Influence of small additives of germanium on the physical properties of chalcogenide glasses based on composition \( \text{As}_{30.5}\text{S}_{44.5}\text{I}_{25} \)

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Abstract. Advanced for the infrared region of the spectrum chalcogenide glass composition \( \text{As}_{30.5}\text{S}_{44.5}\text{I}_{25} \) with small germanium additives were investigated. The concentration dependences of some physical and chemical properties indicate an increase in the performance of glasses due to the modification of the glass network. The character of the change in the short-wavelength absorption edge with an increase in the content of germanium atoms had an exponential character, shifting from 597 to 582 nm. A non-monotonic dependences were also found for the values of density, refractive index, and glass transition temperature. A joint analysis of the results obtained and structural studies described in the literature for similar glass systems made it possible to propose possible structural groups of glass compositions under investigation.

1. Introduction
The mid-infrared (IR) spectral region is of high practical importance for various spheres of human activity: laser and thermal imaging equipment, environmental monitoring, biomedicine, space technologies, fiber-optic communication lines, material processing and optoelectronics [1 - 2]. The nomenclature of existing materials for the mid-IR region is limited, mainly used are expensive and laborious to obtain and process crystalline materials, such as: ZnSe, ZnS, Ge, TlBr-TlI [3]. Their alternative can be chalcogenide glasses, which provide the required level and spectral IR range of transmission [4].

In recent years, a technologically demanded area of research in IR materials is the development of thermoplastic compositions of glasses, which make it possible to obtain optical components (lenses, windows, prisms) using polymer optics methods: casting into molds, hot pressing, and layer-by-layer fusion [4]. For these purposes, low-melting chalcogenide glasses are also promising, the softening temperature of which can be in the range of \((60 - 400) \, ^\circ\text{C}\). The main feature of the majority of chalcogenide glass compositions limiting their practical application in optical instrumentation is a high tendency to crystallization. The presence of bulk or surface crystallization leads to degradation of the optical characteristics of glasses. Despite the large number of publications devoted to chalcogenide systems, currently there are only 3 commercially produced glass compositions: AMTIR – 1 (based on Ge – As – Se), AMTIR – 3 (Ge – Sb – Se), AMTIR – 7 (As – Se) [5].

Chalcogen halide iodine-containing glasses are also known, which have a low melting point, high refractive index, but also prone to crystallization. It is known that small additions of \(p\)-elements can act as stabilizers of the amorphous structure. In this work, germanium was chosen as such an element. The
study presents the results of studying the optical characteristics of glasses based on the As-S-I composition with small additions of Ge. The initial composition was $\text{As}_{30.5-x}\text{Ge}_x\text{S}_{44.5}\text{I}_{25}$, where $x = 0, 1, 3, 5$ (mol. %), located in the centre of the glass formation region of the ternary system. Note that there are no studies in the literature on the effect of small additives of Ge on the properties of glass system As-S-I.

2. Experimental details
The synthesis of glasses was carried out according to the standard technology for chalcogenide materials: fusion of the initial components in an evacuated quartz ampoule. Elemental arsenic, sulfur, iodine, and germanium of the "high purity" grade were used for synthesis. The weighed portion was placed in a quartz ampoule and was pumped out to a pressure of $10^{-2}$ Pa using a fore-vacuum pump and sealed. Then the ampoules were placed in a tubular furnace of a special design, which ensured mixing of the melt. The synthesis temperature did not exceed 600 °C.

The glass densities $\rho$ were determined at Normal Temperature and Pressure conditions (NTP) (20°C, pressure 101.325 kPa, relative air humidity - 50%) by using Archimedes method. Xylene was used as a reference. The following equation was used to estimate the glass densities:

$$\rho = \frac{W_a}{W_a - W_x} \rho_x,$$

where $\rho_x$ – is the xylene density, $W_a$ and $W_x$ are the sample weights in air and xylene, respectively.

The measurements were carried out using Vibra HT-224RCE analytical balance.

The glass transition temperature was determined by a method of differential thermal analysis (DTA) on a Thermoscan 2 apparatus with a heating rate of 10 °C / min, using a powder of Al2O3 as a reference sample.

For optical measurements, the samples were shaped as plane-parallel with a thickness of 1-2 mm. Fourier spectrometer FSM 1201 was used to record infrared transmission spectra in the range of $(400 - 5000) \text{ cm}^{-1}$, the resolution was set at 4.0 cm$^{-1}$.

The refractive index was measured by the Fraunhofer least displacement angle method using a laser ($\lambda = 635$ nm), the sample was prepared in the form of a prism with an angle of 30° [8].

The optical absorption spectra were calculated from the transmission spectra, which were measured using an AvaSpec-2048L fiber spectrometer (Avantes, Netherlands) and a deuterium-halogen radiation source AvaLight-DH-S (Avantes, Netherlands). The absorption coefficient ($k(\lambda)$) was calculated using the following equation:

$$k(\lambda) = \frac{1}{d} \ln \left( \frac{1}{T(\lambda)} \right) = \frac{1}{d} \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right),$$

where $T(\lambda)$ is transmission and $d$ is the thickness of the glass sample, $I_0(\lambda)$ and $I(\lambda)$ signal intensity without sample and with it, respectively.

3. Experimental results
Areas of glass formation in ternary systems As-S-Hal (Hal – Cl, I, Br) have been known since the 70s [6 - 7] and since they have remained practically unchanged. In system As-S-Hal, iodine has a higher glass-forming ability than other halogens, in addition, such glasses have a higher refractive index and high chemical durability. The main problem of these glasses is their hydrolytic instability and low microhardness, which limits their practical use in IR optical instrumentation. Additives of various atoms can be used to improve the thermodynamic and mechanical characteristics of glasses by modifying the initial glass network structure. Such atoms can be p-elements of IV and V groups of the Periodic Table. In this work, germanium atoms (up to 5 mol. %) were used as modifying additives.

Table 1 shows the chemical compositions and some physical and chemical properties of the studied glasses. As can be seen from the values presented in the table, even small additions of Ge lead to changes
in the characteristics of the glass. Let us consider the concentration dependences shown in figure 1 in more detail.

Table 1. Glass compositions and some physical and chemical properties of the studied glasses.

| Composition, mol. % | Density, g/cm³ (±0.005) | Molar volume, V_m, cm³/mol | Refractive index at λ=635 nm, n_635 (±0.004) | Glass transition temperature T_g, °C (±3 °C) |
|---------------------|--------------------------|----------------------------|---------------------------------------------|------------------------------------------|
| As₃₀.₅GeₓS₄₄.₅I₂₅ | 3.626                    | 18.98                      | 2.37                                        | 57                                       |
| As₃₀.₅Ge₁S₄₄.₅I₂₅ | 3.646                    | 18.88                      | 2.39                                        | 75                                       |
| As₃₀.₅Ge₃S₄₄.₅I₂₅ | 3.598                    | 19.12                      | 2.33                                        | 73                                       |
| As₃₀.₅Ge₅S₄₄.₅I₂₅ | 3.581                    | 19.19                      | 2.31                                        | 70                                       |

As can be seen from the presented dependences, with the first additions of germanium, a sharp increase in the values of density, glass transition temperature, and refractive index is observed. In this case, the further course of the dependences has a descending character. The greatest effect of germanium additives was on the value of the glass transition temperature, which significantly increased by more than 30%. An increase in the values of characteristic temperatures (T_g) when another glass-forming atoms are introduced into the glass matrix is a natural and frequent phenomenon. This is due to a change in the glass structure as a result of the formation of a mixed glassy network.

Figure 1. Concentration dependences of density, refractive index and glass transition temperature for glass composition As₃₀.₅₄GeₓS₄₄.₅₁₂₅, where x = 0, 1, 3, 5 (mol. %).

It should be noted that the dependences of the ρ and n₆₃₅ have a clearly pronounced maximum at 1 mol. % of Ge, a further increase in its content leads to decrease, and the obtained values of density and refractive index for samples with 3 and 5 mol. % of Ge are even lower than for the initial glass composition. In glassy materials, the density characterizes the compactness of the arrangement of structural groups during the formation of a glass network, with the addition of atoms with a molecular mass exceeding the value of the average molecular weight of the glass, in the absence of phase transitions, an increase in the density value is usually observed [9]. Since the molecular weights of arsenic (74.9 g/mol) and germanium (72.6 g/mol) atoms practically coincide, the change in the density value can be associated exclusively with the modification of structural groups as a result of the different charge capabilities of the atoms. The refractive index of an optical material in the visible region of the spectrum is related to the electronic polarizability of atoms [9]; therefore, its change also characterizes the short-range order of the glass structure.

Thus, such a significant change in the density, refractive index and glass transition temperature are due to the different roles of atoms As and Ge in the formation of the short-range order of the glassy network.

In investigation [10] by neutron scattering was shown that glass with composition As₃₀S₄₅.₂I₂₄.₈ is formed by pyramids of [AsS₃] connected by bridges of –S– and pyramids [AsI₃]. In this case, iodine acts as chain terminator, bonding to As in place of sulphur. Thus, the structure of the glass consists of
[AsS₃] pyramids connected by bridges of –S– and pyramids with partially replaced S with iodine [–S–As⁻¹–S].

At the same time, the work [11] describes the structure of Ge-As-S glasses, which is formed by a tetrahedra [GeS₄], trigonal pyramids AsS₃ and S-S homopolar bonds. In another work [12], the structure of the glasses of the system Ge-S-I is investigated and it is shown that the structure is formed by are mixed [GeI₄] and [GeS₄] units connected by S-S homopolar bonds. Thus, for the glasses under study, we can assume the presence of a mixed frame consisting of the following structural groups: [–S–As⁻¹–S], [AsS₃], [GeI₄] and [GeS₄]. Taking into account the values of the bond length [10 - 12], the most likely groups in compositions under investigation are following: [GeS₄], [AsS₃] and [GeI₄]. Therefore, in comparison with the original glass without Ge additives, glass network is formed by mixed pyramid-tetrahydric groups in which iodine atoms locate in the first coordination sphere of germanium.

Figure 2 shows the optical absorption spectra of the samples of the studied glasses, taking into account the corrections for reflection from both faces based on the previously obtained values of n₆₅₅. As can be seen from the spectra presented, with an increase in the germanium content, the fundamental absorption edge shifts to the region of shorter wavelengths. The concentration dependence of short-wave absorption edge on the Ge content is shown on figure 2 b). The dependence was approximated by an exponential function, which had a high correlation coefficient (>0.99).

Figure 2. a) Optical absorption spectra, corrected for reflection from both glass faces, b) Dependence of the values of the short-wavelength absorption edge on the Ge content.

The shift in the value of the short-wavelength absorption edge was 15 nm for the sample with the maximum concentration of germanium. The difference in the absorption spectra between the samples containing 1 mol. % Ge and 3 mol.% Ge is noticeably visible. The difference between glasses with 3 and 5 mol. % of Ge is not significant.
Figure 3 shows the IR transmission spectra for a series of studied samples. Spectra did not show significant differences, both in the spectral transmission region and in the number and position of absorption bands. Analysis of the IR spectra of the samples revealed the presence of characteristic absorption bands.

Table 2 shows the values of the wavenumber of the detected absorption bands and the corresponding groups [13, 14]. The presence of absorption bands associated with oxygen-containing groups (~1300, ~1580 and ~3550 cm\(^{-1}\)) in the IR transmission spectra is determined by the degree of purification of the initial components, as well as by the vacuum depth achieved when the quartz ampoules are sealed. Thus, the presence of bands with maxima at about 3550 cm\(^{-1}\) in the transmission spectra of chalcogenide glasses is due to the presence of molecularly adsorbed water in the glass composition in the form \([\text{H}_2\text{O}]\) [15].

### Table 2. Position of absorption bands of impurities and their assignment [14].

| Composition       | Impurity compound or functional group | Maximum of absorption band, cm\(^{-1}\) |
|-------------------|---------------------------------------|-----------------------------------------|
| \(\text{As}_{30.5}\text{Ge}_{x}\text{S}_{44.5}\text{I}_{25}\) | C-O-H, [AsO\(_{3/2}\)], [Ge-O]        | 250-650                                 |
|                   | C-O                                   | 1000                                    |
|                   | S-O, [AsO\(_{3/2}\)]                  | 1300                                    |
|                   | \(\text{H}_2\text{O}\)                | 1580                                    |
|                   | \(\text{H}_2\text{S}\)                | 2330                                    |
|                   | S-H                                   | 2490                                    |
|                   | O-H                                   | 3500-3600                               |

Let us consider the changes in the intensities of absorption bands around 3550, 2330, 2490 and 1580 cm\(^{-1}\) with an increase in the germanium content. With an increase of germanium content, the intensity of the bands in the region of 3550 cm\(^{-1}\) and 1580 cm\(^{-1}\) decreased. In this case, the bands corresponding to the vibration of the \([\text{H}_2\text{S}]\) (2330 cm\(^{-1}\)) and \([\text{S-H}]\) (2490 cm\(^{-1}\)) increased. Since the synthesis of a series of studied glasses was carried out under the same conditions (vacuum depth, purity of the initial components, and temperature conditions), the reason for the concentration changes in the ratio of absorption bands associated with [OH] and [HS] groups may be the effect of germanium additives in the oxygen distribution in the glass matrix.

According to [14, 15] the introduction into the glass composition such additives as Al, Mg, Be and Ge can promote the preferential binding of oxygen to the atoms of these additives. Thus, there is a
redistribution of molecular water and the formation of group type [=Ge-O-] with the release of hydrogen atoms, which form bonds with sulphur [H2S] and [S-H]. The absorption bands of bonds [Ge-O] located around 500 – 600 cm⁻¹ are overlapped in the spectra by [C-O-H] and [AsO₃;₂] bonds, therefore the latter assumption cannot be proved on the basis of the spectra presented.

4. Discussion
The results obtained in the study affect the optical, physical and chemical properties of chalcogenide glasses and clearly demonstrate changes in both the density of arrangement of structural groups (density, molar volume), overlap of wave absorption bands of hydroxyl groups in the IR region). The dependences of density and refractive index have a non-monotonic character: they demonstrate an increase at minimal concentration of Ge additives (1 mol. %), and at 3 and 5 mol. % of Ge the values become lower than the initial glass. For the concentration dependence of the Tg, an increase by more than 30% at 1 mol. % of Ge was found. Such a significant change in the characteristics of the glassy material is associated with changes in the structure of the glass upon the introduction of strong glass former - germanium.

5. Conclusion
Experimental results demonstrate that Ge additives cause significant changes in optical and structural characteristics of chalcogenide glass based on composition As₅₀₋₅₋Ge₃₄₋₅₋I₂₅. The dependence of the short-wavelength absorption edge position has an exponential character in the investigated range of compositions, and demonstrate shift from 597 to 582 nm.

Also, with an increase in the content of Ge, a significant decrease in the intensity of absorption bands associated with molecular water and hydroxyl groups was observed (3550 cm⁻¹ and 1580 cm⁻¹). At the same time, for the bands corresponding to the [H₂S] and [S-H] vibrations, the intensity increased. These results were interpreted due to the inclusion of oxygen atoms in the first coordination sphere of germanium, while separated hydrogen atoms form bonds with sulphur.

Based on the results obtained in this work, as well as studies of short-range order in similar glassy systems described in literature, the following units can be proposed as structural groups in As₅₀₋₅₋Ge₃₄₋₅₋I₂₅ glass: [GeS₄], [AsS₃] and [GeI₄].

Acknowledgments
This work was supported by the grant of the President of the Russian Federation for young scientists No. MK-2869.2021.1.2.

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