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CHARACTERISTICS OF COMPLEX NON-CRYSTALLINE CHALCOGENIDES FROM THE Ge-As-S-Se-I SYSTEM

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In the first part of the paper we summarize the results of our research in technology of obtaining complex five–component non-crystalline glasses of the $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ type. In the second part of this paper we report results from studying general mechanical, thermal, spectral and optical properties of these complex amorphous materials.

1. Introduction

As a rule, the nature and composition of the components of the given system determine the structural units forming the glass lattice. With increase in the number of components the glass formation capability increases too, since this enhances the possibility of forming various structural units.

Multicomponent chalcogenide glasses are widely applicable in the field of semiconductor techniques.

Five–component systems offer special possibilities because one can substantially alter the properties of the system simply by changing the ratio of their components.

With the aim of raising the possibilities of preparing new materials with predefined physical characteristics, studies were made of the five-component system Ge-As-S-Se-I [1]. Starting from the results of investigation of four-component systems Ge-As-S-I and Ge-As-Se-I [2], it could be expected that the five-component system for prospective application of this type of materials would be the cut $Ge_{20}As_{14}(S_xSe_{1-x})_{52}I_{14}$ [3].

However, the later investigations of complex systems have shown that iodine as a component important for the formation of elementary structural units may have an unfavourable effect on the stability and preservation of the sample homogeneity with time. This was one of the main reasons for undertaking studies of the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$, with the aim of examining the effect of iodine introduction and technological procedure involved in the synthesis on physico-chemical properties of the material.

2. Experimental

2.1. Technology of glass preparation

The choice of the methodology to synthesize glasses from the system Ge-As-S-Se-I was influenced by the characteristics of the elementary components forming the binary and tertiary compounds that could be expected as a result of interaction of these components, as well as by the magnitude of the area of amorphous state in the phase diagram. The area of the non-crystalline phase that can be realized in the quaternary system involving sulphur is presented in Fig. 1 and for the system with selenium in Fig. 2 [4].

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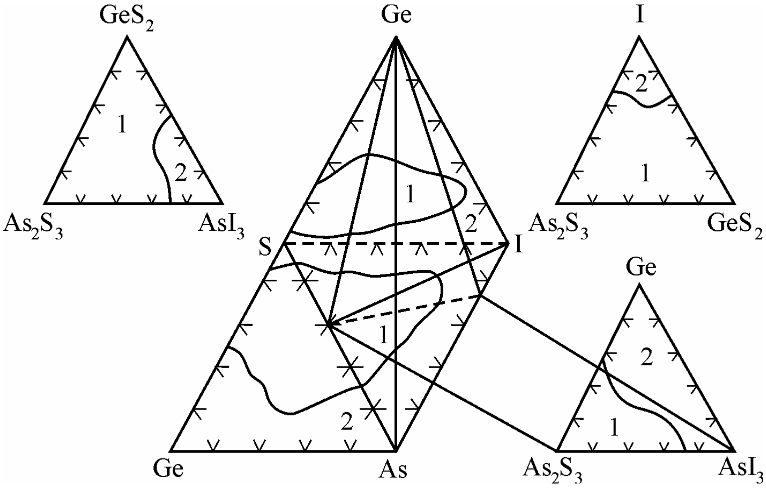


Fig. 1. The glass-forming region in the system Ge-As-S-I: 1 – glass; 2 –crystal.

As can be seen from Figs. 1 and 2, the amorphousness area in the tetrahedron Ge-As-S(Se)-I occupies its relatively large portion and comes out to the lateral planes of the three-component systems As-S(Se)-I, Ge-As-S(Se) and Ge-S(Se)-I. The low tendency to crystallization of the glasses in these systems is primarily a consequence of the possibility of formation of a larger number of compounds of different structures such as GeX_2, As_2X_3, AsXI (X=S, Se) with relatively low melting temperatures.

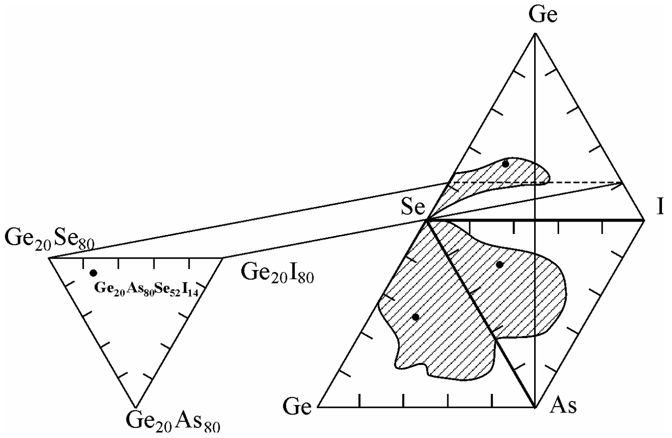


Fig. 2. The glass-forming region in the system Ge-As-Se-I.

The synthesis was conducted according to a special program, in cylindrical quartz ampoules evacuated to a pressure of the order of magnitude of 1×10^{-3} Pa. The ampoule length was usually about 15 cm, its diameter 15 mm, and the wall thickness 2 mm, in order to be able to withstand the relatively high pressures in the ampoule during the synthesis.

The synthesis was carried out in semiautomatic horizontal tube furnaces *Carbolite*, Model *CTF 12/65*, with a temperature controller *Eurotherm 91-3*, according to the empirically defined regimes shown in Fig. 3.

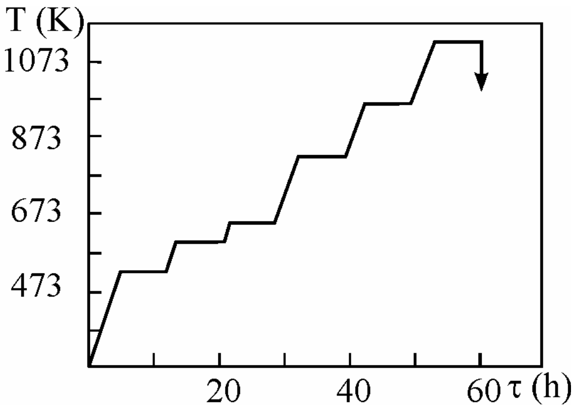


Fig. 3. Diagram of process for obtaining glasses of $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ type.

Melting temperatures of the starting components of this five-component system are markedly different and heating during the synthesis was carried out in several stages [5-7]. Heating of the starting components in evacuated ampoules yields first to melting and evaporation of iodine and sulphur. This, however, produces a high pressure of iodine and sulphur vapours, and the purpose of the first temperature plateau at 523 K is to enable reaction of these two elements, which reduces the pressure. Analogously, at the plateau of 923 K, molecules of As_2S_3 and As_2Se_3 are formed, and at 1073 K the molecules GeS_2 and $GeSe_2$.

The relatively high temperatures of the synthesis (1143-1203 K) were needed to prevent liquefaction in the melts with higher sulphur contents. In order to achieve its homogenization, the melt was kept at the maximal temperature for 25-30 hours, and then cooled at a rate of 873 K/min. In some cases, samples were kept for additional 10-15 hours at a temperature that was 20-30 K lower than the softening temperature, T_g.

The temperature conditions presented in Fig. 3 were used to synthesize samples of the type $Ge_{20}As_{14}(Se_{0.5}S_{0.5})_{66-x}I_x$. The procedure yielded the glasses for x=2, 4, 6, 8, 10, 12, 14 and 18 [8, 9].

2.2. Experimental methods

As the result of successful syntheses the corresponding amorphous materials in the form of oval rods with no visible fissures or defects, were obtained in appropriate yields. Amorphous character of samples was checked by x-ray diffraction and polarization microscopy.

For determining the thermal characteristics and defining the range of existence of each individual phase a *Paulik-Paulik-Erdey* Derivatograph, *type 1000* was used. Samples were heated to 1273 K in open ceramic crucibles in air atmosphere, using Al_2O_3 as inert standard. The heating rate was 10 K/min and the mass of the samples was 100 mg. Before measurement the samples were powdered.

The x-ray diffraction (XRD) measurements were performed on a conventional x-ray diffractometer PW 1373-PW 1065/50 (*Philips*), using step-scanning mode and monochromatic CuK_α radiation. XRD spectra at higher temperatures were recorded using a high temperature attachment *HTK 10 (Paar)* and automatic control bar *HTK 2-HC (Paar)*. Experiments were carried out up to maximum temperature of 873 K. The rate of sample heating was 10 K/min.

Dilatometric studies of samples were carried out on a *Perkin Elmer TMA 7* thermomechanical analyzer in the range from room temperature to the temperature of the beginning of the material deformation by its own mass. Changes in sample length were measured with an accuracy of $\pm 10^{-4}$ mm, rate of sample heating was 10 K/min, and the furnace was cooled with water. In view of the fact that the measuring equipment required a defined form of samples, they were prepared mechanically in the form of plates whose initial thickness was about 5 mm.

The rate of sample dissolving in a chemical reagent of different concentration was determined by indirect method by measuring mass and using the formula:

$$w = \frac{\Delta m}{S \cdot M \cdot \Delta t} \qquad \left[\frac{mol}{m^2 s}\right] \tag{1}$$

where Δm is the mass change during the dissolution time Δt, S is the sample surface and M is the molecular mass of the conditional chemical unit. Chemical stability of glasses was estimated on the basis of their dissolution rate in potassium hydroxide of concentrations 2 [mol/dm^3] and 5 [mol/dm^3]. Estimated accuracy of dissolution rate is 5%-10%

Transmission spectra in the range of 400-1000 nm were recorded using an *SPM-2* monochromator (*Zeiss-Jena*) with quartz optics. The light source was a bulb with tungsten filament; an EMI 9684 B photomultiplier served as detector, and the current signal was measured using a universal instrument Philips PM-2436/06.

Reflection spectra in the IR range from 2.5 to10 μm were taken (KBr pellet) on a *Perkin Elmer Infracord* spectrometer.

Because of the large values of the refractive index of chalcogenide glasses, the determination of this physical parameter and its spectral dependence requires, as a rule, non-standard methods. In this sense, use is often made of the so-called direct prism method, i.e. a method based on the optical beam refraction on specially prepared prisms, made of the corresponding glasses [10].

The refractive index values for all the bulk samples described in this work were obtained by this procedure. Use was made of the normal incidence beam and the acute angle of the prism was bounded by the relation *arc sin(0.8/n)*. The angle between the polished prism planes was determined by reflection method on an *Enraf Nonius Y-881* two-circle optical goniometer, with an accuracy of $\pm 1'$.

Frequency dependence of the refractive index was analyzed using a laboratory setup. Measurements were carried out at room temperature in the wavelength range from the absorption edge to 1150 nm. An *Osram XBO 450 W* xenon bulb served as source of electromagnetic radiation, monochromatic beam was obtained using an *SPM-2* monochromator, and a silicon photodiode was used as detector.

Samples were polished mechanically, using carborundum powder of different grain fineness (from 260 μm to 28 μm) to obtain regular geometric shapes (prism, rectangle, cube) for different experimental measurement. Final polishing was carried out with the powder of grain size of 0.3 μm.

Density was determined by the method of hydrostatic balance using bulk homogeneous samples. Sample mass was measured in air and in distilled water at room temperature, using a *″Metler B-6″* balance with an accuracy of $\pm 5 \times 10^{-8}$ kg.

Microhardness was measured using the Vickers method. Measurements were performed for different masses of the indenter, viz. 9, 20, 30, 40 and 50 g and using a *Reichert MeF2* microscope with the corresponding accessories.

3. Results and discussion

Density and microhardness as important parameters of materials were measured to characterize the glasses of the investigated system. Measurements showed that the density increases linearly as a consequence of replacing lighter selenium and sulphur atoms with heavier iodine atoms (Table 1).

The obtained results enabled the analysis of the effect of the difference in magnitude of covalent radii of the exchanged atoms. The calculated changes of relative molar mass and relative volume due to partial replacement of S atoms with Se atoms allowed the calculation of the expected change in density of the material. In Fig. 4 is presented the correlation of thus calculated and experimentally determined densities of the material as a function of iodine concentration. It can be seen that there is a significant difference in the rate of change of these quantities, and that the influence of covalent radius of iodine is smaller than expected. This suggests that the introduction of iodine and increase in its content yield formation of new structural units if compared with the four-component Ge–As–S–Se system, causing thus a somewhat slower increase in density [11].

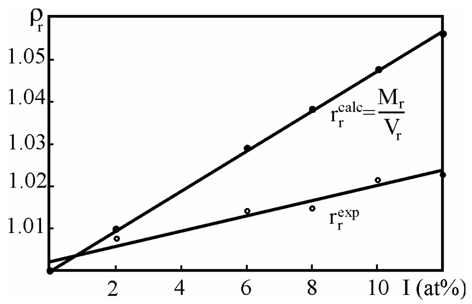


Fig. 4. Experimental (ρ_r^{exp}) and calculated (ρ_r^{calc}) relative densities of the glasses in the $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ system as a function of iodine content.

Measurements of the other physical quantity important for the assessment of mechanical properties, microhardness, gave the expected values for such type of material. The measured values of the Vickers microhardness for different loads of the indenter are also presented in Table 1.

Table 1. Values of density and microhardness of the glasses in the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$.

iodine conten x [at%]	ρ [kg/m^3]	H_V [10^7 Pa]				
		9 g	20 g	30 g	40 g	50 g
0	3698.6 ± 1.5	259±24	235±13	219±8	216±6	211±5
2	3727.2 ± 1.5	240±22	219±9	202±6	198±4	194±3
4	/	223±20	205±9	192±6	184±4	184±3
6	3750.5 ± 0.8	210±19	188±7	177±5	173±4	172±3
8	3752.6 ± 1.1	197±18	177±7	167±5	163±4	163±3
10	3777.2 ± 2.3	185±17	167±7	155±4	154±3	149±3
12	3782.1 ± 0.7	167±15	154±6	146±4	141±3	140±2
14	/	156±14	143±6	137±4	131±3	130±2
18	3791.3 ± 1.4	141±13	128±5	123±3	114±2	110±2

In Fig. 5 is presented the dependence of microhardness on the mass of the indenter load. It can be noticed that in the major part of the investigated range microhardness shows a mild decrease with load, the change being faster at small loads. Such a behaviour is usual for such materials and can be explained in terms of the occurrence of microstrains, invesrsely proportional to the magnitude of the applied force. These microstrains arise because of special physical properties of the surface layer of the material. At lower loads, the external pressure is comparable with the magnitude of surface microstrain, the consequence being another form of functional dependence [12].

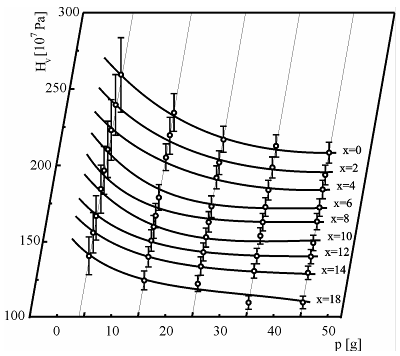


Fig. 5. Dependence of microhardness of the glasses from the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ on the indenter mass load.

The relationship between the microhardness and percentage of iodine in the composition of the glass $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ for the indenter load corresponding to 30 g is presented in Figure 6. Such linear decrease of H_v from 250×10^7 to 125×10^7 Pa with increasing iodine content is a consequence of the redistribution of population of particular structural units in the glass network. Most probably, the ratio of the entities that have lower binding energies (chain and discrete structural units) such as AsSI, AsSeI and AsI_3 increases, while population of the tetrahedral units GeS_2 and $GeSe_2$ decreases. Similar conclusion can also be drawn on the basis of thermal investigations.

Previous investigations of similar chalcogenide and halide glasses showed that they, as a rule, exhibit high chemical stability with respect to air, water vapour and acidic solutions; certain instability being observed in basic solutions [13]. Analogous results have also been obtained in the investigations presented in this work. The dependence of dissolution rate of the samples with different iodine contents in 2 [mol/dm^3] and 5 [mol/dm^3] KOH solutions as a function of time at room temperature is presented in Fig. 7.

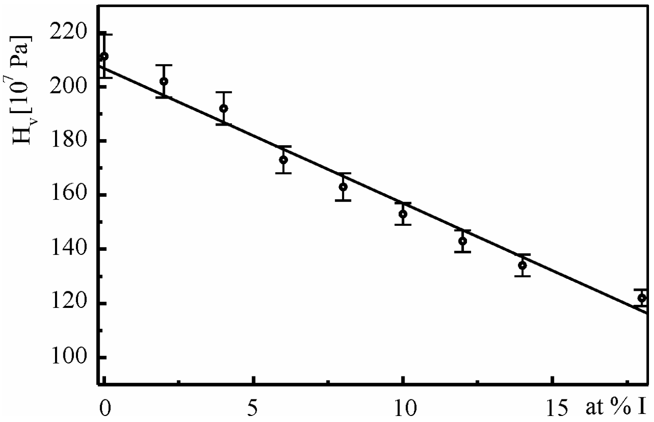


Fig. 6. Dependence of microhardness of the glasses from the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ on iodine content.

It can be seen that the dependence of the rate of dissolution on time is of exponential form, which can be explained by saturation of the solutions in which samples were treated. On the basis of the obtained results it can be concluded that the increase in iodine content in the glass composition yields an increase of dissolution rate in KOH solutions.

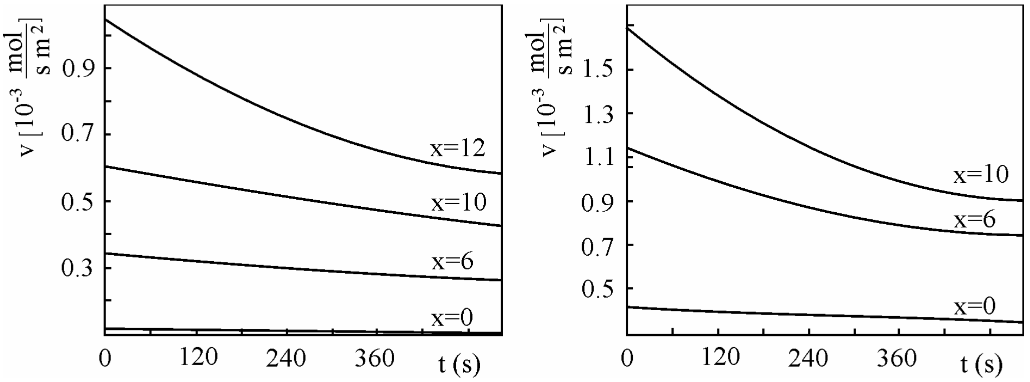


Fig. 7. Rate of dissolution of glasses of the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ as a function of time a) in 2 [mol/dm^3] KOH; b) in 5 [mol/dm^3] KOH.

In view of the fact that thermal stability is essentially important for the application of chalcogenide semiconductors, these characteristics have also been included in the investigations. In Fig. 8 are given TG, DTG and DTA curves of the samples with x = 2 and x = 18 at% I, while in Fig. 9 are presented the curves of differential thermal analysis of all the investigated samples.

The TG and DTG curves enabled the determination of the temperature of the beginning of decomposition of these glasses. The dependence of this quantity on iodine concentration is presented in Fig. 10.a. In the temperature interval of decomposition, a number of successive changes can be seen on the TG, DTG and DTA curves, indicating a very complex character of the process. With the samples containing more than 8 at% I it is possible to notice a new effect at about 573 K, denoted by T_{ox}, whose dependence on iodine concentration is presented in Fig. 10.b. Most probably, this exothermic effect stands for the process of oxidation of the excess of iodine. Namely, at about 573 K the weakly-bound portion of iodine forms the oxide I_2O_5, which decomposes in the interval of the subsequent 40-50 K and leaves the system. Also, it can be seen that the temperature of this process decreases significantly with increase of iodine content in the sample.

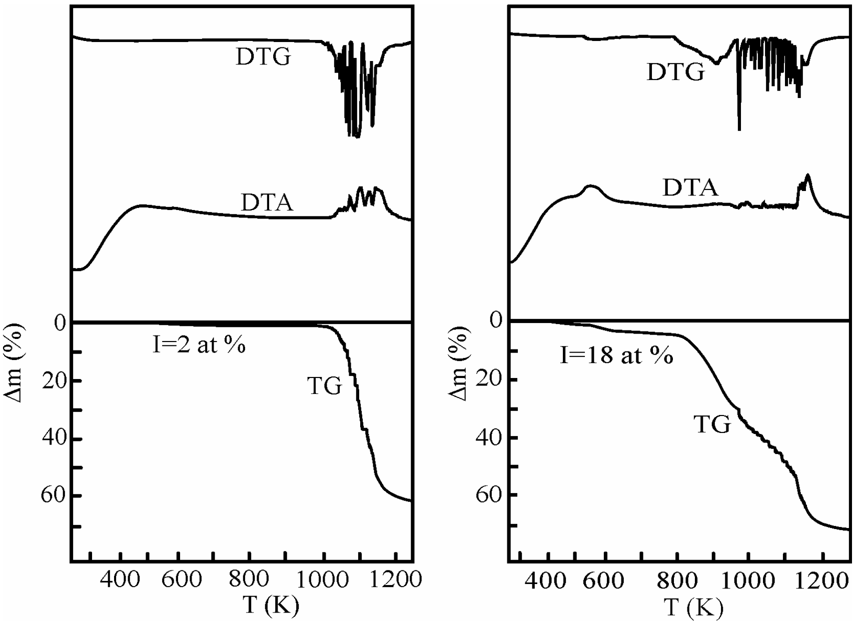


Fig. 8. DTG, TG and DTA curves for $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$.

Taking into account that sulphur and selenium have the same valence and assuming equal probabilities of forming molecules of all the elements involved, it can be supposed that the relation between the elementary structural units in the four-component system without iodine can be presented as follows:

$$3Ge_{20}As_{14}X_{66} \rightarrow 58GeX_2+2GeX+20As_2X_3+2AsX+ +18X \text{ (i.e.}9X_2) \qquad (2)$$

The introduction of iodine brings about the formation of new structural units of the type AsXI and AsI_3 instead of AsX (X = S, Se), so that the ratio of elementary structural units would be:

$$3Ge_{20}As_{14}X_{66-x}I_x \rightarrow k_1GeX_2+k_2GeX+k_3As_2X_3+ +k_4AsXI+k_5AsI_3+k_6X+k_7I, \qquad (3)$$

Coefficients k_i (i = 1-7) are given in Table 2.

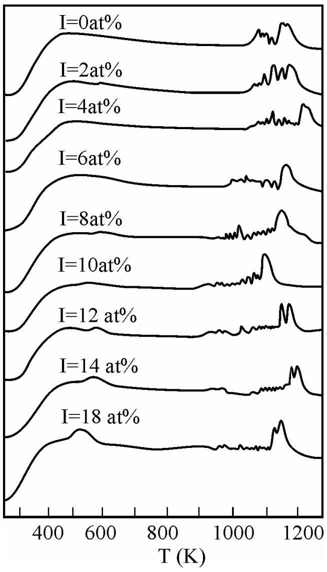


Fig. 9. DTA curves for the glasses of the type $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$.

Table 2. Values of coefficients k in formula (3).

Sample	k_1	k_2	k_3	k_4	k_5	k_6	k_7
$Ge_{20}As_{14}S_{32}Se_{32}I_2$	58	2	19	3	1	14	-
$Ge_{20}As_{14}S_{31}Se_{31}I_4$	58	2	18	3	3	11	-
$Ge_{20}As_{14}S_{30}Se_{30}I_6$	58	2	17	3	5	8	-
$Ge_{20}As_{14}S_{29}Se_{29}I_8$	58	2	16	3	7	5	-
$Ge_{20}As_{14}S_{28}Se_{28}I_{10}$	58	2	15	5	7	-	4
$Ge_{20}As_{14}S_{27}Se_{27}I_{12}$	54	6	14	6	8	-	6
$Ge_{20}As_{14}S_{26}Se_{26}I_{14}$	50	10	13	7	9	-	8
$Ge_{20}As_{14}S_{24}Se_{24}I_{18}$	42	18	10	12	10	-	12

In the samples containing up to 8 at% of iodine, a redistribution of structural units takes probably place, so that the number of units of the type As_2S_3 and As_2Se_3 decreases and the number of AsI_3 units increases. Also, the increase in iodine content in all compositions brings about a decrease in contents of elementary S and Se, whereby iodine appears in excess.

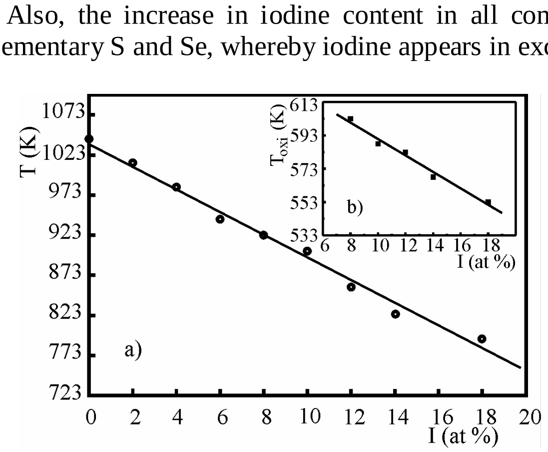


Fig. 10. Temperatures of the beginning of decomposition (a) and iodine oxidation in the glass $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ (b).

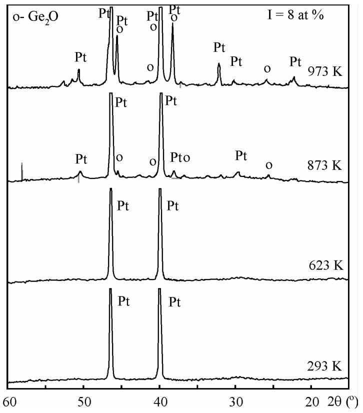


Fig. 11. High-temperature diffractogram of the glass $Ge_{20}As_{14}S_{29}Se_{29}I_8$.

A series of successive changes observed in the process of thermal treatment of glasses, especially pronounced on the DTG curves, can be ascribed to the existence of four structural units involving germanium (GeX and GeX_2) that are successively decomposed. The dissociation of GeX proceeds with the evolution of X and dissociation of GeX_2 is accompanied by evolution of X_2. These dissociation processes take place in parallel with the oxidation of Ge, which starts at 873–973 K. The arguments supporting this reasoning are: first, the decomposition processes terminate by formation of the polycrystalline GeO_2 as a stable residue, and second, each recording gives complex DTA and DTG patterns. With the samples containing more than 8 at% of iodine, part of iodine that is weakly bound forms at about 573 K (T_{ox}) the oxide I_2O_5, which decomposes in the subsequent interval of 40-50 K and leaves the system. The accompanying mass effect is proportional to the increase in iodine content in the glass. The diffraction peaks of polycrystalline GeO_2 appear on high-temperature x-ray recordings from about 873 K. The high-temperature diffractograms of the sample with 8 at% of iodine are given in Fig. 11. The further course of decomposition at high temperature is the degradation of arsenic compounds, oxidation and evolution of gaseous products to the end of the process. All other glass samples gave analogous x-ray diffractograms.

Table 3. Contents of compounds in the glasses from the series $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ and calculated and experimental values of decomposition residue (GeO_2).

x (at %)	GeS_2	$GeSe_2$	GeS	GeSe	As_2S_3	As_2Se_3	AsSI	AsSeI	AsI_3	I	S	Se	m_{teor} (%) (GeO_2)	m_{exp} (%) (GeO_2)
0	21.4	36.1	0.57	0.82	13.3	20.9	0.6	0.8	-	-	1.6	3.8	33.9	35
2	21.0	35.3	0.55	0.80	12.4	19.4	1.8	2.2	2.4	-	1.2	2.9	33.2	38
4	20.5	34.5	0.54	0.78	11.4	18.0	1.8	2.2	7.0	-	0.9	2.2	32.4	35
6	20.2	33.8	0.53	0.77	10.6	16.6	1.8	2.1	11.5	-	0.6	1.6	31.7	28.5
8	19.6	33.1	0.52	0.75	9.7	15.3	1.7	2.1	15.7	-	0.4	0.98	31.1	33
10	19.2	32.4	0.5	0.7	8.9	14.1	2.8	3.4	15.4	2.5	-	-	30.4	28.5
12	17.5	29.5	1.5	2.2	8.2	12.9	3.3	4.0	17.2	3.6	-	-	29.8	31.5
14	15.9	26.8	2.4	3.5	7.4	11.7	3.8	4.5	19.0	4.7	-	-	29.2	30
18	12.8	21.7	4.2	6.1	5.5	8.7	6.2	7.4	20.3	6.8	-	-	28.1	28.5

In Table 3 are presented the calculated contents of particular molecular forms expressed in mass percents, along with experimentally determined values of percentage of mass residue after the completed thermal decomposition. The masses of residues after the decomposition are in good agreement with the calculated masses of the GeO_2 formed.

On the basis of the results of measuring thermal expansion of the glasses of the investigated system thermal coefficients of linear expansion of solid (α_g) and viscoplastic (α_ℓ) phases were determined from the linear parts of the functional dependence $\Delta\ell/\ell$=f(t) (Fig. 12).

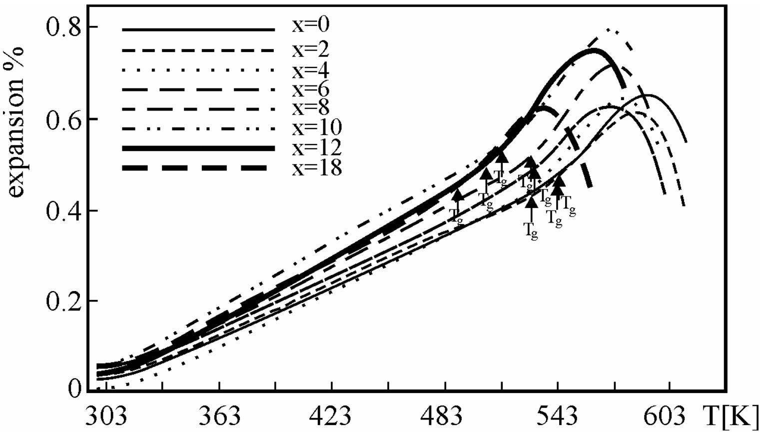


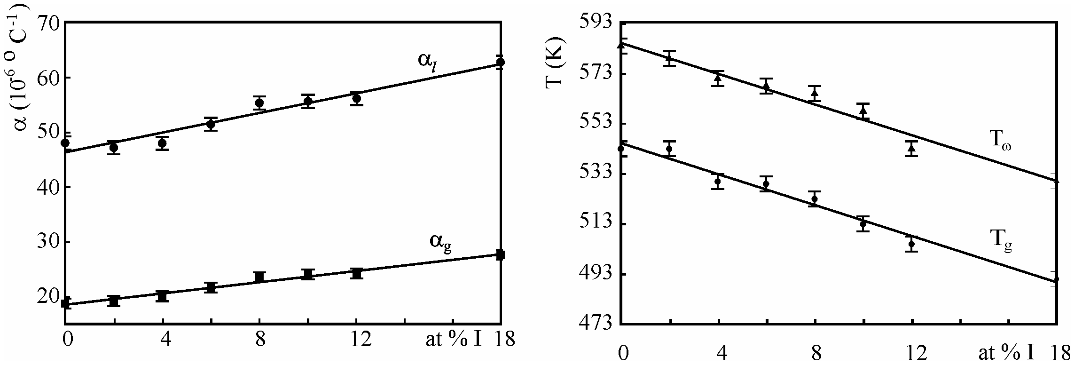
Fig. 12. DTD curves of the glasses $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$.

In Table 4 are given the data for T_g, T_ω, α_g and α_ℓ.

Table 4. Results of dilatometric measurements of glasses $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ type: T_g – softening temperature, T_ω– temperature of the beginning of deformation, α_g and α_ℓ – thermal coefficient of linear expansion of solid viscoplastic phase, respectively.

Iodine content x [at%]	T_g [K]	T_ω [K]	α_g $[10^{-6}\ K^{-1}]$	α_ℓ $[10^{-6}\ K^{-1}]$
0	543	584	18.8	48.1
2	543	579	19.3	47.2
4	530	571	20.2	48.05
6	529	568	21.7	51.5
8	523	565	23.6	55.4
10	513	558	24.1	55.7
12	505	543	24.3	56.2
18	491	530	27.7	62.8

In Fig. 13a is presented the dependence of α_g and α_ℓ on iodine concentration and in Fig. 13b the analogous concentration dependence of the softening temperature T_g and temperature of the beginning of deformation T_ω.



a) b)

Fig. 13. Dependence of thermal coefficient of linear expansion (a) and of T_g and T_ω (b) of the glass $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ on iodine content.

It can be seen that the coefficient of linear expansion of solid phase, α_g, increases and the softening temperature T_g decreases with increase in iodine content in the material, indicating thus the weakening of the structural network of the glass. The weaker structural skeleton and lower softening temperatures mean a lower thermal stability of the material. The fact that iodine weakens internal stability of the glass has already been suggested by the correlation of microhardness and iodine content. The temperature of the beginning of deformation (T_ω) follows the change in the softening temperature (T_g) and also decreases linearly with increase in iodine content. At the same time, it can be also noticed that the coefficient of viscoplastic phase α_ℓ has a trend of linear increase with increase in iodine concentration, like that observed for α_g.

When concerning optical characteristics of the investigated materials, it was found that the samples showed high transparency in a wide range of optical and IR part of the electromagnetic spectrum. The IR spectrum for the samples with 6 and 12 at% of iodine is given in Figure 14. The absorption band at about 3450 cm^{-1} is due to the presence of absorbed water, which is a consequence of the experimental technique employed [14]. The vibration energies corresponding to the possible bonds of the most probable molecular structural units involved (S_8, Se_8, $AsS_{3/2}$, $AsSe_{3/2}$, $GeS_{4/2}$, $GeSe_{4/2}$, AsI_3) are in the far-infrared region [15].

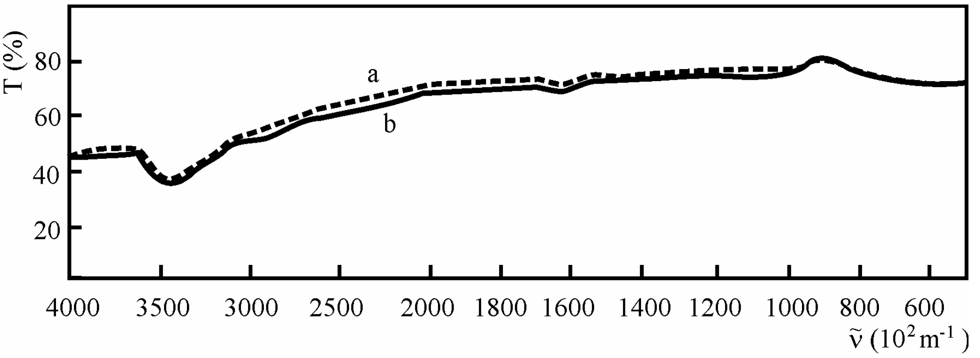


Fig. 14. IR spectrum of $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$, for x = 6 (a) and x=12 (b).

The transparency spectra allowed the determination of the corresponding absorption coefficients. Fig. 15 shows the correlation between the coefficient of absorption and wavelegnth of electromagnetic radiation for some glassy samples of the investigated system. Extrapolation of the linear parts of the curves showing the dependence $\alpha=\alpha(\lambda)$ enabled the determination of the absorption edge and optical bandgap (Fig. 16).

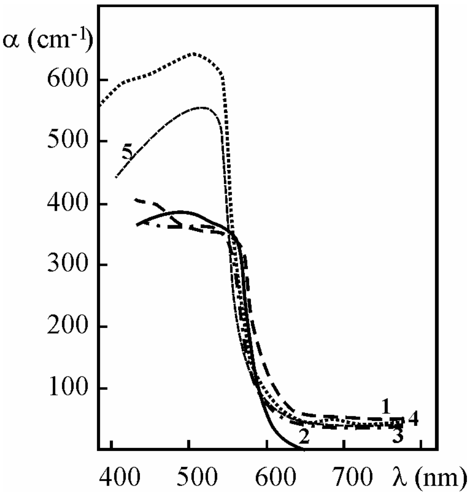


Fig. 15. Dependence of the absorption coefficient on wavelenth for the galsses of the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$, for: 1) x = 0; 2) x = 2; 3) x = 6; 4) x = 10; 5) x = 14.

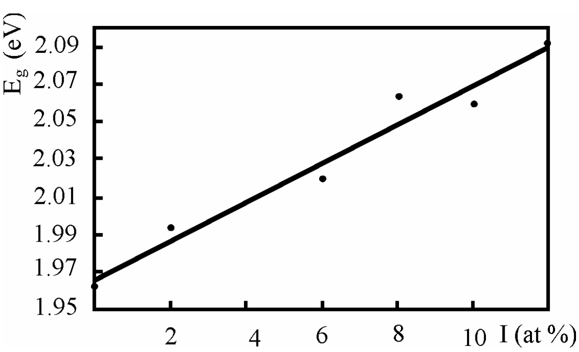


Fig. 16. Optical bandgap as a function of iodine concentration for the glasses of the system $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$.

It can be seen that the increase in iodine content yields a linear increase in the value of optical bandgap according to the expression:

$$E_g = 1.97 + 0.01 \cdot c \ [\text{eV}] \tag{3}$$

where, c - iodine content (at %) in the sample.

This simple formula gives the possibility of determining analytically the percentage of particular components in the glasses of the general formula $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ that would result in the predefined value of optical bandgap in the interval from 1.97 to 2.17 eV.

The index of refraction of the investigated materials showed also dependence on the content of iodine, i.e. on the content of chalcogenide elements in their composition (Table 5).

Table 5. Indices of refraction and the corresponding standard deviations.

No.	Sample	n ± Δn
1	$Ge_{20}As_{14}S_{33}Se_{33}$	2.564 ± 0.001
2	$Ge_{20}As_{14}S_{32}Se_{32}I_2$	2.507 ± 0.002
3	$Ge_{20}As_{14}S_{30}Se_{30}I_6$	2.444 ± 0.003
4	$Ge_{20}As_{14}S_{29}Se_{29}I_8$	2.405 ± 0.003
5	$Ge_{20}As_{14}S_{28}Se_{28}I_{10}$	2.386 ± 0.002
6	$Ge_{20}As_{14}S_{27}Se_{27}I_{12}$	2.358 ± 0.004
7	$Ge_{20}As_{14}S_{26}Se_{26}I_{14}$	2.274 ± 0.004
8	$Ge_{20}As_{14}S_{24}Se_{24}I_{18}$	2.244 ± 0.003

Fig. 17 shows graphical dependence of the refraction index as a function of iodine concentration in the samples. It is evident that increase in iodine content yields a linear decrease of the refraction index. The observed monotonicity of the functional dependence of these quantities indicates that the investigated system can be treated as a solid solution [17].

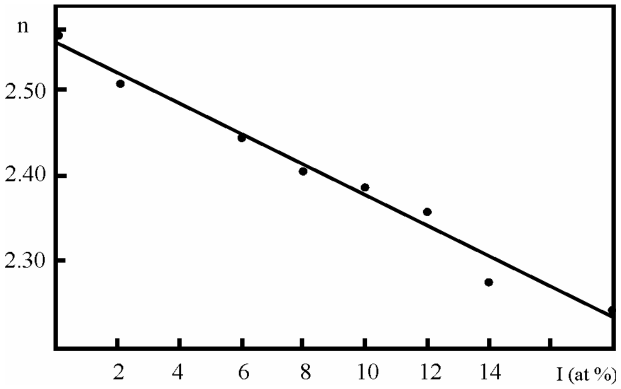


Fig. 17. Dependence of the refraction index on percentage of iodine in the sample.

On the basis of the established linear dependence it was possible to derive an analytical expression for the dependence of n on the iodine concentration in the form:

$$n = 2.55 - 0.017 \cdot c \qquad (4)$$

where, c - iodine content (at %) in the sample.

4. Conclusions

New materials of the five-component system Ge-As-S-Se-I, belonging to chalcogenide, i.e. halide, glasses were synthesized and investigated for the cut $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$, (x = 0, 2, 6, 8, 10, 12, 14 and 18). This cut was selected on the basis of previous studies that showed that the samples with equal contents of sulphur and selenium have some very interesting optical characteristics. At the same time, it was necessary to establish optimal concentration of iodine in order to preserve time stability of these favourable properties. It appeared that the relevant properties and physical quantities can be correlated to the iodine content in the glass composition.

It was found that the density of these glasses shows a linear increase and microhardness a linear decrease with iodine content in the material. Also, it was shown that these chalcohalides are stable in air, water vapour, and acidic solutions, whereas in basic solutions the observed dissolution rate is characteristic of chalcogenide glasses. It was also found that these glasses have high indices of refraction that show usual dispersion (normal dispersion), as well as that the value of refraction index at a fixed wavelength decreases with increase in iodine content.

Values of optical bandgap were calculated and an analytical expression was derived for the dependence of this quantity on iodine concentration in the glass composition. The values of optical bandgap in the range from 1.97 to 2.17 eV obtained for the samples of the investigated system in the given interval of concentrations are characteristic of semiconducting materials.

Derivatographic and dilatometric measurements showed that the increase in iodine content in the composition of the given glass results in a decrease of the temepratures of softening and beginning of decomposition, whereas the coefficients of thermal expansion show an increase. This suggests that the making of the composition more complex reduces the strength of binding of the unordered network of the internal structure of the investigated material. This trend could be expected bearing in mind the known fact that the introduction of halogen elements causes disturbances in the tridimensional continuous network, as the systems invloving halogen elements are characterized by chain-like structure.

The fact that it was possible to establish certain correlations between a number of physical parameters and composition as a monotonous function indicates that these glasses within the selected cut behave as solid solutions.

On the basis of DTA measurements it was possible to postulate a degradation scheme of the glasses involving various structural units, which would mean that the structure of the glass of the type $Ge_{20}As_{14}(S_{0.5}Se_{0.5})_{66-x}I_x$ is formed of several structural units. These are primarily the following:

- tetrahedral:	- $GeX_{4/2}$	(GeX_2)
	- $Ge_2X_{4/2}$	(GeX)
	- $As_2XX_{4/2}$	(As_2X_3)
- trigonal:	- $AsX_{3/2}$	(1/2 As_2X_3)
- chain-like:	- $AsX_{2/2}I$	(AsXI)
	- $X_{2/2}$	(X- S or Se)
- discrete:	- AsI_3	
	- I	

In view of the fact that the different literature sources mention also discrete structural units formed by bonding of two structural units $AsS_{2/2}I$ with two sulphur atoms in the bridge between As atoms, such combination can be also expected for the compound AsSeI in these glasses. All these facts point to the complexity of the investigated series of these chalcogenide semiconductors.

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