^{-1}$ for As_2Se_3 and to $-0.4 \times 10^{-5} \text{ K}^{-1}$ for As_2S_3 , i.e. there is the inversion of the TCRI sign (the TCRI passes through zero). The composition dependence of the temperature increase in n is a linear function of the content and is well described by the relation

$$\partial n/\partial T(x) = \partial n/\partial T(0) + x[\partial n/\partial T(1) - \partial n/\partial T(0)], \quad (2)$$

where $\partial n/\partial T(x=0) \equiv \partial n/\partial T(0)$ and $\partial n/\partial T(x=1) \equiv \partial n/\partial T(1)$ are the TCRI values for the initial compositions of vitreous alloys. According to expression (2), the zero value of the TCRI has to be attributed to the composition $(\text{As}_2\text{S}_3)_{88}(\text{As}_2\text{Se}_3)_{12}$. The experimental results for the content $x = 10$ (an unannealed specimen) are practically in agreement with the calculation ones ($\partial n/\partial T = -0.14 \times 10^{-5} \text{ K}^{-1}$).

Refraction is caused by merely electronic processes, and its variation, which accompanies a change of the alloy content (Fig. 3), reflects changes in the effective dimensions of the electron shells of alloy atoms. Therefore, the substitution of smaller, by dimensions, S atoms in the structural grid of alloys by Se ones leads to its growth. Moreover, the valence electrons of selenium atoms are more weakly bound to the atomic core than those in sulfur atoms, which results in an extra contribution to the refraction of the alloys enriched with selenium.

In order to analyze the interrelations between optical, refractometric, and thermo-optical parameters of alloys concerned, we used the optical-refractometric relation (ORR) [18, 19]. First, the ORR eliminates the main shortcoming of known empirical relations of Moss, Ravindra, Gladstone–Dale, Lorenz–Lorentz, Wemple–Di Domenico, and so on, in which the conditions

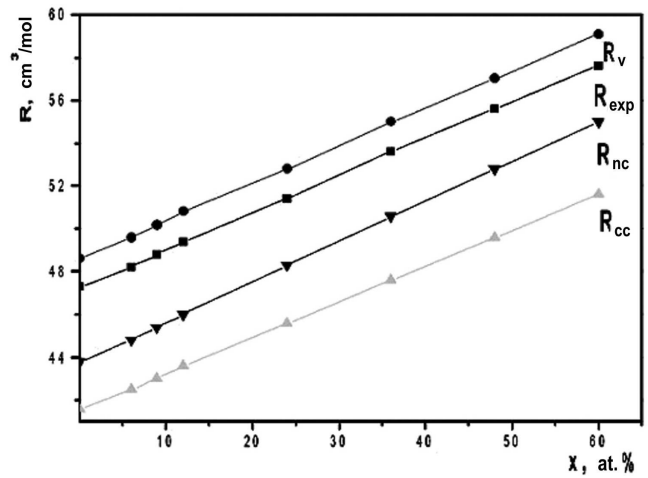


Fig. 4. Composition dependences of the experimental, R_{exp} , and calculated (vitreous, R_v , normal covalent, R_{nc} , and crystal covalent, R_{cc}) refractions of vitreous alloys of the As–S–Se system

$\partial n/\partial T = 0$ and $\partial E_g^*/\partial T = 0$ are interrelated. Second, it gives a relation between the refractometric parameters $n(\lambda)$ and ρ , the energy position of the intrinsic absorption edge E_g^* , and the chemical composition of the material (the molar weight μ and the refraction R); it also takes the refraction dispersion into account. The ORR looks like

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

where $s = 2$ for the mid- and 3 for the high-energy section of the transparency range (i.e. in the range of strong dispersion at $h\nu \approx E_g^*$), η_s and E_s are fitting parameters, $E_{p\sigma} = 28.82\sqrt{n_v\rho/\mu}$ is the energy of plasma oscillations for valence electrons, n_v is the number of valence electrons per formula unit of the substance, and μ is the molar weight. The parameters η_s and E_s were determined from the experimental values of the quantities E_g^* , n , and ρ , using the dependences $L_s(h\nu) = f[(h\nu)^s]$. The relevant values for initial compounds are quoted in Table. For the calculation of molar refractions $R(x)$ by the formula

$$R(x) = \frac{\mu(x)n^2(x) - 1}{\rho(x)n^2(x) + 2}, \quad (4)$$

we used the values of $n(x)$ in the range of low dispersion and the experimental values of $\rho(x)$. The corresponding concentration dependences are shown in Fig. 4.

The values of optical-refractometric parameters for binary alloys As_2S_3 and As_2Se_3

Substance	Refractive index $n(\lambda = 5 \mu\text{m})$	Optical pseudogap E_g^* , eV	Energy of plasma oscillations E_{pv} , eV	Fitting parameters			
				E_2 , eV	E_3 , eV	η_2	η_3
As_2S_3	2.410	2.324	17.42	11.9	5.47	1.291	1.409
As_2Se_3	2.773	1.775	16.67	11.8	5.51	1.256	1.418

The comparative analysis of experimental composition dependences $R(x)$ and those calculated making use of both the values for crystalline covalent, R_{cc} , and normal covalent, R_{nc} , refractions recommended in work [20] and the values R_v obtained in the framework of the “vitreous” refraction model [21] showed that these dependence are symbatic. While calculating the refraction making use of the R_{cc} and R_{nc} values, we obtain the values that are underestimated with respect to experimental ones; the use of the R_v value gives rise to the overestimated result (Fig. 2). In order to obtain valid refraction values for the components of the studied alloys (As, S, and Se), we measured n and ρ for vitreous selenium and, using Eq. (3), obtained $R_v = 11.8 \text{ cm/mol}^3$. Proceeding from the principle of additivity and taking the linear behavior of the concentration dependences $n(x)$ and $\rho(x)$ into account, we obtained the following values for the covalent refractions of As and S: $R_{\text{As}} = 11.2 \text{ cm/mol}^3$ and $R_{\text{S}} = 8.3 \text{ cm/mol}^3$. This enables the refraction value to be calculated for a specimen with an arbitrary composition, provided that this composition belongs to the system under examination. We carried out the experimental researches of the spectral and temperature dependences of the refractive index for four compositions only. Therefore, since the ORR describes well the experimental dependences $n(\lambda, T)$, we made the calculations of such dependences for several intermediate compositions with low selenium contents ($x \leq 20\%$) (Fig. 2).

Thus, the results of our experimental researches of the optical-refractometric and thermo-optical parameters of vitreous alloys belonging to the As–S–Se system evidence for a practically linear character of the concentration dependences of their optical-refractometric parameters. This fact allowed us to make a conclusion about the formation of a continuous set of solid solutions. The interrelation between the quantities E_g^* , n , and ρ is well described by the ORR, so that, in the framework of structural-chemical and optical approaches, the ORR can be used for the synthesis of vitreous materials with prescribed optical-refractometric parameters.

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КОМПОЗИЦІЙНА ЗАЛЕЖНІСТЬ ТА ВЗАЄМОЗВ'ЯЗОК
ОПТИКО-РЕФРАКТОМЕТРИЧНИХ І ТЕРМООПТИЧНИХ
ПАРАМЕТРІВ СКЛОВИДНИХ СПЛАВІВ
(As₂S₃)_{100-x}(As₂Se₃)_x

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Резюме

Досліджено вплив композиційного розупорядкування на енергетичне положення краю власного поглинання і диспер-

сії показника заломлення скловидних сплавів системи As—S—Se по розрізу (As₂S₃)_{100-x}(As₂Se₃)_x. Експериментально визначено адитивні величини рефракцій миш'яку, сірки і селену в сплавах та встановлено взаємозв'язок концентраційної поведінки ширини оптичної псевдоцілини, показника заломлення і рефракції вихідних компонентів досліджуваних скловидних сплавів.