# Peculiarities of refractive index temperature dispersion of Ge-As-S-I glasses system

P.P.PUGA[1]*, V. T. MASLYUK[1] I.Y. ROSOLA[2], G.D. PUGA[2], B. M. GUNDA[2]

[1]Institute of Electron Physics, Ukrainian Academy of Sciences, Uzhhorod, Ukraine
[2]Uzhhorod State University, Uzhhorod, Ukraine

*The temperature dependence of the refractive index of glass-like disordered alloys of Ge-As-S-I was studied by a prism, normal incident beam, technique in the range from 4.2 K till 420 K. Two quasi-binaries of this material system, i.e., $(As_2S_3)_x(GeS_2)_{1-x}$ and $(AsSI)_x(GeS_2)_{1-x}$, with $0 \leq x \leq 0.51$, were investigated. As the result of the performed experiments it has been evidenced that in both cases, of the chosen binaries, the value of ionicity of the chemical bonds in the alloys increses when the content of $GeS_2$ increases (x decreases). It has also been shown that glasses of the Ge-As-S-I material system can be synthesized which exhibit positive-, negative-, or zero-valued temperature increment $\Delta n/\Delta T$ of the refractive index in fairly wide temperature and wavelength regions.*

## 1. Introduction

An increased interest in the application of multi-component chalcogenide and chalcohalogenide glasses and films for the construction of optical and especially acousto-optical devices, emphasizes the importance of their optical studies. Such glass materials differ from other transparent solids by their optical parameters and are characterized by relatively high refraction index n values and low dispersion coefficient.

In this paper the results of the temperature investigation of refractive index dispersion in the disordered alloys of Ge-As-S-I glass-like system along $As_2S_3$-$GeS_2$ and AsSI-$GeS_2$ quasibinary section are given. It was shown that the chemical bond's degree of ionicity in the studied systems rises with the increasing of $GeS_{4/2}$ structure complexes number in the matrix of glass-generating compounds – $As_2S_3$ and AsSI.

The possibility for synthesis of glasses with positive, nought and negative values of refractive index temperature increment $\Delta n/\Delta T$ in the wide temperature and spectrum regions was established.

## 2. Experimental results

The results of temperature dependence studies of refractive index dispersion in disordered alloys on the basis of Ge-As-S-I system along $(As_2S_3)_x$ $(GeS_2)_{1-x}$ and $(AsSI)_x$ $(GeS_2)_{1-x}$ directions in the medium infrared spectral range are reported.

Refractive index dispersion was studied by a prism technique (normal incident beam technique) with a setup, based on an IKS-21 spectrometer and a ODH-10 optical division head [1]. The refractive index was measured within +0.001. Low-temperature and high-temperature studies of the refractive index dispersion were performed using a special purpose helium cryostate. The sample temperature was controlled within ±1 K. The refraction angle $\phi$ of the prismatic sample was chosen as about 15° and determined within ± 2″, using a GS-1,5 goniometer.

The refractive index value was calculated as:

$$n = \frac{\sin(\phi + \delta)}{\sin\phi}$$

where $\delta$ is the deviation angle of the beam, passing through the prismatic sample. The results of the refractive index dispersion studies in $As_2S_3$-$GeS_2$ system glasses for various x values are given in Fig.1a. The

* corresponding author: P. P. Puga, Institute of Electron Physics, Ukrainian Academy of Sciences, Uzhhorod, Ukraine
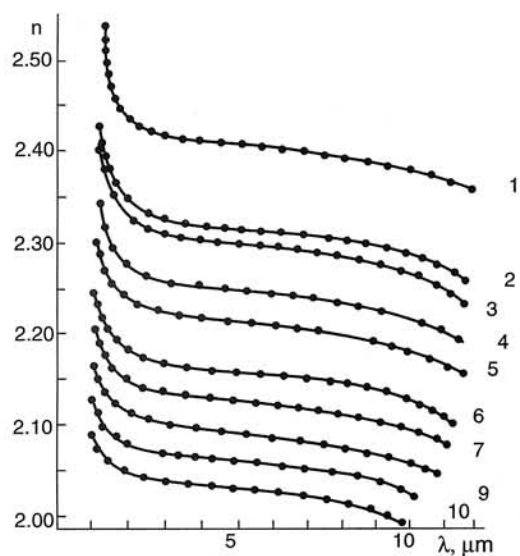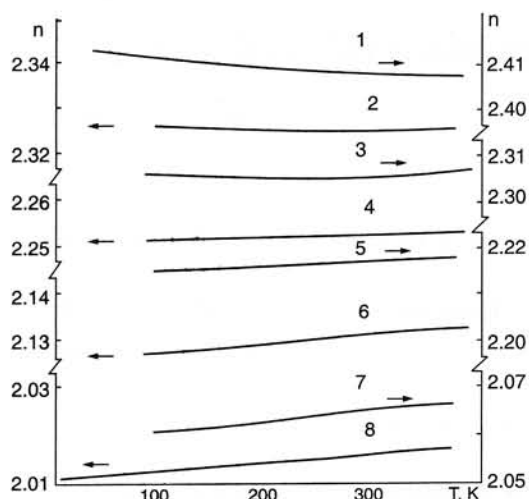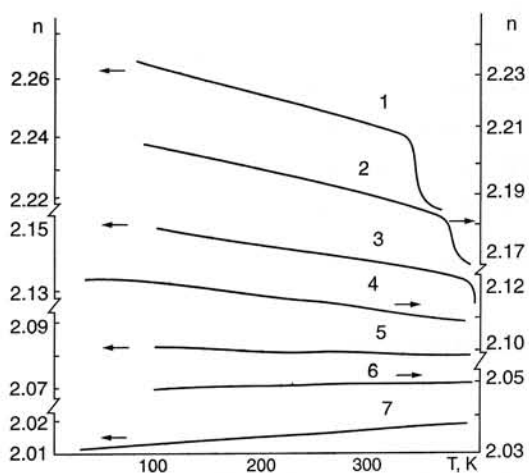
a)
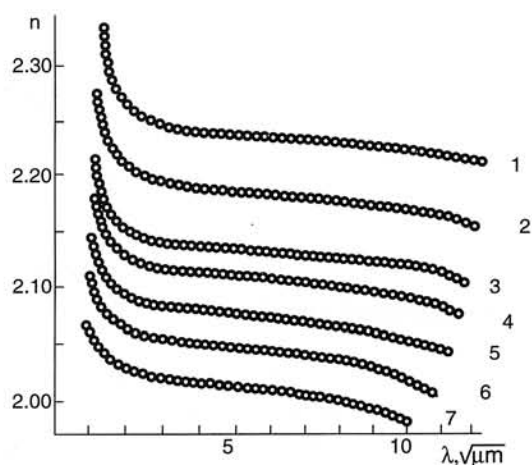


b)

Fig. 1. Refractive index in the glassy alloys:
a – $(As_2S_3)_x (GeS_2)_{1-x}$, x= 1.0(1); 0.9 (2); 0.75(3); 0.6(4); 0.5(5); 0.4(6); 0.3(7); 0.2(8); 0.1(9); 0.0(10).
b – $(AsSI)_x (GeS_2)_{1-x}$, x=1.0(1); 0.8(2); 0.6(3); 0.5(4); 0.4(5); 0.2(6); 0.0(7).



a)



b)

Fig. 2. Refractive index temperature increment of the glassy alloys:
a – $(As_2S_3)_x (GeS_2)_{1-x}$, x= 1.0(1); 0.9 (2); 0.75(3); 0.6(4); 0.5(5); 0.4(6); 0.1(7); 0.0(8).
b – $(AsSI)_x (GeS_2)_{1-x}$, x = 1.0(1); 0.8(2); 0.6(3); 0.5(4); 0.4(5); 0.2(6); 0.0(7) (=5 m).

obtained results indicate that the $As_2S_3$ binary compound exhibits a maximum value of refractive index. The increase of $GeS_2$ concentration in $As_2S_3$ glass-forming matrix leads to a corresponding decrease in the refractive index value. In the short-wavelength range ($\lambda < 2$ μm) a sharp increase in the refractive index due to the beginning of the fundamental absorption band, is observed. The refraction index dispersion is characterized by normal behaviour at $\lambda < 11$ μm. At higher wavelengths singularities in the refractive index dispersion are observed due to a variety of local vibrations, typical for glassy alloys in this spectral range.

A similar dependence in n dispersion is also revealed for the glasses of $(AsSI)_x(GeS_2)_{1-x}$ system (Fig.1b). For all compositions of Ge-As-S-I system at shorter wavelengths a gradual decrease in the refractive index is observed. With the increase of GeS content the refractive index value varies from 2.243 for AsSI to 2.016 for $GeS_2$ ($\lambda < 5$ μm).

The refractive index temperature increments of the $(As_2S_3)_x (GeS_2)_{1-x}$ glassy alloys are given in Fig. 2a. As follows from the analysis of the obtained plots it can be concluded that, in the glasses of this system, $\Delta n/\Delta T$ sign is changed under transition from trigonally (typical for AsS) to tetrahedrally (typical for GeS)

44       

bound structural units. For the $(As_2S_3)_{0.75}$ $(GeS_2)_{0.25}$ composition (2a, curve 3) the $\Delta n/\Delta T$ value is practically zero within 150 to 320 K.

The results of temperature variation for the $(AsSI)_x$ $(GeS)_{1-x}$ glassy alloys refractive index is shown in Fig. 2b. As in the preceding case, for the AsSI-GeS$_2$ system of glasses the $\Delta n/\Delta T$ sign is changed and its value varies vs composition. For the alloys of this system a sharp decrease of refractive index in the range of softening temperatures Tg is observed, which is probably due to the thermodynamic instability of glasses, where structural units typical for AsSI compound, prevail [2]. On the basis of n=f(T) relations we have plotted dispersion dependences of the refractive index temperature increment for $(AsSI)_x$ $(GeS_2)_{1-x}$ glasses at different x values. The $\Delta n/\Delta T = f(\lambda)$ dependence (Fig.3) reveals the following features. For $(AsSI)_x(GeS_2)_{1-x}$ glassy alloys at $0.18 \leq x \leq 0.22$ mol% GeS$_2$ the ratio $\Delta n/\Delta T$ appears to be independent of temperature within 5 to 420 K in a relatively broad spectral range. It should be noted that at present the parameters and properties necessary for the quantitative description of the refractive index temperature increment $\Delta n/\Delta T$ of the glasses of the system under investigation, are not available, therefore we restrict ourselves to the qualitative description of the observed phenomenon.
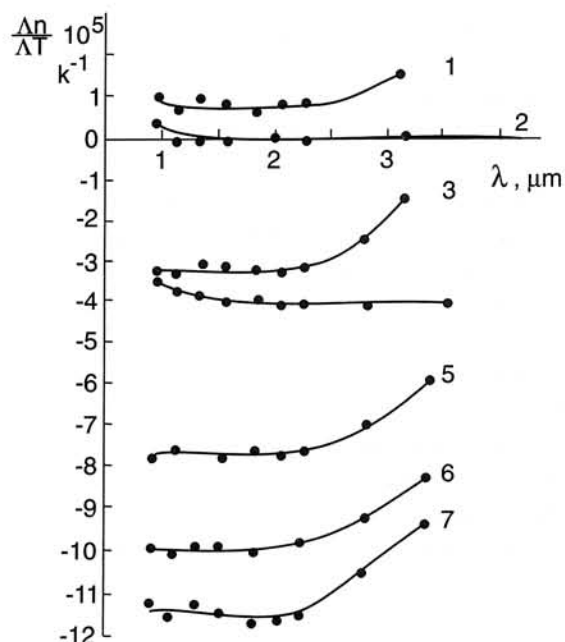


Fig. 3. Dispersion of $(AsSI)_x$ $(GeS_2)_{1-x}$ glassy alloys refractive index temperature increment; x = 1.0(1); 0.8(2); 0.6(3); 0.5(4); 0.4(5); 0.2(6); 0.0(7).

## 3. Discussion

In Ref.3 two types of physical effects, affecting the $\Delta n/\Delta T$ sign and value, are considered. The first is the thermal expansion: with the increase in temperature the

Table 1. Compositional dependences of pseudogap ($E_{g\mu}$), plasmon energy ($E_{pv}$), $\mu$ parameter, oscillator strength (F), chemical bond ionicity degree ($f_i$), dispersion energy ($E_d$), average coordination number ($N_c$) and refractive index temperature increment ($\Delta n/\Delta T$) for Ge-As-S-I glassy alloys.

| Composition | x | $E_{g\mu}$ [eV] | $E_{pv}$ [,eV] | $\mu$ | F [eV$^2$] | $f_i$ [%] | $N_c$ | $E_d$ [eV] | $\Delta n/\Delta T$ $10^5 K^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $(As_2S_3)_x(GeS_2)_{1-x}$ | 1.0 | 2.42 | 17.42 | 1.29 | 114 | 45 | 4.3 | 23.5 | –0.7 |
| | 0.9 | 2.51 | 17.41 | 1.30 | 113 | 48 | 4.2 | 22.5 | –0.4 |
| | 0.75 | 2.58 | 17.28 | 1.31 | 119 | 48 | 4.3 | 22.7 | 0.0 |
| | 0.6 | 2.66 | 17.21 | 1.32 | 124 | 49 | 4.4 | 22.6 | 0.6 |
| | 0.5 | 2.74 | 17.15 | 1.32 | 128 | 50 | 4.5 | 22.5 | 1.0 |
| | 0.4 | 2.79 | 17.14 | 1.34 | 119 | 52 | 4.3 | 20.8 | – |
| | 0.3 | 2.84 | 17.06 | 1.35 | 128 | 53 | 4.5 | 21.3 | 1.9 |
| | 0.2 | 2.90 | 17.03 | 1.36 | 130 | 54 | 4.6 | 21.2 | – |
| | 0.1 | 2.97 | 16.86 | 1.36 | 132 | 55 | 4.7 | 20.9 | 2.0 |
| | 0.0 | 3.10 | 16.38 | 1.37 | 128 | 56 | 4.7 | 20.0 | 1.5 |
| $(AsSI)_x(GeS_2)_{1-x}$ | 1.0 | 2.35 | 15.89 | 1.32 | | | | | –9.5 |
| | 0.8 | 2.46 | 15.82 | 1.33 | | | | | –8.4 |
| | 0.6 | 2.56 | 16.00 | 1.35 | | | | | –6.0 |
| | 0.5 | 2.62 | 16.04 | 1.35 | | | | | –4.5 |
| | 0.4 | 2.72 | 16.10 | 1.36 | | | | | –1.5 |
| | 0.2 | 2.90 | 16.28 | 1.36 | | | | | 0.0 |
| | 0.0 | 3.10 | 16.38 | 1.37 | 128 | 56 | 1.7 | 20.0 | 1.5 |

material expands and becomes less dense. If this mechanism was the only one, a trend to obtain a negative $\Delta n/\Delta T$ would be observed. The second effect consists in variation of the electronic polarisation of the material vs temperature. In the case of diamond-type and zincblende-type semiconductors the electronic contribution prevails in the whole transparency range apart from a narrow range in the vicinity of TO phonon energy, by virtue of $dE_{g\mu}/dT$ term contrary to the contribution from the thermal expansion effects. For such materials $\Delta n/\Delta T$ has a positive sign and a value on the order of $10^{-4}$ $K^{-1}$.

For ionic crystals the main contribution to the frequency dependence of value $\Delta n/\Delta T$ is made by the thermal expansion variation effect, prevailing over the electronic contribution, and $\Delta n/\Delta T$ has high negative values of about $3 \times 10^{-5}$ $K^{-1}$. Having compared our results (Fig.3) with those for NaCl, NaF, KCl, CsI, we observe similar plots of $\Delta n/\Delta T = f(\lambda)$. Such similarity enables one to assume that in our case phonon dispersion also favours the $\Delta n/\Delta T$ value determination, starting from $l = 4$ mm. For glasses, possessing zero value of $\Delta n/\Delta T$ according to [3], the polarisation variation effects in the discussed temperature range is compensated by the density variation effect.

Using the optical refractometric formula for isotropic substances, relating pseudogap $E_{g\mu}$, the refractive index and electron-plasma vibration energy $E_{pv}$ [5] taking into account the internal field, we have determined a quasiconstant $\eta$, characterizing a ratio between the energy of intrinsic electronic (polarizational) vibrations of the corresponding equivalent oscillator and the mean arithmetic value of $E_{pv}$ and $Eg\mu$. A value of $\eta$ increases with the degree of ionicity of binding with a transition from trigonal (chain-like) to tetragonal structural units.

Note that the refractive index dispersion data for the chalcogenide glasses can be used for studying their structure dependence on composition. From this point of view the conclusions of [6] seem to be the most interesting, where an expression, relating the refractive index n, the oscillator strength F and the oscillator intrinsic vibration energy $E^0$, is proposed for the transparency range within a one-oscillator model approximation. By means of this relation, some energy parameters of the glassy alloys and compounds under investigation were determined, their values being listed in the Table. Using F and $E_0$ values, we have calculated $E_d$ value, determining the electronic dielectric constant dispersion in non-metal solids depending on their chemical nature. When $E_d$ is known, according to [7], the degree of ionicity of chemical bonds $f_i$ in the disor-

dered alloys under investigation can be determined. The results of the analysis in the Table 1 shows the bond ionicity degree to increase with the transition from trigonal to tetrahedrally bound structural units. Besides, when these parameters are known, the coordination number $N_c$ of the central atom with respect to the anion can be determined. Note that the calculations of the coordination number for $AsSI$-$GeS_2$ glasses within the framework of [6] model appeared to be difficult due to the complicated structure of the system under investigation.

## 4. Conclusions

The results of temperature refractometric studies of Ge-As-S-I have shown that glassy alloy systems exhibit along $As_2S_3$-$GeS_2$ and $AsSI$-$GeS_2$ directions the chemical bond ionicity degree of the considered alloys increasing with the amount of $GeS_{4/2}$ structural complexes in $As_2S_3$ and $AsSI$ glass-forming matrices. The principal possibility of the glasses with positive, zero and negative $\Delta n/\Delta T$ value in a broad spectral range is stated, which enables the studied glasses to be suggested for manufacturing of non-untuning optical system elements.

## References:

1. P.P. Puga, D.Sh. Kvach, V.A. Zubany and A.N. Boretz: *The thermal refractometrie installation based on optical dividing mount O.D.G. – 10 type. Metrologicheskoje obespieczenie proizvodstva i kontrolno – izmeritelnaja technika.* Uzhhorod. (1984) 43.
2. P.P. Puga, I.D. Sejkovskij, A.N. Boretz: *IR-absorbtion instability of the semicondoctoring AsSI, AsSeI glasses in the soften temperature range.* Ukr. Fiz. Zhurnal **17** (1972) 1738.
3. A. R. Hilton, C. E. Jones: *The thermal change in the nondispersive index of optical materials.* Appl. Optics **6** (1967) 1513.
4. Y.F. Tsay, B. Bondow, S. S. Mitra: *Theory of temperature derivative of refractive index in transparent crystals.* Phys. Rev. B. **8** (1973) 2688.
5. O.M. Boretz: *The some optical and refractometrial regularities in nonmetallic isotropic substances.* Ukr. Fiz. Zhurnal **28** (1983) 1346.
6. S.H. Wemple, M. Di-Domenico: *Behaviour of the dielectric constant in covalent and ionic materials.* Phys. Rev. B. **3** (1971) 1338.
7. M. P. Tubbs: *A spectroscopic interpretation of crystalline ionicity.* Phys. Stat. Sol. **41** (1970) k61.