

Article

Glass Formation and Properties of Multicomponent Glasses of the As₂Se₃-Ag₂Te-GeTe System

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Abstract: Chalcogenide alloys of As₂Se₃-Ag₂Te-GeTe were synthesized using the melt-quenching technique. By the visual and XRD analyses, the state of obtaining alloys was proven (glass, crystalline, glass + crystalline), and the glass formation region in the system was established. The thermal characteristics of some samples were determined—temperatures of glass transition (T_g); crystallization (T_{cr}); and melting (T_m). The basic physicochemical parameters, such as density (d) and Vickers microhardness (HV), were measured. Compactness (C), as well as some thermomechanical characteristics, such as module of elasticity (E), volume (V_h), and formation energy (E_h) of micro-voids, were calculated, and the influence of the composition on these characteristics was investigated. The addition of silver telluride resulted in a decrease in T_g and HV values and an increase in d and V_h values. No thermochemical effects of crystallization or melting were detected in some of the alloys. The obtained results were in agreement with the available literature data for similar systems.

Keywords: chalcogenide glasses; physicochemical properties; thermomechanical properties



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1. Introduction

Chalcogenide glasses (ChGs), with their characteristic properties—low glass transition temperature; low phonon energy; transparency in the middle infrared region of the electromagnetic spectrum; high refractive index; semiconductor properties; and photosensitivity; combined with their relatively easy production in bulk and thin-film form; have long been widely used in sensors and electronics as active membranes for various types of sensors [1–3]; information storage and transmission media [4]; threshold switches [5]; low-cost solar cells [6]; and many other electronic elements.

The interest in glassy chalcogenides with a high content of tellurium is determined by the ability of this class of compounds to transmit light in the middle and far infrared regions of the electromagnetic spectrum—up to 28 μm [7–9]. Based on them, optical sensors with good selectivity and sensitivity were obtained for the registration of molecules, biomolecules, bacteria, viruses, and proteins whose absorption bands are located in the region above 12 μm.

The pronounced tendency to crystallize tellurium makes it difficult to obtain stable glasses with its participation. It was established that the introduction of certain components in the composition, such as arsenic, selenium, and gallium—Ge-Te-Se [10,11]; Te-Ge-I and Te-Ge-Ga [7] Ge-As-Te, Ge-As-Te-Se [12]; (GeTe₄)_{100-x}(AgI)_x [13]; as well as additional purification of the obtained alloys [14]; improve the preparation of compositions in glassy form and reduce their tendency to crystallize.

Jovari studied the structure of GeTe₄-Ag glasses and reported that the concentration of charge carriers increased with increasing Ag content, while the topology of the GeTe₄ host framework was largely preserved. Other authors report the structure-terahertz (THz) property relationship for various non-oxide chalcogenide glasses. This comprehensive

study combined Raman spectroscopy to examine structural units, connectivity, and glass networks and terahertz time-domain spectroscopy (THz-TDS) to record the THz refractive index, $n(\text{THz})$, across a broad THz bandwidth. Research shows that Ge-Se binary glasses measure increased THz refractive index as $\langle r \rangle$ increases, with the maximum at $\langle r \rangle = 2.8$. Ternary Ge-As-Se glasses record the maximum THz refractive index value at $\langle r \rangle = 2.5$ for $\text{Ge}_{10}\text{As}_{30}\text{Se}_{60}$. Such a correlation is valuable for predicting and designing chalcogenide glasses for integrated optical applications across the THz and IR regions.

Studies for glass forming ability with high thermal stability of glass with composition $\text{Ge}_x\text{Te}_y\text{Se}_{(100-x-y)}$ and the studied properties prove strongly depending on the Ge/Se ratio and the concentration of Te. The glasses with $15 \leq x \leq 40$ are the most suitable compositions for applications for making IR lenses and optical fibers [11,15,16].

Multicomponent systems built on the basis of a good glass former, such as As_2Se_3 and chalcogenide compounds with different properties, imply the creation of a more disordered structure, which increases the probability of obtaining glassy materials in wider areas and with changing properties depending on the composition.

In this regard, the object of the present study is ChGs from the multicomponent system $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te-GeTe}$.

The compound As_2Se_3 is a high-resistance semiconductor. It exists in a crystalline and glassy state. At $T = 300 \text{ K}$, the crystalline As_2Se_3 has electrical conductivity $\sigma \approx 10\text{--}13 \text{ S cm}^{-1}$, and the glassy— $\sigma \approx 10\text{--}12 \text{ S cm}^{-1}$. The thermal band gap of the crystalline one is 1.84, and that of the glassy one is 1.90 eV. Under normal synthesis conditions and slow cooling of the melt to room temperature, As_2Se_3 is obtained in a glassy state [17]. Ismailov et al. study the electrical conductivity of glassy As_2Se_3 . The electrical conductivity of As_2Se_3 at 300 K is $6 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$. The thermal bandgap calculated from the slope of the conductivity curves is $\Delta E = 1.96 \text{ eV}$ [18].

GeTe is a promising material in both crystalline and amorphous forms. Crystalline GeTe is a semiconductor with $\Delta E = 0.1\text{--}0.2 \text{ eV}$ [19], has a high specific electrical conductivity at room temperature (3.103 S cm^{-1} [20]), as well as a high reflection coefficient (65% at 633 nm [21]). On the other hand, amorphous GeTe is a semiconductor with a band gap of 0.8 eV, a low electrical conductivity (almost 106 lower than that of crystalline GeTe [19]), and a lower reflection coefficient (~40% at 633 nm [21]). Ge-Te-based glassy materials are characterized by permeability in the range of 2–20 μm [22]. Germanium is known to increase the network connectivity of glass because it forms relatively strong chemical bonds and improves its thermal and mechanical properties.

Silver (I) telluride is a narrow-bandgap semiconductor with good thermoelectric properties. It exhibits effects of magnetoresistance and high electrical conductivity, which is why it is used in magnetic, electronic, and thermoelectric devices [23]. The inclusion of silver chalcogenides leads to an increase in the plasticity of the material [24], a valuable property in infrared technology. The inclusion of silver chalcogenides leads to an increase in the plasticity of the material, a valuable property in infrared technology for the production of optical fibers and as a material for the optical recording of information. The preparation of As_2Se_3 -based ChGs by the addition of two compounds with different properties— Ag_2Te and GeTe—is expected to lead to more stable ChGs in a wider range with improved or new properties.

In this regard, the aim of the present communication is related to the synthesis and investigation of the composition-properties dependence of basic physicochemical and thermomechanical characteristics of ChGs from the $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te-GeTe}$ system.

2. Experimental Procedure

2.1. Materials

Arsenic powder (As, 99.999% Sigma-Aldrich Chemie GmbH, Steinheim, Germany); Silver shot (Ag, 99.999%, Thermo Scientific Chemicals, Alfa Aesar Avocado Research Chemicals, Ltd., Ward Hill, MA, USA); Germanium powder (Ge, 99.999%, Thermo Scientific Chemicals, Fisher Scientific UK); Tellurium powder (Te, 99.999%, Alfa Aesar); Selenium

powder (Se, 99.999%, Thermo Scientific Chemicals, Alfa Aesar Avocado Research Chemicals, Ltd., Ward Hill, MA, USA); all these reagents were used without purification.

2.2. Preparation of Glass Samples

The alloys of the As_2Se_3 - Ag_2Te - GeTe system, as well as their constituent components, were obtained by direct, three-step, one-temperature synthesis. Se, Te, As, Ag, and Ge of 5N purity were used for the synthesis of the starting materials As_2Se_3 , GeTe , and Ag_2Te . The investigated samples with chemical composition $(\text{As}_2\text{Se}_3)_x(\text{Ag}_2\text{Te})_y(\text{GeTe})_z$, where x , y , and z —mol%; were synthesized in amounts of 4 g. For this purpose, the starting substances were weighed on an analytical balance with an accuracy of ± 0.0002 g in quantities corresponding to the chemical composition of the samples, after which they were transferred into quartz ampoules 100 mm long and 10 mm in diameter. The ampoules, evacuated to a residual pressure of 0.133 Pa and soldered on the flame of an oxygen propane-butane torch, were placed in an electric resistance furnace equipped with a vibrating device. The temperature-time characteristics, as well as the method of cooling the melts, are presented in Table 1. The rate of heating from step to step— $3\text{--}4$ $^\circ\text{C min}^{-1}$, $2\text{--}3$ $^\circ\text{C min}^{-1}$, and $2\text{--}3$ $^\circ\text{C min}^{-1}$, respectively. Vibration stirring was applied at each isothermal stage as well as at the maximum heating temperature, for better homogenization of the melt. At the end of the last stage, the ampoules are cooled in air to $900\text{--}950$ $^\circ\text{C}$ and sharply quenched in a mixture of water + ice, which provides a cooling rate of $10\text{--}15$ $^\circ\text{C s}^{-1}$ (depending on the size of the ampoules).

Table 1. Regimes of synthesis of the initial compounds and samples of the As_2Se_3 - Ag_2Te - GeTe system.

Compound	Isothermal Steps								Cooling
	$T_1, ^\circ\text{C}$	t_1, min	$T_2, ^\circ\text{C}$	t_2, min	$T_3, ^\circ\text{C}$	t_3, min	$T_4, ^\circ\text{C}$	t_4, min	
As_2Se_3	300	60	550	60	750	60	450	30	Furnace off
GeTe	500	60	950	60	750	60	-	-	Furnace off
Ag_2Te	500	60	1000	60	900	-	-	-	Furnace off
$(\text{As}_2\text{Se}_3)_x(\text{Ag}_2\text{Te})_y(\text{GeTe})_z$	450	30	770	60	1000	120	950	-	Ice + water mixture

2.3. Characterization of Materials

The surface of the freshly synthesized alloys, revealed by mechanical breaking of the ingot, was visually analyzed using a binocular magnifier with a magnification of $4\times$.

The X-ray phase analysis of the starting substances and samples from the system was carried out on a TUR-M 62 apparatus with a $\text{K}\alpha$ -Cu and Ni filter.

The diffractograms of the studied compositions were obtained under the following conditions: 750 mg of the studied alloy was previously ground in an agate mortar and sieved to obtain a powder sample with particle sizes no larger than 63 μm . The samples were prepared on aluminum cuvettes with a layer thickness of 2 mm.

The thermograms of the vitreous alloys were recorded on a derivatograph with a three-channel Y — t recorder from the company Kutesz; Type 1040. The accuracy of measuring the temperatures of phase transformations is ± 5 $^\circ\text{C}$. Pre-calcined Al_2O_3 served as reference material for this study. The characteristic temperatures of the obtained chalcogenide glasses—softening temperature— T_g ; crystallization temperature— T_{cr} ; and melting temperature— T_m of the system were determined during non-isothermal heating carried out in the temperature range from room temperature to 1000 $^\circ\text{C}$, at a rate of 15 $^\circ\text{C}\cdot\text{min}^{-1}$.

The density of the chalcogenide glasses in the investigated systems was determined by the hydrostatic method [25]. Working fluid—toluene. Five samples of each composition, with approximately the same mass, were measured. Density values were calculated using the formula:

$$d^t = d_{\frac{4}{V}}^t \cdot Q_{\frac{4}{V}}^{\text{H}_2\text{O}} \cdot \left(\frac{m \cdot d_{\text{T}}^t (Q_{\text{H}_2\text{O}}^t - \lambda)}{m - m_{\text{T}}} \right) + \lambda, \text{ gcm}^{-3} \quad (1)$$

where m —weight of the air sample; m_{T} —sample weight in toluene; d_{T}^t —relative density of toluene at the measurement temperature; $Q_{\text{H}_2\text{O}}^t$ —relative density of water; at the measurement temperature; $d_{\frac{4}{V}}^t$ —relative density of the sample at temperature t ; $Q_{\frac{4}{V}}^{\text{H}_2\text{O}}$ —water density at $t = 4^\circ\text{C}$ and $V = \text{const.}$; λ —relative air density—0.0012. The error of the method used is $\pm 5\%$.

The compactness— C —of the glasses is a structurally sensitive characteristic that reacts to the occurring changes in the structure. It is calculated by the formula [26]:

$$C = d \left\{ \sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d} \right\} \left[\sum_i M_i x_i \right]^{-1}, \quad (2)$$

where: d —density of glass; d_i ; M_i ; x_i —density; molar mass; and mole fraction of the i -th component.

The microhardness of the voluminous vitreous samples was determined by the Vickers method using a MIM-7 microscope with a PMT-3 microhardness meter built into it. The load on the pyramid was selected experimentally.

The microhardness values were calculated using the formula:

$$\text{HV} = \frac{P}{F} = \frac{2 \cdot P \cdot \sin \frac{\alpha}{2}}{d^2} = \frac{1854 \cdot P}{d^2}, \quad (3)$$

$$d = d_1 + d_2 / 2N \cdot 0.315; 1 \text{ kg f} = 9.81 \text{ N}, \quad (4)$$

where: P —load force, g; d —diagonal of the footprint, μm^2 ; N —scale division/1 scale division = 0.315 μm ; F —surrounding surface from the impression; α —angle at the top of the pyramid; -136° .

The microhardness of the samples was calculated based on 20 impressions per sample with a measurement accuracy of $\pm 5\%$.

Sanditov [27] offers the following formula for the microhardness of glasses:

$$\text{HV} = \frac{E_h}{V_h} \quad (5)$$

where: V_h и E_h are, respectively, the volume of microvoids in chalcogenide glasses and the energy for their formation.

The moduli of elasticity— E ; V_h и E_h are calculated using the formulas:

$$E = 15\text{HV kgf mm}^{-2} \quad (6)$$

$$V_h = 5.04 \frac{T_g}{\text{HV}} 10^{-3}, \text{ nm}^3 \quad (7)$$

$$E_h = 30,729 T_g, \text{ kJ mol}^{-1} \quad (8)$$

where: T_g , K.

3. Results and Discussion

3.1. Synthesis and State of the Obtained Alloys—Delineation of the Glass Formation Region in the As_2Se_3 - Ag_2Te - GeTe System

Forty compositions of the As_2Se_3 - Ag_2Te - GeTe system were synthesized. The resulting samples are dark gray in color. Their condition was determined by visual and X-ray phase analysis according to generally accepted criteria. Vitreous alloys have a smooth, shiny

surface; their X-ray patterns are distinguished by a characteristic amorphous “halo” and the absence of diffraction lines. On the surface of the glass crystal samples, two phases are observed—crystalline and vitreous. The X-ray phase analysis registered weak diffraction lines of low intensity. The crystalline samples have a matte and rough surface, and X-rays show the absence of an amorphous “halo”. Well-defined diffraction lines characteristic of the crystalline state are observed in —Figure 1.

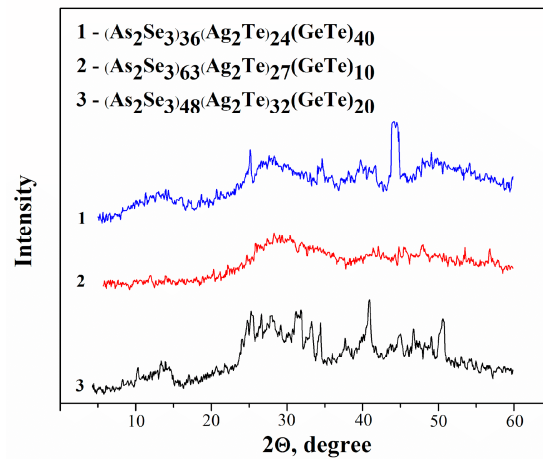


Figure 1. XRD patterns of the alloys from the $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te-GeTe}$ system.

As a result of the conducted analyses, the condition of the obtained alloys was established—Table 2 and the area of glass formation in the $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te-GeTe}$ system was outlined Figure 2.

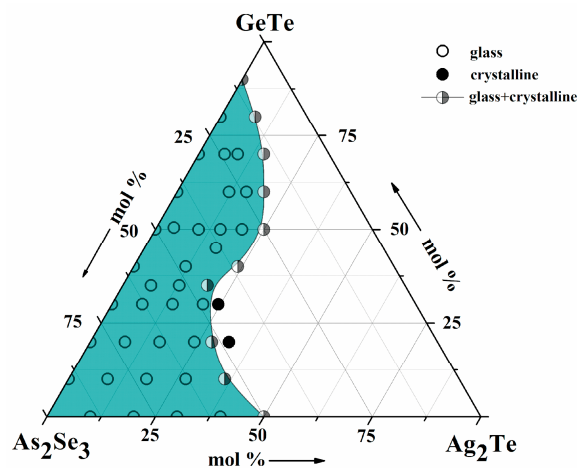


Figure 2. Glass-forming region in the $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te-GeTe}$ system.

Condition of the samples in the system:

- Specimens in a glassy state (vitrification region)—29 compositions: SG1–SG4; SG6–SG9; SG12–SG15; SG17–SG18; SG20–SG21; SG24–SG28; SG30–SG32; SG34–SG36; SG38;
- Specimens in glass crystal state—SG5; SG10; SG19; SG22–SG23; SG29; SG33; SG39–SG40;
- Samples in the crystalline state, located outside the glass formation region—2 compositions: SG11, SG16.

The glass formation region—Figure 2 is drawn to As_2Se_3 (peak in the Gibbs concentration triangle). It is located in the range from 0 to 50 mol % Ag_2Te [28] in the $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te}$ system and from 0 to 90 mol % GeTe [29] in the $\text{As}_2\text{Se}_3\text{-GeTe}$ system. Glasses in the $\text{Ag}_2\text{Te-GeTe}$ system, under the given conditions, were not obtained. The $\text{As}_2\text{Se}_3\text{-Ag}_2\text{Te}$ couple

dissolves up to 70 mol % GeTe. Its solubility in the system has a maximum value in sample SG36 with composition $(As_2Se_3)_{21.0}(Ag_2Te)_{9.0}(GeTe)_{70.0}$.

Table 2. Composition (mol %) and condition of the synthesized alloys.

Sample	Composition, mol %			State
	As ₂ Se ₃	Ag ₂ Te	GeTe	
	x	y	z	
SG1	90.0	-	10.0	glass
SG2	81.0	9.0	10.0	glass
SG3	72.0	18.0	10.0	glass
SG4	63.0	27.0	10.0	glass
SG5	54.0	36.0	10.0	glass + crystalline
SG6	80.0	-	20.0	glass
SG7	72.0	8.0	20.0	glass
SG8	64.0	16.0	20.0	glass
SG9	56.0	24.0	20.0	glass
SG10	52.0	28.0	20.0	glass + crystalline
SG11	48.0	32.0	20.0	crystalline
SG12	70.0	-	30.0	glass
SG13	63.0	7.0	30.0	glass
SG14	56.0	14.0	30.0	glass
SG15	49.0	21.0	30.0	glass
SG16	45.5	24.5	30.0	crystalline
SG17	58.5	6.5	35.0	glass
SG18	52.0	13.0	35.0	glass
SG19	45.5	19.5	35.0	glass + crystalline
SG20	60.0	-	40.0	glass
SG21	48.0	12.0	40.0	glass
SG22	36.0	24.0	40.0	glass + crystalline
SG23	38.5	16.5	45.0	glass + crystalline
SG24	50.0	-	50.0	glass
SG25	45.0	5.0	50.0	glass
SG26	40.0	10.0	50.0	glass
SG27	35.0	15.0	50.0	glass
SG28	30.0	20.0	50.0	glass
SG29	25.0	25.0	50.0	glass + crystalline
SG30	40.0	-	60.0	glass
SG31	28.0	12.0	60.0	glass
SG32	24.0	16.0	60.0	glass
SG33	20.0	20.0	60.0	glass + crystalline
SG34	30.0	-	70.0	glass
SG35	24.0	6.0	70.0	glass
SG36	21.0	9.0	70.0	glass
SG37	15.0	15.0	70.0	glass + crystalline
SG38	20.0	-	80.0	glass
SG39	12.0	8.0	80.0	glass + crystalline
SG40	10.0	-	90.0	glass + crystalline

Studies by Chen et al. [30] show a solubility of 88 mol % GeTe in the As₂Se₃-GeTe binary system, which is probably due to the difference in the melt cooling mode—air quenching.

3.2. Study of the Dependence Composition—A Property of Vitreous Samples with a Common Composition $(As_2Se_3)_x(Ag_2Te)_y(GeTe)_z$

To facilitate the analysis of the composition-property relationship, the magnitude has been introduced: $m = \frac{\chi_{Ag_2Te}}{(\chi_{As_2Se_3} + \chi_{Ag_2Te})}$, where: χ_{Ag_2Te} —the molar fraction of Ag₂Te; $\chi_{As_2Se_3}$ —the molar fraction of As₂Se₃.

3.2.1. Thermal Characteristics

The thermal analysis was carried out under the conditions described in point 2.2.

It is noticed that in some of the studied compositions, the effects related to crystallization and melting processes are absent—Table 3.

Table 3. Characteristic temperature of the same of the studied glass samples.

Sample	Composition, mol %			m	$T_g, ^\circ\text{C}$	$T_{cr}, ^\circ\text{C}$	$T_m, ^\circ\text{C}$
	As_2Se_3	Ag_2Te	GeTe				
	x	y	z				
SG1	90.0	-	10.0	0	202	-	299
SG2	81.0	9.0	10.0	0.1	189	249	297
SG3	72.0	18.0	10.0	0.2	174	232	295
SG4	63.0	27.0	10.0	0.3	160	213	295
SG6	80.0	-	20.0	0	203	-	-
SG7	72.0	8.0	20.0	0.1	192	-	280
SG8	64.0	16.0	20.0	0.2	178	242	295
SG9	56.0	24.0	20.0	0.3	165	217	293
SG12	70.0	-	30.0	0	205	-	-
SG13	63.0	7.0	30.0	0.1	198	-	-
SG14	56.0	14.0	30.0	0.2	184	251	294
SG15	49.0	21.0	30.0	0.3	170	222	298
SG24	50.0	-	50.0	0	215	-	297
SG26	40.0	10.0	50.0	0.2	202	-	293
SG27	35.0	15.0	50.0	0.3	186	-	297
SG28	30.0	20.0	50.0	0.4	170	246	387
SG34	30.0	-	70.0	0	222	-	292
SG35	24.0	6.0	70.0	0.2	208	-	-

Glass transition temperature (T_g) [29], depending on the composition of ChGs, varies in the range from 160 to 222 $^\circ\text{C}$ —Table 3. The introduction of Ag_2Te into the system leads to an increase in the metal component of the chemical bond in ChGs, and when its amount increases (at $z = \text{const.}$), the softening temperature decreases. With increasing GeTe content, at $m = \text{const.}$, T_g increases. The softening temperature reflects the structure of the glass [31], and a decrease in its value indicates that the integrity of the structure is deteriorating. The pure components As_2Se_3 и GeTe have $T_g = 453\text{--}473\text{ K}$ и 413 K , respectively. It can be expected that, at $m = \text{const.}$, the addition of GeTe to As_2Se_3 will lower the T_g . However, in reality, the exact opposite effect is observed (Figure 3).

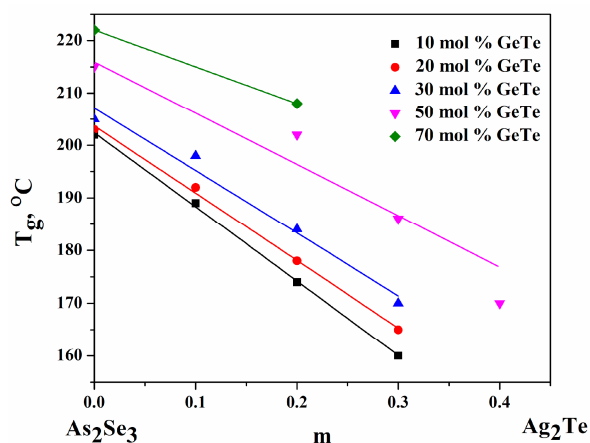


Figure 3. Dependence of T_g on the contents of Ag_2Te , $z = \text{const.}$, and GeTe , $m = \text{const.}$

The crystallization temperature (T_{cr}) varies between 213 and 251 (246) °C, and the melting temperature (T_m) varies between 287 and 387 °C. With increasing concentrations of Ag_2Te (at $z = \text{const.}$), T_{cr} decreases. Crystallization and melting effects were not observed in some of the studied glass compositions— $(As_2Se_3)_{80.0}(Ag_2Te)_0(GeTe)_{20.0}$; $(As_2Se_3)_{70.0}(Ag_2Te)_0(GeTe)_{30.0}$; $(As_2Se_3)_{63.0}(Ag_2Te)_{7.0}(GeTe)_{30.0}$; $(As_2Se_3)_{24.0}(Ag_2Te)_{6.0}(GeTe)_{70.0}$. The absence of exothermic effects associated with the crystallization process is an indicator of the good thermal resistance of glassy alloys. For compositions where no crystallization is observed, the endoeffects associated with the melting process are unclear and fuzzy.

3.2.2. Density, Microhardness, Compactness, and Thermo-Mechanical Characteristics

The density (d) depends on the composition of ChGs and varies between 4.31 and 5.58 g cm^{-3} . When increasing the content of Ag_2Te (at $z = \text{const.}$) and $GeTe$ ($m = \text{const.}$), respectively, the density of the glasses increases, which is expected since the density of the starting components decreases in the order: $d(Ag_2Te) > d(GeTe) > d(As_2Se_3)$, respectively $8.5 > 6.2 > 4.75 \text{ g cm}^{-3}$ —Figure 4.

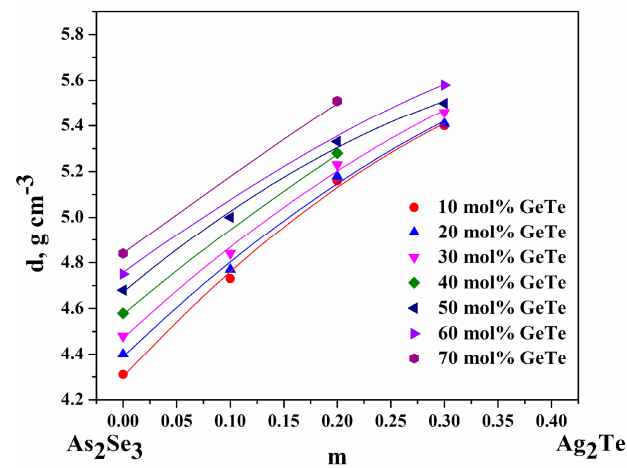


Figure 4. Dependence of density (d) on glasses' content.

The microhardness HV of the glasses varies from 73 to 133 kgf mm^{-2} —Table 4. As m increases (at $z = \text{const.}$), HV decreases. As z increases (at $m = \text{const.}$), it increases. This course of the dependences $HV(m)$ and $HV(z)$ is expected because: $HV_{As_2Se_3} = 150 \text{ kgf mm}^{-2} > HV_{GeTe} = 143 \text{ kgf mm}^{-2}$ [32] $> HV_{Ag_2Te} = 38 \text{ kgf mm}^{-2}$ —Figure 5.

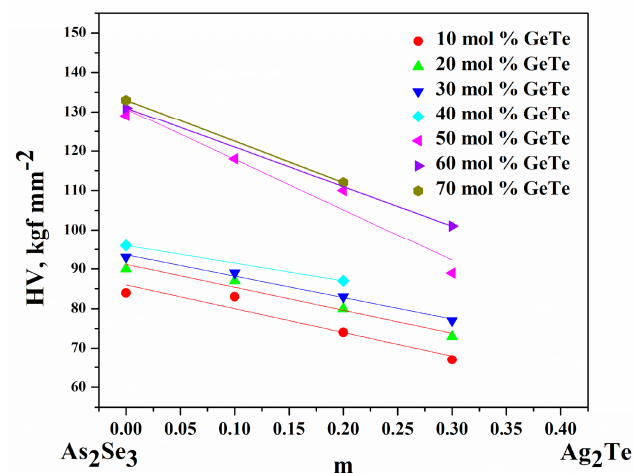


Figure 5. Dependence of microhardness (HV) on contents of m ($z = \text{const.}$) and z ($m = \text{const.}$).

Table 4. Measured density (d), microhardness (HV), and compactness (C) of some glass samples.

Sample	Composition, mol %			m	d, g cm ⁻³	HV, kgf mm ⁻²	C
	As ₂ Se ₃	Ag ₂ Te	GeTe				
	x	y	z				
SG1	90.0	0	10.0	0	4.31	84	-0.1042
SG2	81.0	9.0	10.0	0.1	4.73	83	-0.0543
SG3	72.0	18.0	10.0	0.2	5.16	74	-0.0100
SG4	63.0	27.0	10.0	0.3	5.40	67	-0.0086
SG6	80.0	0	20.0	0	4.40	90	-0.0985
SG7	72.0	8.0	20.0	0.1	4.77	87	-0.0581
SG8	64.0	16.0	20.0	0.2	5.18	80	-0.0165
SG9	56.0	24.0	20.0	0.3	5.41	73	-0.0146
SG12	70.0	0	30.0	0	4.48	93	-0.0969
SG13	63.0	7.0	30.0	0.1	4.84	89	-0.0577
SG14	56.0	14.0	30.0	0.2	5.23	83	-0.0185
SG15	49.0	21.0	30.0	0.3	5.46	77	-0.0144
SG20	60.0	0	40.0	0	4.58	96	-0.0936
SG21	48.0	12.0	40.0	0.2	5.28	87	-0.0221
SG24	50.0	0	50.0	0	4.68	129	-0.1052
SG25	45.0	5.0	50.0	0.1	5.00	118	-0.0593
SG26	40.0	10.0	50.0	0.2	5.33	110	-0.0275
SG27	35.0	15.0	50.0	0.3	5.50	89	-0.0282
SG30	40.0	0	60.0	0	4.75	131	-0.1022
SG31	28.0	12.0	60.0	0.3	5.58	101	-0.0269
SG34	30.0	0	70.0	0	4.84	133	-0.1114
SG35	24.0	6.0	70.0	0.2	5.51	115	-0.0209

The modulus of elasticity E (Table 5) varies from 1005 to 1995 kgf mm⁻² and reproduces the microhardness of the glasses, following Equation (6).

Table 5. Thermo-mechanical characteristics—minimum volume of micro-voids (V_h); energy of their formation (E_h); and module of elasticity (E) of some glass samples.

Sample	Composition, mol %			m	V _h , 10 ⁻³ nm ³	E _h , kJ mol ⁻¹	E
	As ₂ Se ₃	Ag ₂ Te	GeTe				
	x	y	z				
SG1	90.0	0	10.0	0	28.50	14.6	1260
SG2	81.0	9.0	10.0	0.1	28.05	14.2	1245
SG3	72.0	18.0	10.0	0.2	30.44	13.7	1110
SG4	63.0	27.0	10.0	0.3	32.57	13.3	1005
SG6	80.0	0	20.0	0	26.66	14.6	1350
SG7	72.0	8.0	20.0	0.1	26.94	14.3	1305
SG8	64.0	16.0	20.0	0.2	28.41	13.9	1200
SG9	56.0	24.0	20.0	0.3	30.24	13.5	1095
SG12	70.0	0	30.0	0	25.90	14.7	1395
SG13	63.0	7.0	30.0	0.1	26.67	14.5	1335
SG14	56.0	14.0	30.0	0.2	27.75	14.0	1245
SG15	49.0	21.0	30.0	0.3	29.00	13.6	1155
SG24	50.0	0	50.0	0	19.07	15.0	1935
SG26	40.0	10.0	50.0	0.2	21.76	14.6	1650
SG27	35.0	15.0	50.0	0.3	25.99	14.1	1470
SG34	30.0	0	70.0	0	18.76	15.2	1995
SG35	24.0	6.0	70.0	0.2	21.64	14.8	1725

The minimum volume of the microvoids (V_h) varies between 18.76 and 32.57 × 10⁻³ nm³. V_h increases with increasing amounts of Ag₂Te (at z = const.) and decreases with increasing

GeTe content ($m = \text{const.}$)—Figure 6. The microvoid formation energy E_h follows the course of T_g and ranges from 13.3 to 15.2 kJ mol⁻¹.

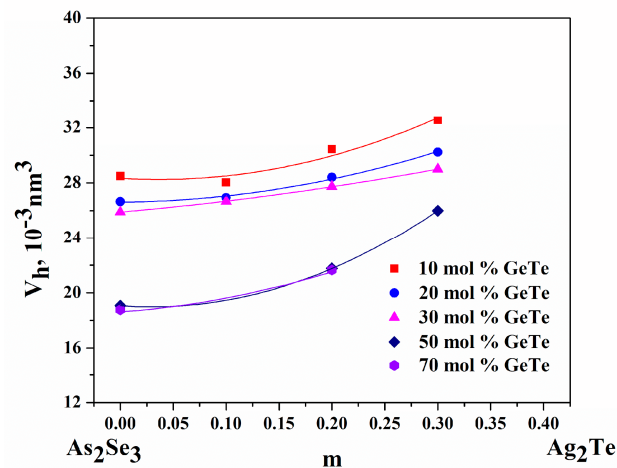


Figure 6. Minimum volume of microvoids (V_h) dependence at m ($z = \text{const.}$) and z ($m = \text{const.}$).

According to Tichý [33], compactness (C) expresses the change in volume that is due to the interactions between the components that make up the glass and is therefore related to the free volume and flexibility of the vitreous network. It can also take negative values, which is an indication of greater free volume and flexibility of the vitreous structure. The compactness (C) of the studied samples increases with increasing Ag_2Te content in the interval $0.0 < m < 0.2$ —(Table 5). At $m = 0.2$, the dependence $C(m)$ at $z = \text{const.}$ passes through a maximum. At $m > 0.2$, the characteristic is weakly dependent on the Ag_2Te content. A similar dependence of compactness on composition is also observed in CHGs from other systems [28]. The concentration of GeTe does not have a significant effect on the compactness of the studied compositions.

This course of dependence of T_g , d , HV , V_h , and $C(m)$ and T_g , HV , V_h , and $C(z)$ is closely related to the characteristics of the output components. By introducing Ag_2Te into the structure of the chalcogenide glass (at $z = \text{const.}$), chemical bonds are broken, and silver atoms and fragments ($-\text{Ag}$; $-\text{Te}-\text{Ag}$) close the broken chains, as a result of which the cross-linking of the structure decreases and the disorder in the system increases, which explains the decrease in T_g and microhardness and the increase in microvoid volume. On the other hand, the introduction of heavier atoms (Ag and Te) to As_2Se_3 leads to an increase in the average molecular weight of the glass and an increase in density and compactness. GeTe (at $m = \text{const.}$) leads to a compaction of the structure and an increase in the connectivity in the glass network, which is expressed in an increase in the value of T_g , d , and HV and a decrease in the volume of microvoids (V_h) [29] in the studied compositions. A similar effect of GeTe on thermal and mechanical properties such as T_g and HV has been observed in other studies [34,35].

4. Conclusions

Forty samples from the As_2Se_3 - Ag_2Te - GeTe system were synthesized by the method of direct mono-temperature synthesis.

With the help of the visual and XRD analyses, the region of the glass formation domain within this system was outlined. Chalcogenide glasses were obtained in the As_2Se_3 - GeTe system in the range of 0 to 90 mol% GeTe, while in the binary As_2Se_3 - Ag_2Te system, from 0 to 50 mol % Ag_2Te . In the Ag_2Te - GeTe system, no glass samples were obtained. It is been found that the maximum solubility is 70 mol % GeTe in the As_2Se_3 - Ag_2Te system.

The characteristics and temperatures of some alloys in the studied system were determined. The thermograms showed clearly expressed effects connected to the glass-transition

process. It is an indicator of the good thermal resistance of glassy alloys. Thermos-effects of crystallization and melting were not observed in some of the samples.

The composition affects the properties of glassy alloys. The introduction of GeTe leads to a densification of the structure and an increase in the values of microhardness (73 to 133 kgf mm⁻²) and density (4.31 to 5.58 g cm⁻³). The values of compactness and thermomechanical characteristics of some of the compositions were calculated, and the influence of the composition on them was investigated. This allows us to suggest that these compounds could be used in the production of thin films for special window glasses or for optical fiber lines for data transmissions.

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