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Polarization properties and a local structure of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses

V.I. Malesh, V.V. Rubish, I.I. Shpak, V.M. Rubish, P.P. Puha*

Uzhhorod National University, 54 Voloshin str., 88000 Uzhhorod, Ukraine

** Institute of Electron Physics, NAS of Ukraine, 21 Universytets'ka str., 88000 Uzhhorod, Ukraine*

Abstract. The results of investigating different parameters (T_g , ρ , H , E_g , n_∞ , ε , $\text{tg}\delta$) of glasses in Ge–Sb–Se system have been given. The values of structural-sensitive molar IR polarization F have been calculated and its concentrational dependence has been constructed. The polarity of chemical bonds has been estimated. It has been shown that with increasing the content of Sb_2Se_3 in the composition of the glasses the polarity of Sb–Se bonds rises. Within the limits of free volume conception the formation energy (E_h) and the volume (V_h) of microcavities have been calculated. E_h and V_h are structural-sensitive parameters of glassy materials.

It has been shown that the inflection is observed in concentrational dependences of investigated and calculated parameters of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses in the vicinity of $x = 0.60$. It testifies to the structural changes in the glasses while changing the composition.

The structure of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses is mainly determined by structural units $\text{GeSe}_{4/2}$ and $\text{SbSe}_{3/2}$, to be statistically distributed into matrices. The increase of Sb_2Se_3 content in GeSe_2 is accompanied by a gradual transition from tetrahedrally co-ordinated structural units in glassy GeSe_2 , to trigonally co-ordinated – in Sb_2Se_3 .

Keywords: chalcogenide glass, polarization, local structure, structural units.

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1. Introduction

As known [1], some correlation exists between a local structure of the glass and its physical and chemical properties, including the dielectric ones. Since the latter are determined by those kinds of the polarization to be formed in the substance under the action of the electric field having a certain frequency, they bear the information on the interaction between particles in the solid. Therefore, the study of polarization properties of glasses allows one in some cases to estimate the polarity of chemical bonds, to establish the type of a chemical interaction between components and kind of structural units, to reveal a mutual influence of structural units different in the composition and symmetry and to make a conclusion about the character of their distribution [1–3]. A combined study of polarization, physical and chemical properties and vibration spectra of the materials under study can give a more thorough and real information on the structural – chemical character of atoms and units.

In the paper, the results of investigating some physical-and-chemical, thermodynamic and polarization properties of Ge–Sb–Se glasses (GeSe_2 – Sb_2Se_3 section) have been presented, on the basis of which the interpretation of glass structures is given.

2. Experimental part

The glasses were synthesized in vacuum quartz tubes from super-pure elementary components in accordance with the methods given in [4]. The characteristic temperatures of thermal effects (glass-formation T_g , crystallization T_c and melting T_m) were determined based on the data of differential-thermal analysis, conducted with the help of a high-sensitive set-up [5] at heating rate ~ 0.08 K/s. The accuracy of the temperature determination made up 0.5 K.

The density of glasses (ρ) was determined by the method of hydrostatic weighing in toluene and the microhardness (H) was measured by using the device PMT–3 while loading the indenter of 20 and 50 g. The measurement error made up: $\rho - 0.5\%$, $H - 5-10\%$.

The gap band E_g was determined from the measurements of a spectral dependence of the fundamental absorption edge in accordance with the procedure given in [4]. While doing this the Urbach rule ($\alpha = \alpha_0 \exp \Gamma(h\nu - h\nu_0)$) is obeyed in a wide spectral region. The spectral resolution is not more than 10^{-3} eV.

The refractive index n was determined at room temperature by the prism method. Over the range of wavelengths λ from 3 up to 11–12 μm for $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$

glasses the refractive index dispersion is practically absent. The determination accuracy of n made up 0.001. The static value of the refractive index (n_∞) was determined by the formula [6].

$$n_\infty = n_1 - \frac{n_2 - n_1}{\lambda_1^2 / \lambda_2^2 - 1}, \quad (1)$$

where n_1 and n_2 are the refractive indices at $\lambda_1 = 5 \mu\text{m}$ and $\lambda_2 = 10 \mu\text{m}$.

The permittivity (ϵ) and dielectric loss tangent ($\text{tg}\delta$) were measured by the resonance method [7] over the range of frequencies of 10^3 – 10^8 Hz within the temperature interval from 170 K up to T_g . The measurement errors made up: ϵ – 3%, $\text{tg}\delta$ – 10%.

3. Results and discussion

The results of measurements are given in Fig. 1. The concentrational dependences of studied parameters of glasses of GeSe_2 – Sb_2Se_3 system are of monotonic character, which is indicative of the absence of fundamental reconstruction of chemical bonds between the components while going from one structural region to another one.

The study of dielectric properties of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses over the range of frequencies of 10^3 – 10^8 Hz has shown the absence of permittivity dispersion (over the temperature range from 170 K to T_g) and the decrease in $\text{tg}\delta$ with increasing the frequency. The study of temperature dependences ϵ and $\text{tg}\delta$ of glasses the results of which are given in Fig. 2 have shown that over the temperature

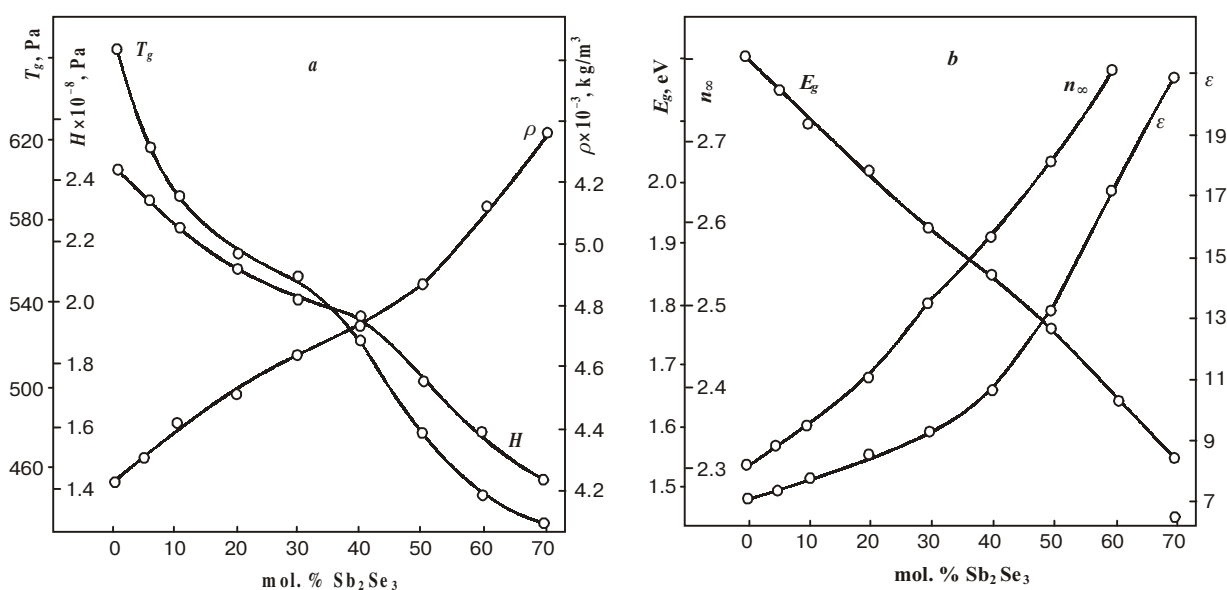


Fig. 1. Concentrational dependences of T_g , H , ρ (a) and E_g , n_∞ , ϵ (at frequency 10^5 Hz) (b) of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses.

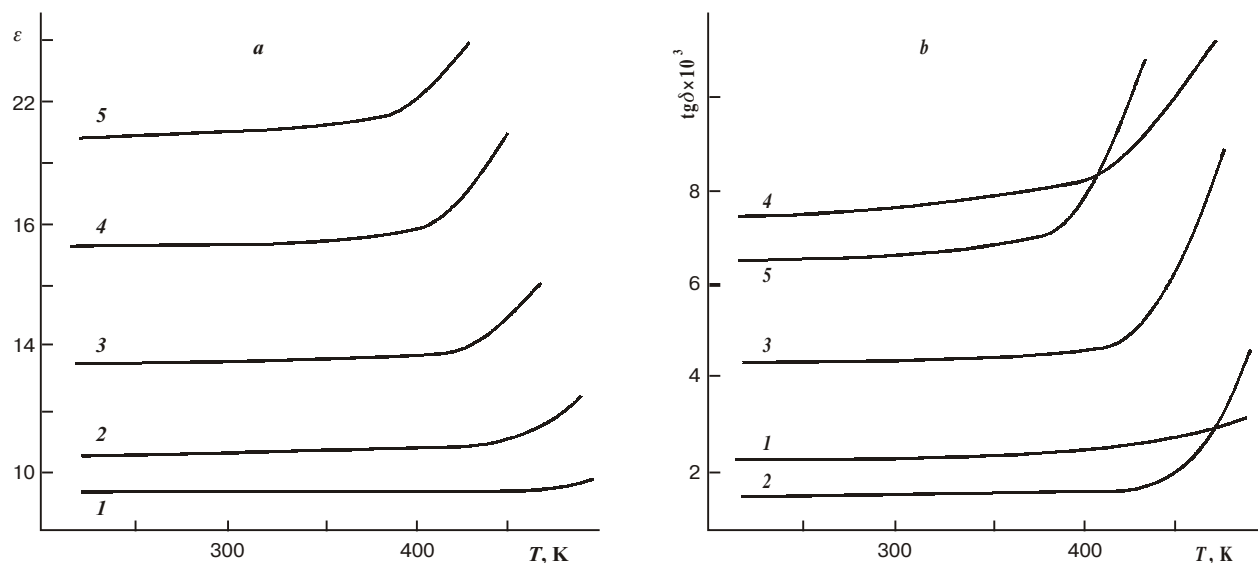


Fig. 2. Temperature dependences ϵ (a) and $\text{tg}\delta$ (b) at frequency 10^5 Hz of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses. x , mol. %: 1 – 0.7; 2 – 0.6; 3 – 0.5; 4 – 0.4; 5 – 0.3.

region of $T < T_g$ for all the samples ε is practically constant and at temperatures close to T_g of respective glasses ε and $\text{tg}\delta$ grow noticeably. When repeating heating-cooling cycles, the character of the $\varepsilon(T)$ dependence does not change, which testifies to the absence of crystallization effect in the glasses of the given system.

The absence of the permittivity dispersion and its weak dependence of the temperature (over the range of $T < T_g$) testify to the fact that the value of ε in glasses of GeSe₂-Sb₂Se₃ system is mainly determined by electron and infrared polarizations [8]. The time of their determination is very small and makes up $\sim 10^{-15}$ and 10^{-3} s, respectively. The shift of electrons and ions with these kinds of the polarization is merely of elastic character. Even at high frequencies they manage to watch the change in the electric field. Inside the dielectric the irrevocable energy absorption does not take place. The low values of $\text{tg}\delta$ for the glasses under study ($\text{tg}\delta$ depending on the composition at $T = 300$ K at the frequency of 10^5 Hz has the value of 10^{-4} - 10^{-3}) testify to this fact.

Over the region of temperatures T_g a considerable increase in ε and $\text{tg}\delta$ (Fig. 2) is observed. Such a behavior of dielectric parameters may be connected both with a partial orientation of dipole structural units in the glass and with the polarization conditioned by the interaction of the field with charge carriers [8]. In the region of glass-formation temperatures the mobility of the glass matrix increases and, as a result, the orientation of structural units forming it becomes easier. However, the main contribution to the increase in ε is made by another component which is conditioned by the transitions of charge carriers between charged defect centers. The similar results have been obtained while investigating the glasses in GeS₂-As₂S₃ and GeS₂-Sb₂S₃ systems [8] isotypical by the composition with the glasses of GeSe₂-Sb₂Se₃ system.

As the permittivity of the studied materials is determined by elastic kinds of the polarization, it is connected with microscopic parameters within the framework of the Lorenz-Lorentz local field model by the equation [2]

$$\varepsilon = n_\infty^2 + 4\pi \left(\frac{n_\infty^2 + 2}{3} \right)^2 \frac{e^2}{4\pi^2 c^2} \times \sum_i N_i v_{ii}^{-2} m_i^{-1} \left(\frac{Z_i e_i^*}{e} \right) \quad (2)$$

Here e is the electron charge; c is the velocity of light; v_{ii} is the wave number which corresponds to the frequency of lateral optical vibrations; m_i is the reduced mass of structural elements of i -type whose number is equal to N_i in the volume unit; $Z_i e_i^*$ is an effective charge of the central atom of i -type structural element. The formula (2) is given for the substances which contain several kinds of structural units. The magnitude N_i [2] may be presented as:

$$N_i = N_A \rho x_i / A, \quad (3)$$

where N_A is the Avogadro number; ρ is the density; A is the average molar mass; x_i is the mole fraction of the element which is the central one in the i -type structural element. By grouping macro- and microscopic parameters in the left and right parts of the equation (2) we will get

$$F = \frac{3A(\varepsilon - n_\infty^2)}{\rho(n_\infty^2 + 2)^2} = \sum_i F_i x_i, \quad (4)$$

where $F_i = 4\pi N_A \alpha_i / 3$. As it is seen from the equation (2) the polarization α_i depends on $Z_i e_i^*$ and v_{ii} .

And as effective charges are determined by the type of a chemical interaction and local structure, they give the possibility of watching the structural-chemical transformations that take place in the glasses when changing the ratio of components in their composition. Therefore (in accordance with (4)), the value of molar infrared polarization F is also structural-sensitive, its concentrational dependences for glasses of Ge-Sb-Se system are given in Fig. 3.

It is seen that the magnitude F increases with increasing the content of antimony in the composition of glasses and F is observed to considerably increase in the regions of compositions $x < 0.60$. While increasing the concentration of Sb₂Se₃ the electronic component of the polarization determined by the formula [9] also increases:

$$R_\infty = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \frac{A}{\rho} \quad (5)$$

The increase of the electronic contribution to total polarization testifies to increasing the average dimensions of electron shells of atoms while going from GeSe₂ to Sb₂Se₃.

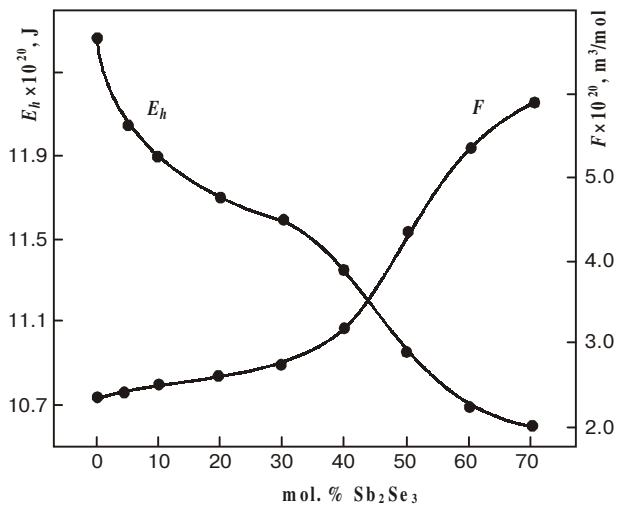


Fig. 3. Concentrational dependences of F and E_h for $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses.

The fact that the values of ϵ in Ge-Sb-Se glasses are much higher than in similar alloys of Ge-As-Se(S) system with respect to the composition [10, 11] draws the attention (in Ge-As-Se system the value of ϵ is within the limits of 7.34–10.2, and in Ge-As-S system it is 5.3–7.25). This may be related with a considerable magnitude of the dynamic effective charge on antimony and selenium atoms. By using experimentally determined ϵ , n_∞ and ρ in accordance with the Szigeti formula [10] the values of effective charges in the fractions of the electron charge per unit of valency, i.e. ionicity degrees of Sb-Se bonds have been calculated:

$$i = \sqrt{\frac{9\pi c^2 v_0 M (\epsilon - n_\infty^2)}{(n_\infty^2 + 2)^2 N z_1 z_2 e^2}} \quad (6)$$

Here v_0 is the frequency of valency vibrations of Sb-Se bond; M is the reduced mass of a pair of atoms; N is the number of dipoles in 1 cm³ of the glass equal to the number of chemical bonds; z_1 and z_2 are valencies of atoms. To calculate the value of i we have used the value $v_0 = 187 \text{ cm}^{-1}$ determined from the study of Raman spectra of Sb-Se glasses [12]. The similar band is obtained while investigating IR transmission spectra of crystalline and amorphous Sb₂Se₃ [13]. This band accounts for the vibration of Sb and Se atoms in SbSe_{3/2} trigonal pyramids. The results of calculations testify to the fact that with increasing the content of antimony in the composition of (GeSe₂)_x(Sb₂Se₃)_{1-x} glasses the polarity of Sb-Se bonds increases steadily from 0.22 up to 0.41. The value of polarity of Ge-Se bonds in accordance with [10] is equal to 0.18 and does not practically depend on the composition of glasses. A good correlation of our data with the results of [14] should be mentioned. The magnitude i for crystalline Sb₂Se₃, calculated according to the Batsanov method [9] makes up 0.43.

The concentrational dependence of ionicity degree of Sb-Se bonds is similar to the dependence F of the composition (Fig. 3). At the case a considerable change in the infrared polarization and polarity of bonds (as well as the dielectric constant) Fig.1b)) is observed over the region of compositions $x < 0.60$.

It was mentioned above that the value of molar infrared polarization is sensitive to the change in the structure. In an ideal system with several kinds of nonexciting each other structural units an additive dependence of F on the composition should take place. The interaction between structural units, which results in the change of polarization α (as well as Ze^* and v_l) conditions the declination from a linear course on “ F -composition” diagram. In case of a stronger interaction of structural elements, which results in a deep reconstruction of chemical bonds between components (for example, the formation of a new compound) a singular point should appear on “ F -composition” diagram [2].

Since both permittivity and gap band are determined by the short-order structure of the material there exists a

definite interconnection between them. Moss has shown that there exists the relationship between magnitudes ϵ and E_g in crystalline semiconductors [3]:

$$1/\epsilon^2 = \text{const} \cdot E_g \quad (7)$$

However, in the works of many authors it was proved that this relationship is true for glassy materials as well. Besides, there is the connection between the magnitude E_g and atomization enthalpy H_A of glasses ($E_g = a(H_A - b)$, where a and b are constants [3]). Then the relation $1/\epsilon^2 \sim H_A$ is valid. And since H_A is determined by the kind of structural units, which form the glass matrix, the dependences “property-atomization enthalpy” bear a certain information on its local structure [1]. Based on this one may consider that the diagrams “ $10^3/\epsilon^2 - E_g$ ” and “ $T_g - E_g$ ” given in Fig. 4 also possess informational possibilities with respect to the structure of glasses and its change while varying the composition. Like concentrational dependences of physical and chemical parameters and polarizations they do not reveal extreme points.

The study of IR transmission spectra of non-crystalline Sb₂Se₃ i GeSe₂ has allowed one to establish [13, 3] that SbSe_{3/2} trigonal pyramids and tetrahedrons GeSe_{4/2} are the main structural units which form their matrix. The intensive absorption band with the maximum at 180–185 cm⁻¹ accounts for the vibrations of Sb-Se bonds and the vibrations of Ge-Se – at 260 cm⁻¹. For the glasses of GeSe₂-Sb₂Se₃ section a two-mode character of IR spec-

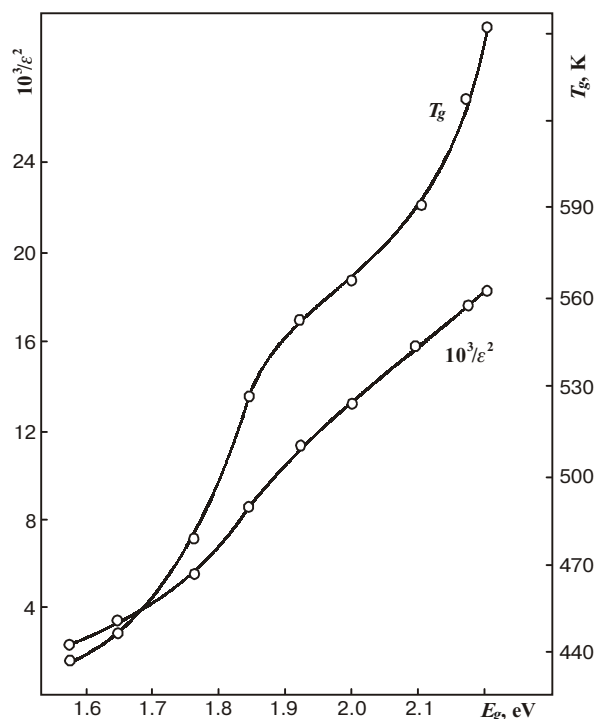


Fig. 4. Diagrams “ $10^3/\epsilon^2 - E_g$ ” and “ $T_g - E_g$ ” of (GeSe₂)_x(Sb₂Se₃)_{1-x} glasses.

tra is revealed. They have two absorption bands over the region of indicated frequencies whose intensity depends on the ratio of components in the composition of glasses. The concentrational dependence of infrared polarization F (Fig. 3) is of monotonic character. This testifies to the fact that when introducing Sb_2Se_3 into GeSe_2 and increasing its quantity a gradual change of the structure from tetrahedral (based on $\text{GeSe}_{4/2}$) to trigonal one (based on $\text{SbSe}_{3/2}$) takes place. A negative declination from a linear course on “ F -composition” diagram testifies to a statistic character of the distribution of $\text{GeSe}_{4/2}$ and $\text{SbSe}_{3/2}$ structural units.

The change in the structure is accompanied by a considerable change in all studied parameters (Fig. 1). The gap band E_g decreases from 2.20 eV for GeSe_2 glass to 1.57 eV for $(\text{GeSe}_2)_{0.30}(\text{Sb}_2\text{Se}_3)_{0.70}$ glass. Such a dependence of E_g on x does not need special explanations, since the values of E_g obtained correlate with the values of the gap band of crystalline GeSe_2 ($E_g^* = 2.30$ eV) and Sb_2Se_3 ($E_g^* = 1.17$ eV) [16]. Besides, such a dependence of E_g on the composition agrees well with the values of strength of single bonds energies (234.5 kJ/mole for Ge-Se and 213.5 kJ/mole for Sb-Se [1]). Depending on the composition of the glasses and respective to the change in E_g and ρ , a statistic refractive index n_∞ changes as well (Fig. 1). The increase in the content of Sb_2Se_3 in the composition of glasses is accompanied by the increase in n_∞ (from 2.301 for GeSe_2 glass to 2.903 for $(\text{GeSe}_2)_{0.30}(\text{Sb}_2\text{Se}_3)_{0.70}$ glass).

The transition from tetrahedral (GeSe_2) to trigonal (Sb_2Se_3) structure of glasses as it is seen in Fig. 1a, is accompanied by a considerable decrease in their microhardness and glass-formation temperature. Such a behavior of the concentrational dependences of H and T_g testifies to the decrease in the connectivity of glass matrix with increasing the antimony concentration in the composition of glasses.

The connectivity of glass matrix within the frame of free volume theory [17,18] is connected with the availability of a considerable quantity of microcavities (“holes”) of atomic or molecular dimensions in their volume. These microcavities are characterized by the volume V_h and the formation energy E_h . The analysis of experimental data shows [18] that the processes of formation and migration of microcavities are mainly connected with the deformation of the glass matrix as a result of thermal fluctuations. The formation energy and volume of microcavities may be estimated from the relations [18]:

$$E_h = 3kT_g; \quad (8)$$

$$V_h = 3kT_g/H. \quad (9)$$

Here k is the Boltzmann constant. As numerical investigations of silicate, borate and chalcogenide (in As-S and As-Se systems) glasses with the growth of the connectivity of the glass matrix have shown, the formation energy of microcavities increases and their volume decreases [18,19]. Silicate and borate glasses possess the smallest volume (4–8 E^3) for which a three-dimensional matrix

structure is characteristic [18]. The volume of microcavities is some times larger for glassy As_2S_3 and As_2Se_3 , which are mainly characterized by a random two-dimensional matrix structure [19].

The volume of microcavities in $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses is within the limits from 10.7 to 12.5 E^3 and increases with increasing the content of Sb_2Se_3 in the composition of glasses. The magnitude E_h is within the limits of $(1.80\text{--}2.75) \cdot 10^{-20}$ J and decreases with the growth of Sb_2Se_3 concentration (Fig. 3). Such a course of concentrational dependences of E_h and V_h testifies to the increase in the connectivity of the matrix of Ge-Sb-Se glasses while going from GeSe_2 to Sb_2Se_3 .

As the study of glassy alloys in Ge-Sb-Se system has shown the concentrational dependences of measured and calculated parameters are of monotonic character that testifies to a gradual character of reconstruction of glasses from tetrahedral to trigonal one. However, the bend is practically observed on all the diagrams “property–composition” over the range of 30–40 mol.% of Sb_2Se_3 . With the content of Sb_2Se_3 higher than 40 mol.% the concentrational dependence is stronger for the majority of parameters. This may be conditioned by the fact that effective charges on antimony atoms are larger than in germanium atoms. Due to this the exciting action of $\text{SbSe}_{3/2}$ trigonal pyramids on the structure of glasses is much higher than that of tetrahedral $\text{GeSe}_{4/2}$ structural units.

4. Conclusions

As a result of investigations it has been ascertained that dielectric properties of $\text{GeSe}_2\text{--Sb}_2\text{Se}_3$ glasses are mainly determined by electron and infrared polarizations. The analysis of concentrational dependences of physical-and-chemical and calculated structural-sensitive parameters (F , E_h , V_h) has allowed one to assume a microheterogenic model of a local structure of glasses. The structure of $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ glasses is mainly determined by $\text{GeSe}_{4/2}$ and $\text{SbSe}_{3/2}$ structural units which are statistically distributed into their matrices. The increase in the content of Sb_2Se_3 in GeSe_2 is accompanied by a gradual transition from tetrahedrally co-ordinated structural units in glassy GeSe_2 to trigonally co-ordinated – in Sb_2Se_3 . The results obtained agree well with the data of refractometric study and vibrational spectroscopy.

References

1. A. Felts, Amorphous and glassy non-organic solids (in Russian) (Nauka, Moskva, 1985), p. 558.
2. M.S. Gutenev, L.A. Baidakov, A chemical bond and local structure in tellurium-containing chalcogenide glasses according to dielcometry data (in Russian) // *Fiz. i. khimiya stekla*, **9** (4) pp.449-460 (1983).
3. I.M. Yurkin, V.S. Bilanich, V.M. Rubish, A local structure and polarization of glasses in Ge-As-S-I system (in Russian) // *V.Sb.: Novije razrabotki v oblasti estestvennykh i gumanitarnykh nauk*, ch.I (Uzhhorod, 1990) p.45-54.
4. I.I. Rosola, V.V. Khiminets, P.P. Puha, D.V. Chepur, Refractometric studies of Ge-Sb-Se glasses (in Russian) // *Fizikal elektronika* **22**, pp.124-130 (1981).

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5. P.P. Shtets, V.P. Terban, N.V. Polazhinets, I.M. Yurkin, The set-up DTA by using a high-frequency temperature regulator BPT-3 (in Russian)// V sb.: Metrologicheskoye obespecheniye proizvodstva i kontrolno-izmeritel'naya tekhnika (Uzhhorod, 1985) p.77-80.
6. V.V. Ioffe, Refractometric methods of chemistry (in Russian) (Khimiya, Leningrad, 1974) p.400.
7. Yu.S. Nakonechny, A.A. Horvat, V.I. Marfidin, The measurement of capacity and active conductivity over the range of radiofrequencies (in Russian)// V.sb.: Slozhnyye poluprovodniki (polucheniye, svoystva, primeneniye) (Uzhhorod, 1981) p.26-34.
8. V.M. Rubish, AC conductivity and dielectric properties of chalcogenide glasses (in Ukrainian)// Zhurn.fiz.doslidzhen **6** (2) p.188-192 (2002).
9. S.S. Batsanov, Structural refractometry (in Russian) (Vysshaya shkola, Moscow, 1976) p.304.
10. A.M. Efimov, V.A. Khariuzov, Dielectric properties and structure of arsenic-selenium and germanium – selenium glasses (in Russian)// V sb.: Stekloobraznoye sostoyaniye (Nauka, Leningrad, 1971) pp.370-373.
11. V.M. Rubish, I.D. Turianitsa, V.V. Khiminets, Dielectric properties of glasses of Ge-As-S system (in Russian)// Ukr.fiz.zhurn., **26** (11), pp.1856-1859 (1981).
12. V. Rubish, I. Yurkin, V. Malesh, V. Fedelesh, M. Trunov, D. Semak, Investigation of glass structure in As(Sb)-S(Se)-I system by the method of Raman spectroscopy and X-ray diffraction // Proc. SPIE, **2618**, pp.531-537 (1995).
13. V.P. Zakharov, V.S. Gerasimenko, Structural peculiarities of semiconductors in amorphous state (in Russian)/(Naukova dumka, Kyiv, 1976) p.280.
14. M.S. Gutenev, I.V. Viktorovskiy, L.A. Baidakov, A.V. Pazin, The peculiarities of structural-chemical construction of Sb-Ge-Se glasses in accordance with the data of investigating dielectric and magnetic properties (in Russian)//Fiz.i khimiya stekla, **1** (4) pp.350-353 (1975).
15. V.S. Gerasimenko, M.S. Gutenev, N.A. Korepanova, The study of magnetic susceptibility, viscosity and vibrational spectra of Sb-Ge-Se glasses (in Russian)//Fiz.i khimiya stekla, **2** (3) (1976).
16. D.I. Chizhikov, V.P. Schastliviyi, Selenium and selenides (in Russian) (Nauka, Moscow,1964) p.
17. Ya.I. Frenkel, Kinetic theory of liquids (in Russian) (Izd-vo AN SSSR, Moscow-Leningrad, 1945) p.424..
18. D.S. Sanditov, G.M. Bartenev, Physical properties on disordered structures (in Russian) (Nauka, Novosibirsk, 1982) p.255.
19. T.M. Melnichenko, V.I. Fedelesh, I.M. Yurkin, V.M. Rubish, The formation energy and volume of microcavities as a function of the glass structure in ternary As-S(Se)-I systems (in Ukrainian)// Visnyk Uzhhorod.Un-tu, ser.Fizyka, **2**, pp.27-30 (1998).