

Structure and thermal properties of Ge-In-S chalcogenide glasses

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Glasses whose compositions can be expressed by $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ ($x=0,10,20,30$) formula were obtained by the melt-quenching technique. The glasses were homogeneous with high optical transmission from visible ($0.65 \mu\text{m}$) to mid infrared region ($10 \mu\text{m}$). The glass structure was studied by Raman and IR spectroscopy. Main structural units of studied glasses are GeS_4 tetrahedra connected to each other by corners and edges, InS_4 tetrahedra and InS_6 octahedra interconnected by sulfur bridges. The thermal stability was evaluated using differential thermal analysis (DTA) combined with differential scanning calorimetry (DSC) for the determination of characteristic temperatures: T_g ~ temperature of glass transition, T_x ~ temperature of onset of crystallization, T_c ~ temperature of crystallization, T_m ~ temperature of melting. The glass-forming ability was estimated using criteria of thermal stability, so-called the glass-forming criteria ($\Delta T = T_c - T_g$; Hruby's criterion, $H_f = (T_c - T_g)/(T_m - T_c)$; Saad and Poulain's criterion, $S = (T_c - T_x)/(T_x - T_g)/T_g$).

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1. Introduction

Chalcogenide glasses have been studied intensively [1-4]. GeS_2 -based chalcogenide glasses containing Ga, La elements, have been shown to provide satisfactory optical and thermal properties [5-7]. Over oxide and halide glasses, GeS_2 -based chalcogenide glasses are recognized as a frequently mentioned glass family with a wider transmission window from visible to infrared (IR) (0.5 - $10 \mu\text{m}$) [8]. Because of broader transmission window in IR spectral region, chalcogenide glasses are applicable for electronic and optoelectronic components not only in visible and near-IR, but also in mid-IR [3,4,9]. Chalcogenide glasses have been considered as promising hosts for doping with rare earth (RE) ions [5-7].

The stability of chalcogenide glasses can be estimated by thermal analysis. Characteristic temperatures (T_g ~ temperature of glass transition, T_x ~ temperature of onset of crystallization, T_c ~ temperature of crystallization, T_m ~ temperature of melting), and subsequently glass-forming criteria ($\Delta T = T_c - T_g$; Hruby's criterion, $H_f = (T_c - T_g)/(T_m - T_c)$; Saad and Poulain's criterion, $S = (T_c - T_x)/(T_x - T_g)/T_g$) were determined. The thermal stability range (ΔT) provides a good estimate of the tendency of the glass to crystallize. It should be larger than $100 \text{ }^\circ\text{C}$ to obtain stable glass samples and use them for applications such as optical fibers. All criteria have been successfully applied for studying stability evolution in a glass family when composition is linearly modified.

For the determination of thermal stability of glasses from ternary Ge-In-S chalcogenide system, differential thermal analysis was already used [10]. Boncheva-Mladenova et al. discussed the glass formation in Ge-In-S

system, in terms of determination of glass-forming boundaries and consequently physical and electrical characteristics of prepared glasses. The calculated values of ΔT ($162 - 365 \text{ }^\circ\text{C}$) predict high thermal stability of Ge-In-S chalcogenide system.

Generally, the structure of GeS_2 -based glasses has been widely studied by various techniques such as Raman and infrared spectroscopy [11,12,13]. The structure of germanium based chalcogenide glasses was described as network of GeS_4 tetrahedral units connected to each other by corners and edges [14].

Tetrahedral and octahedral positions of indium were found in $\beta\text{-In}_2\text{S}_3$ modification [16] Spinel type structure with ordered vacancies resulting in tetragonal symmetry corresponds to $\beta\text{-In}_2\text{S}_3$ modification. There are three successive layers in a unit cell. Some indium atoms are coordinated in these layers, some of them are situated between the layers. Indium atoms occupy two types of sites, octahedral and tetrahedral metal positions. One third of tetrahedral indium sites remain empty, it leads to the presence of vacancies.

In this work, the thermal stability and structural analysis of Ge-In-S chalcogenide glasses, is reported and discussed.

2. Experimental

Bulk $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses, where $x=10, 20$ and 30 were synthesized from high-purity elements (Ge, In, and S, all of 5N-purity) in sealed and evacuated silica ampoules in a rocking furnace ($970 \text{ }^\circ\text{C}$, 8 hours). Under same conditions, glassy sample of GeS_2 and crystalline sample of In_2S_3 were prepared as well. After the synthesis,

the ampoules with the melt were quenched in undercooled salt water. The homogeneity of the obtained glasses and absence of any observable crystalline phase was confirmed by optical transmission measurements, optical, electron microscopy and by X-ray diffraction. The transmission spectra of cut and polished plan-parallel plates of prepared glasses were measured using spectrophotometer Perkin-Elmer Lambda 9 (VIS, NIR), FT spectrophotometer BIORAD FTS 175C (NIR,MID) and FT spectrophotometer BIORAD FTS 45 (FAR). The room temperature Raman spectra were recorded by FT-IR spectrophotometer IFS 55 provided with Raman FRA-106 accessory (Bruker). A back scattering method with the YAG:Nd³⁺ laser line (1064 nm) was used for the excitation.

For correction of temperature dependent population of phonon levels, the reduced Raman spectra were calculated using Gammon-Shuker formula [17]

$$I^{\text{red}}(\omega) = (\omega_L - \omega)^{-4} \omega (1 - \exp(-\hbar\omega/kT)) I(\omega) \quad (1)$$

where ω_L and ω are frequencies of radiation of the laser and scattered light, respectively, T is the temperature, \hbar is reduced Planck constant, k is Boltzmann constant, and I is the intensity of scattered light.

The individual Raman bands were determined by peak fitting modul (Origin 6) using Voigt method assuming spectral line shapes resulting from a superposition of independent Lorentzian (homogeneous) and Doppler (inhomogeneous) line broadening mechanisms in real systems:

$$Y = A \left[m_u \cdot \frac{2}{\pi} \cdot \frac{w}{4(x-x_c)^2 + w_L^2} + (1-m_u) \cdot \frac{\sqrt{4 \ln 2}}{\sqrt{\pi w_G}} \cdot e^{-\frac{4 \ln 2}{w_G^2} (x-x_c)^2} \right] \quad (2)$$

Table 1. Thermal properties of (GeS₂)_{100-x}(In₂S₃)_x chalcogenide glasses: Glass composition (x), density (h), glass transition temperature (T_g), onset temperature of crystallization (T_x), midpoint temperature of crystallization (T_c), temperature of melting (T_m), difference ΔT ($\Delta T = T_{c1} - T_{gmid}$, Hruby's criterion ($H_r = (T_c - T_g)/(T_m - T_g)$), Saad and Poulain's criterion ($S = (T_c - T_x)/(T_x - T_g)/T_g$). Note that temperatures are given in °C.

x	h [g/cm ³] (±0.01)	T _g onset (±1)	T _g endset (±1)	T _g midpoint (±1)	T _x (±1)	T _{c1} (±1)	T _{c2} (±1)	T _{m1} (±1)	T _{m2} (±1)	T _{c1} -T _{gmid}	H _r	S
0	2.81	428	492	460	539	545	-	817	-	85	0.31	1.03
10	3.13	381	420	400	497	503	-	734	778	103	0.45	1.46
20	3.31	332	389	360	415	440	541	734	-	80	0.27	3.82
30	3.56	327	372	349	381	425	555	734	-	76	0.25	4.03

The glass transition temperature (T_g midpoint) is in 349-460 °C temperature range. The crystallization of glasses with composition (GeS₂)₈₀(In₂S₃)₂₀ and (GeS₂)₇₀(In₂S₃)₃₀ proceeds in two stages described by two crystallization peaks. The first one (T_{c1}) can be found in 425-545 °C range, the second one (T_{c2}), is located in 541-555 °C region (Tab. 1). Only one crystallization peak was found for glass (GeS₂)₉₀(In₂S₃)₁₀. The temperature of melting of studied glasses (T_m) was located in 734-817 °C region.

The glass-forming ability was estimated using criteria of thermal stability: ΔT ($\Delta T = T_{c1} - T_{gmid}$), Hruby's criterion

where Y is the intensity of the band, A is the amplitude, w_G is full width at half maximum (FWHM) of the intensity of Gauss band, w_L is FWHM of the intensity of Lorentz band, x is wavenumber, x_c is midpoint of band, m_u is factor including ratio of Gauss and Lorentz components.

The thermal properties were evaluated with combined differential thermal analysis instrument (R.M.I.-DTA 03, temperature range ~ 25-900 °C, heating rate ~ 10K/min.) and differential scanning calorimeter (DSC 12E, Mettler Toledo, temperature range ~ 50-400 °C, heating rate ~ 10K/min.).

3. Results

Glass samples with composition (GeS₂)_{100-x}(In₂S₃)_x (x=10,20,30) can be described as stoichiometric compounds consisting of GeS₂ and In₂S₃. Because of reliable determination of the properties of studied samples, GeS₂ glass and In₂S₃ crystals were studied as well.

Samples with In₂S₃ content up to 30 mol% were amorphous. Samples containing more than 30 mol% of In₂S₃ were partly crystalline as results from X-ray diffraction analysis.

Prepared (GeS₂)_{100-x}(In₂S₃)_x glasses with x=0-30 were homogeneous and well transparent. Their color was orange to dark-red depending on their composition. The density of studied glasses increased with increasing In₂S₃ content, $\rho = 2.81-3.56$ g/cm³.

The results of thermal analysis (characteristic temperatures: T_g, T_c, T_m, T_x) of individual glasses together with criteria of thermal stability (ΔT , H_r, S) are given in Table 1.

($H_r = (T_{c1} - T_{gmid}) / (T_m - T_{c1})$), Saad and Poulain's criterion ($S = (T_{c1} - T_x) / (T_x - T_{gmid}) / T_{gmid}$) [18]. The values of criteria of thermal stability are summarized in Table 1.

The optical transmission of studied glasses was high in spectral range from visible to infrared region (up to 900 cm⁻¹). The position of short-wavelength absorption edge is located between 450-650 nm in the visible region of the spectrum and it is shifted to the near infrared with increasing content of In₂S₃ (Fig. 1). The long-wavelength absorption edge was found near 900 cm⁻¹ and it can be assigned to the multiphonon Ge-S vibrations. In₂S₃ content

does not change the position of the long-wavelength absorption edge.

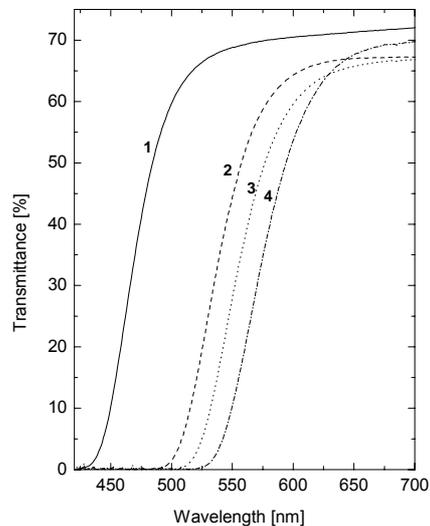


Fig. 1. The short-wavelength absorption edge of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses: 1. $x = 0$ (0.22 mm), 2. $x = 10$ (0.31 mm), 3. $x = 20$ (0.29 mm), 4. $x = 30$ (0.14 mm).

There are weak absorption bands in $1400\text{--}1700\text{ cm}^{-1}$ region in the IR spectra of studied glasses. Such absorption bands can be assigned to the breathing vibration of O-H groups of adsorbed water. A weak absorption band near 2509 cm^{-1} corresponds to the vibrations of S-H bonds [19].

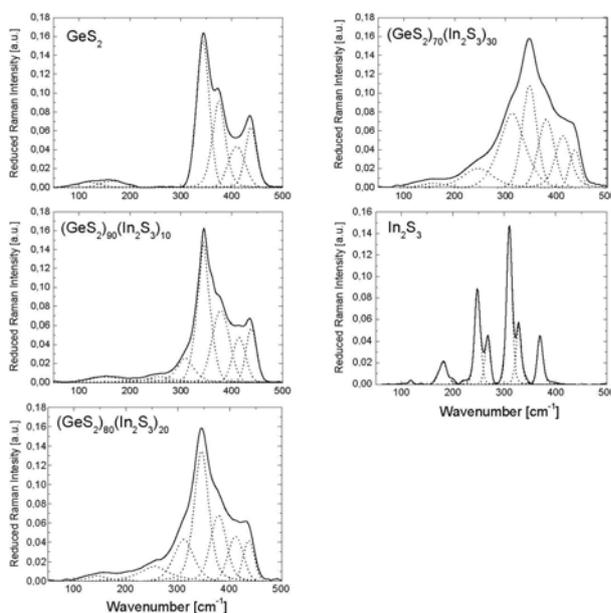


Fig. 2. Room-temperature reduced Raman spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses and In_2S_3 crystals.

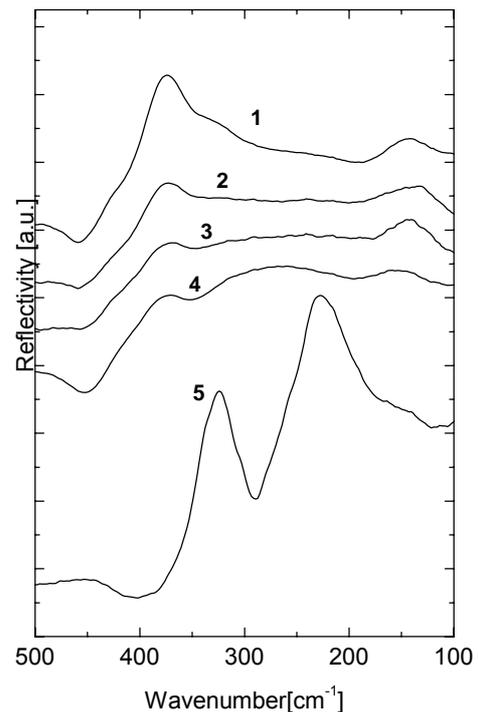


Fig. 3. Room-temperature far-IR reflectance spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses samples: 1. GeS_2 , 2. $(\text{GeS}_2)_{90}(\text{In}_2\text{S}_3)_{10}$, 3. $(\text{GeS}_2)_{80}(\text{In}_2\text{S}_3)_{20}$, 4. $(\text{GeS}_2)_{70}(\text{In}_2\text{S}_3)_{30}$, 5. crystalline In_2S_3 .

The structure of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ ($x=0\text{--}30$) glasses and crystalline In_2S_3 was studied by Raman and far-IR spectroscopy (Figs. 2,3). Reduced Raman spectrum of pure GeS_2 glass contains 6 bands with maxima near 114 , 162 , 345 , 375 , 407 and 437 cm^{-1} . Raman spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses consist of 7 predominant bands with maxima at 162 , 267 , 311 , 345 , 375 , 407 and 437 cm^{-1} . Raman bands of crystalline In_2S_3 were observed at frequencies 117 , 183 , 243 , 267 , 311 , 329 and 369 cm^{-1} . The assignment of all Raman bands found in Raman spectra of individual samples will be discussed in next part.

4. Discussion

The composition of studied glasses $((\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$, where $x=0,10,20$ and 30), is located near the centre of glass-forming region in Ge-In-S system, which predicts good glass-forming ability and possibility of preparation of stable and homogeneous glasses.

According to thermal analysis, two crystallization peaks (T_{c1} and T_{c2}) were located in the DTA curve of $(\text{GeS}_2)_{80}(\text{In}_2\text{S}_3)_{20}$ and $(\text{GeS}_2)_{70}(\text{In}_2\text{S}_3)_{30}$ glasses. The first one ($T_{c1} \sim 425\text{--}545\text{ }^\circ\text{C}$) can be assigned, according to X-ray diffraction, to the crystallization of $\beta\text{-In}_2\text{S}_3$ modification. The second one ($T_{c2} \sim 541\text{--}555\text{ }^\circ\text{C}$) is probably connected with crystallization of GeS_2 .

The highest values of characteristic temperatures were observed for the GeS_2 glass (Table 1). Incorporation of

In_2S_3 thus leads to decrease of the values of characteristic temperatures. This fact can be connected with the formation of eutecticum in $\text{GeS}_2\text{-In}_2\text{S}_3$ system.

Glass stability can be evaluated using semi-empirical relations (criteria of thermal stability: ΔT , H_r , S) based on characteristic temperatures. It is well known that mentioned relations of thermal stability allow one to predict the glass-forming ability of studied samples.

The first criterion ΔT (the difference between T_{c1} and T_{gmid}), which is critical to analyze the thermal stability of a glass, has relatively large values ($\Delta T \sim 76\text{-}103$ °C) in all studied glasses. This fact indicates good glass-forming ability and possibility of drawing fibers from studied glasses.

The other popular stability scale is based on the Hruby's criterion (H_r). In addition to T_{c1} and T_{gmid} , it also includes the temperature of melting (T_m). Generally speaking, the values of $H_r \leq 0.1$ results in difficult preparation of the glass, good glass formers usually have H_r higher than 0.1 [20]. The values of Hruby's criterion were in 0.25-0.45 range in Ge-In-S glasses. According to these results, mentioned in Table 1, we can conclude that studied samples have good glass forming ability.

The results of the criteria ΔT and H_r may be ambiguous, when there are several crystalline peaks in the DTA curve [13]. DTA curves of $(\text{GeS}_2)_{80}(\text{In}_2\text{S}_3)_{20}$ and $(\text{GeS}_2)_{70}(\text{In}_2\text{S}_3)_{30}$ compositions contain two crystallization peaks (Table 1). The criterion which is more sensitive and probably more suitable for the determination of the thermal stability of such glasses is Saad and Poulain's criterion. This relation takes into account the difference between T_{c1} and T_x and depends on the width of the crystallization peak [21]. The values of Saad-Poulain's criterion for Ge-In-S glasses were in 1.03-4.03 range.

According to the values of all thermal criteria, the result is, that prepared samples with composition $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ ($x=0,10,20,30$) exhibit good thermal stability.

The room-temperature reduced Raman spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ samples ($x=0,10,20,30$) are shown in Fig. 2. The individual Raman bands were determined by peak fitting using Voigt method. Individual Raman bands of all studied compositions (Fig. 2) were fitted and assigned using the results of deconvoluted spectra of pure GeS_2 glass and crystalline In_2S_3 sample.

In the Raman spectra of studied glasses, the most intensive is the band with maximum near 345 cm^{-1} . This Raman band can be assigned, in accordance with the literature [14,22,23], to the symmetrical stretching vibrations (ν_1) of GeS_4 tetrahedra (A_1 mode).

The Raman bands at 407 and 162 cm^{-1} are associated with asymmetrical stretching ν_3 (F_2 mode), and asymmetrical bending ν_4 (F_2 mode) vibrations of GeS_4 tetrahedra, respectively [14,22,23].

Two different ways of connecting of GeS_4 tetrahedra provide two additional Raman bands. The first one is located near 437 cm^{-1} and it originates from vibration of two tetrahedra connected through a bridging sulfur at the corner, i.e. corner-sharing units $\text{S}_3\text{Ge-S-GeS}_3$ [5,14]. The other one at 375 cm^{-1} is known as a companion band (A_{c1})

and probably corresponds to the vibration of two edge-shared GeS_4 tetrahedra.

In Raman spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ ($x=10,20,30$) glasses (Fig. 2); bands which can be assigned to the vibrations of structural units present in $\beta\text{-In}_2\text{S}_3$ modification, were found [15,24,25]. We suppose, that the structure of $\beta\text{-In}_2\text{S}_3$ modification belongs to the defect spinel lattice with ordered vacancies in the tetragonal symmetry unit cell. Indium atoms occupy octahedral and tetrahedral metal sites. The Raman bands connected with the vibrations of structural units of $\beta\text{-In}_2\text{S}_3$ modification were located near 311 and 267 cm^{-1} . Raman band with maximum near 311 cm^{-1} is associated with InS_4 tetrahedra, the band at 267 cm^{-1} can be attributed to InS_6 octahedra [15].

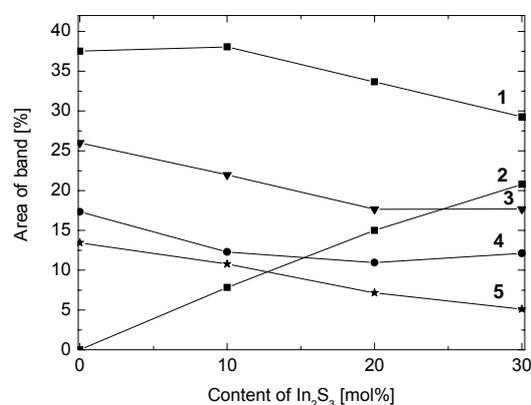


Fig. 4. Concentration dependencies of areas of predominant Raman bands assigned to vibrations of GeS_2 and In_2S_3 in $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses: 1. 345 cm^{-1} , 2. 311 cm^{-1} , 3. 377 cm^{-1} , 4. 407 cm^{-1} , 5. 437 cm^{-1} .

We assume, that the presence of In_2S_3 can change glassy network (connectivity) of studied Ge-In-S glasses. The effect of In_2S_3 addition were examined by the interpretation of integrated areas of observed Raman bands in studied $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses (Fig. 4). The integrated area of the dominant Raman band with maximum near 345 cm^{-1} decreases with increasing of In_2S_3 content, it means that relative proportion of GeS_4 tetrahedra is decreasing. On the other hand, the integrated area of Raman band with maximum at 311 cm^{-1} increases with raising content of In_2S_3 . We thus suppose increasing fraction of tetrahedral (InS_4) structural units. Intensity of two dominant Raman bands with maxima near 407 and 437 cm^{-1} slightly decrease with increasing of In_2S_3 content. We suppose that this behavior can be assigned to relative decrease of GeS_4 tetrahedra fraction and also to the decrease of 3D network connectivity due to decrease of number of corner-sharing GeS_4 tetrahedra ($\text{S}_3\text{Ge-S-GeS}_3$). Intensity of the last intensive Raman band at 375 cm^{-1} , corresponding to edge-sharing GeS_4 tetrahedra ($\text{Ge}_2\text{S}_{8/2}$), does not change with increasing of In_2S_3 content.

The structure of glasses of Ge-In-S system was also analyzed using spectroscopy in the far infrared region. The

IR reflectivity spectra are given in Fig. 3. The reflectivity spectra of $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ glasses contained an intensive band with maximum near 376 cm^{-1} . As mentioned above, this band probably corresponds to the vibration of two edge-shared tetrahedra GeS_4 , companion band (A_{c1}) [14,22] (Fig. 3).

The absorption spectra in the far IR region were calculated from reflectivity spectra by Kramers-Kronig analysis [14,22]. The absorption band with maximum near 376 cm^{-1} can be deconvoluted into 4 bands with maxima near $431, 376, 336$ and 164 cm^{-1} . The assignment of far IR absorption bands to individual vibrations is analogous with Raman spectra analysis. The absorption bands at 431 cm^{-1} , 336 cm^{-1} and 164 cm^{-1} can be assigned to the vibrations of corner-sharing units $\text{S}_3\text{Ge-S-GeS}_3$ (A_1 mode), symmetrical stretching vibrations $\nu_1(A_1$ mode) and asymmetrical bending $\nu_4(F_2$ mode) vibration of GeS_4 tetrahedra, respectively [14,22].

5. Conclusion

Chalcogenide glasses from Ge-In-S family were prepared and studied. According to thermal analysis, studied glasses with $(\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x$ ($x=0-30$) composition form stable and homogeneous glasses.

The structure of Ge-In-S system is formed by corner- and edge-shared GeS_4 tetrahedra as results from Raman spectra analysis. With incorporation of In_2S_3 , Raman bands corresponding to the vibrations of structural units present in $\beta\text{-In}_2\text{S}_3$ modification were observed; we assume the presence of tetrahedral (InS_4) and octahedral (InS_6) structural units in studied Ge-In-S glasses. The presence of In_2S_3 leads to the changes of network connectivity in studied glasses.

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