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Influence of temperature regimes of synthesis on the structure of glassy GeS_2

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The effect of synthesis temperature regimes on the structure and some physical properties of glassy germanium disulfide was examined using the methods of dilatometry and Raman scattering of light. It is concluded that the bond angle disorder increases and the formation of stronger Ge–S bonds in the tetrahedral structure depends on the increase in the synthesis temperature of glassy GeS2. Significant changes in the structural grid of glass also occur when the thermal history of the sample varies in the temperature interval of vitrification.

Keywords: germanium disulfide, linear expansion, Raman scattering, structural units.

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Introduction

The binary compound GeS_2 was studied by many authors, a detailed overview of whose works is given in [1]. Considering the presence of several structural modifications of crystalline germanium disulfide [1, 2], one should expect a certain short-range polymorphism of the glasses of the Ge-S system near the stoichiometric composition of GeS_2, depending on the synthesis modes, which can affect the physical properties of the samples. The situation is significantly complicated when taking into account the possible presence of an average order, since in covalently bonded amorphous solids there is a significant degree of short-range order in the form of well-defined polyhedra, which, in turn, are connected together and form the so-called average order. However, the question of the length of the middle order is currently controversial.

In glassy materials of the MX_2 type (where M=Ge, Si; X=O, S, Se), the short-range order of which is formed from MX_4 tetrahedra, the average order and dimensionality of the glass structure depend on the way such tetrahedra are combined. In the case of GeO_2 and SiO_2, the tetrahedra are connected to each other through a common vertex, forming a three-dimensional continuous random network (CRN) [3]. The authors of [4] proposed that in these glasses the length of the average order is greater than in the model of the CRN due to the formation of planar rings of 3 or 4 connected tetrahedra.

This publication presents the results of dilatometric measurements, which in many cases are effective for the qualitative analysis of structural changes [5], as well as Raman scattering (RS) spectra of GeS2 glasses obtained in the quenching mode from different synthesis temperatures.

I. Experiment

The synthesis of GeS_2 glasses was carried out from the corresponding elementary components in vacuumed quartz containers at different temperatures T_1, T_2, T_3, which are equal to 1170, 1270 and 1370 K, respectively, by quenching the melt in water. The weight of the initial components did not exceed 10 g.

Measurements of the temperature dependence of the relative elongation $\Delta l/l(T)$, where Δl is the absolute elongation, l is the initial length of the sample, were carried out on a quartz dilatometer with a capacitive sensor of the remote type [6]. The peculiarity of this automated device is a small measuring force on the sample (no more than 0.3 N), which made it possible to carry out measurements at temperatures above the glass transition temperature Tg and the possibility of simultaneously recording the dependence of temperature on time and elongation of the sample on temperature. Heating was carried out by a high-precision temperature regulator, which implements the proportional-integral-differential law of regulation. To ensure uniform heating at different speeds, a digital linear-alternating voltage generator with wide functionality regarding the sweep time of the output signal was used as a reference voltage source for the thermostat. This made it possible to change the rate of linear heating in the range of 0.1÷20 degrees/min, to anneal the samples at a given temperature, and to cool them at given rates.

Raman spectra were studied at room temperature using the He-Ne laser and diffraction spectrometer with a 90-degree laser excitation configuration. The spectral separation of the device was $\Delta\nu \approx 1 \div 2\ \text{см}^{-1}$.The relative error of measuring the intensity and half-width of the band did not exceed 3% [7].

II. Thermal expansion

Fig. 1 illustrates the peculiarities of thermal expansion of GeS_2 samples with different thermal histories. As a rule, the coefficient of linear thermal expansion (CLTE) $\alpha=\Delta l/(l\cdot\Delta T)$ of the samples decreases slightly after annealing, and at temperatures above Tg, it increases sharply. This regularity is observed for curves 1, 2 of Fig. 1. However, for GeS_2, a peculiarity was revealed, which consists in a significant difference in the CLTE of the samples in the state of an amorphous solid with different thermal history: the value of the CLTE varies from $8{,}0\cdot10^{-6}$ to $12.0\cdot10^{-6}$ K^{-1}, which indicates significant changes in the structural grid of the glass.

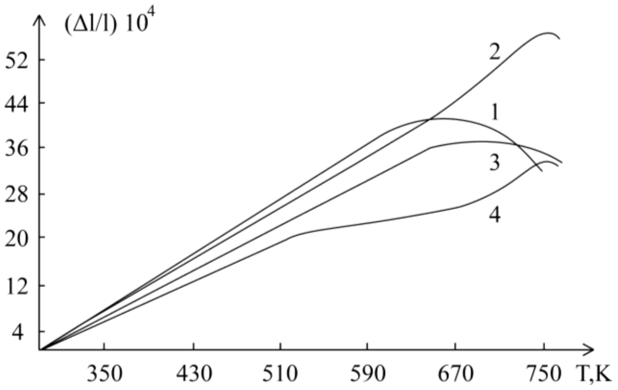

Fig. 1. Temperature dependences of the relative elongation of GeS_2 glass: 1 – the sample is tempered from the synthesis temperature of 1170 K; 2 – the sample is cooled from 780 K at a rate of 3.0 degrees/min; 3, 4 – the sample is tempered from 750 and 650 K, respectively.

It should be noted that the high crystallization ability of this composition does not allow for annealing. As is known, the glass transition temperature Tg can be measured only for annealed samples [8]. However, a certain stabilization of the structure is observed for sample 2 on Fig. 1, which is manifested in an increase in the CLTE in the glass transition interval and makes it possible to experimentally determine Tg≈685 K. This value correlates with Kausmann's two-thirds rule for crystalline GeS_2 α-modification with a melting temperature of 1070 K.

For tempered glasses, the activation temperature of the structural relaxation processes Ta is fixed on the temperature dependence of the relative elongation. For sample 4, the temperature Ta≈530 K≈0.8 T_g can be characterized as the limit of the glass transition interval, below which thermal expansion is caused mainly by anharmonicity of the vibrations of atoms or other elementary components of the structural lattice of glass. The temperature of the beginning of deformation of all samples during measurements on this dilatometer was ~770 K, regardless of the mode of preliminary heat treatment.

III. Raman spectra

In certain crystal forms of GeS_2 and $GeSe_2$, $GeS(Se)_4$ tetrahedra can be connected in two ways: through a common vertex or through a common edge. Two different crystalline forms of $GeS(Se)_2$, one with a layered structure and the other obtained at high pressure, which is three-dimensional, show a significant difference in the behavior of optical properties as a function of applied pressure: the absorption edge of a two-dimensional crystal shifts to the long-wavelength region of the spectrum, while a high-energy shift is observed for a three-dimensional crystal [1]. The fact that amorphous phases show a red shift of the eigenabsorption edge due to applied pressure confirms the existence of a two-dimensional structure of glassy GeS_2.

Experiments on Raman light scattering of vitreous $GeS(Se)_2$ confirm the existence of an average order in these compounds. The authors of [9] proposed that the elements of the two-dimensional structure of the crystal are preserved in glasses with the additional feature of chalcogen-chalcogen bonds that limit the layer. The cluster model [9] is not alone in considering the structure of glass from the point of view of the lack of continuity of the vitreous structure. One of these models is the model of tension of mixed clusters [10], according to which the volume structure is the result of the destruction of the continuum of the structure as a result of the existence of two or more different crystal polymorphs. Glass, therefore, is a mixture of two or more types of clusters, none of which reaches a critical size.

In glasses with tetrahedral short-range order, the circular structures of $Ge_6S_6(Se_6)$ were initially proposed as possible atomic clusters [11]. Lines at 353 cm^{-1} (GeS_2) observed near the A1 mode in addition to four normal vibrations (A1, E, F2) of free tetrahedra were attributed to their symmetric vibrations. However, in the works on the study of reverse quasicrystallization [12] and the study of the dependence of Raman spectra on pressure [13], preference was given to the cluster model [9], according to which the glass structure is formed by clusters with an average diameter and thickness of 10–20 Å, which consist of stacked one-on-one layers of germanium covered with chalcogens. The structure of the cluster is very similar to the structure of the high-temperature modification of crystalline GeS2. However, from the outside of the layer, each divalent chalcogen atom of the cluster is connected to only one germanium atom (Ge–S–). Therefore, it is possible to form S–S bonds. An additional line in the Raman spectra at 353 cm^{-1}, which is shifted relative to the

A1 mode by 11 cm^{-1}, is attributed to the valence vibrations of these bonds. The inconsistency of this value with the one observed in crystalline GeS_2 allowed the authors [9] to conclude that the satellite mode is not completely tetrahedral, however, like the tetrahedral mode, it covers mainly the displacement of chalcogen. This is confirmed by comparing the isotopic shift of the satellite mode from Ge S_2 to $GeSe_2$.

Figure 2 compares the Raman spectra of samples of glassy GeS_2 HH (curves 2) and VH (curves 1) configurations synthesized at temperatures T1 (Fig. 2e), T2 (Fig. 2d), T3 (Fig. 2b) and the Raman spectra of glasses Ge–S systems of non-stoichiometric compositions with an excess of sulfur ($Ge_{0.30}S_{0.70}$, Fig. 2e) and germanium ($Ge_{0.37}S_{0.63}$, Fig. 2a) relative to the composition of germanium disulfide. Curves 3 – the depolarization spectrum ρ, which shows the degree of polarization of the corresponding bands. In the high-frequency region of the spectrum, its lowest value is observed for GeS_2 synthesized at temperature T2 ($\rho \sim 0.1$), and when the synthesis temperature increases (decreases) relative to T2, ρ increases and for vitreous GeS_2 synthesized at temperature T3 $\rho \approx 0{,}3$. All spectra are normalized relative to the band of ~342 cm^{-1}, which was chosen as a reference, which made it possible to follow the change in the relative intensities of the bands that appeared.

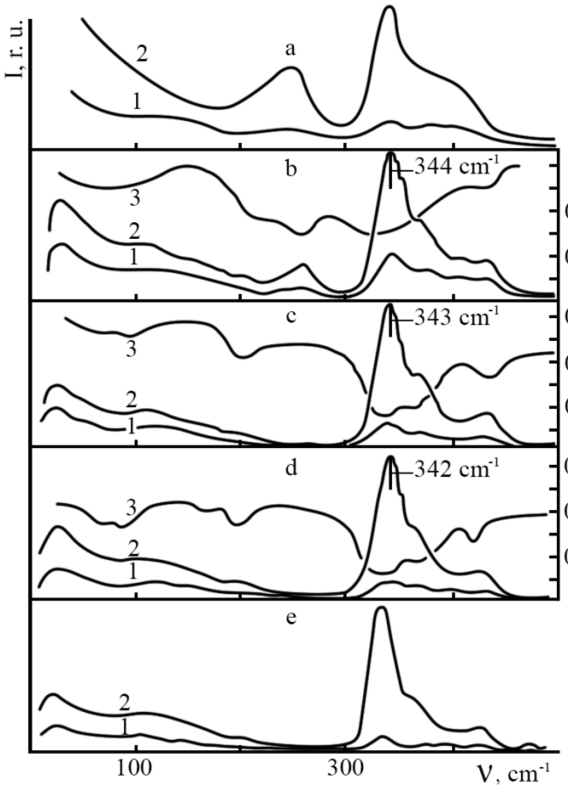

Fig. 2. Raman spectra of glasses of the Ge–S system VH (curves 1) and HH (curves 2) of composition configuration: a – $Ge_{0.37}S_{0.63}$; b, c, d, – vitreous GeS_2, synthesized at temperatures T3, T1, T2, respectively; e – $Ge_{0.30}S_{0.70}$. Curves 3 – spectrum of depolarization ρ.

Analysis of the high-frequency part of the Raman spectrum, which corresponds to intralayer vibrations of glassy GeS_2, shows that the bands have an asymmetric shape. This is possibly due to the presence of non-equivalent Ge–S bonds in the $GeS_{4/2}$ tetrahedral structural units, which form the short-range order of the glass. As the synthesis temperature (T3) increases, the band maximum shifts from 342 to 344 cm^{-1}. At the same time, the degree of polarization of the band in the region of 340 cm^{-1} decreases, and the half-width of the Raman spectrum band in the high-frequency region of the spectrum also increases from 19 to 22 cm^{-1}. This is direct evidence of thermally enhanced disorder in the atomic configuration of glassy GeS_2. The degree of increase in the half-width of the dominant Raman spectrum band, similar to that observed in the dominant band of infrared absorption in the Ge–Se system [14], corresponds to the increase in the disorder of the bond angle of the tetrahedral structure.

In addition, the increase in the intensity of the Raman spectrum band in the region of 245-260 cm^{-1} is a consequence of the presence of ethane-like $Ge(Se_{1/2})_6$ clusters in the glass matrix [9]. The rapid quenching of these clusters, which contain excess germanium, is compensated by the non-stoichiometry of large clusters enriched with sulfur, which is evidenced by the increase in the intensity of the spectrum band in the region of 353 cm^{-1}. A similar situation was observed when studying the Raman spectra of As_2S_3–Ge section glasses with small additions of Ge (Fig. 3). For these glasses, the Raman spectrum consists of a continuous continuum. Introduction to As_2S_3 1 at. % Ge leads to an increase in the relative intensity of the band with a maximum at 188 cm^{-1} and a shift of the band at 340 cm^{-1}, which is responsible for the valence vibrations of the pyramidal structural units of $AsS_{3/2}$, to the region of 345 cm^{-1}, that is, to the region of the valence vibrations of the tetrahedral structural $GeS_{4/2}$ units.

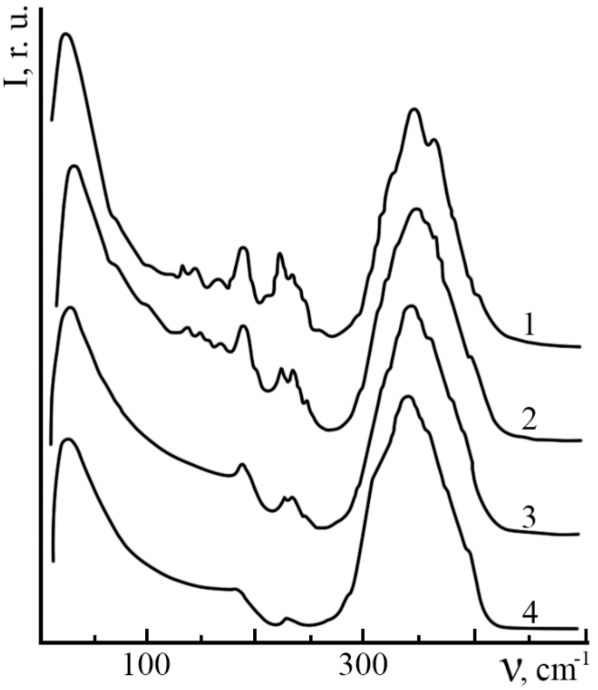

Fig. 3. Raman spectra of glasses of the $(As_2S_3)_{1-X}Ge_X$ system: 1 – X=0.03; 2 – X=0.02; 3 – X=0.01; 4 – X=0.00

In the region of 245 cm^{-1} there is also an emerging feature that is responsible for the oscillations of the Ge–S bonds of structural elements with triple coordination of germanium atoms to sulfur [15].

This means that the formation of Ge–S bonds leads to a decrease in the number of As–S bonds and the appearance of new structural elements containing As–As bonds (bands with maxima at 188, 225, 234 cm^{-1}), accumulation which, with increasing Ge concentration, leads to the formation of clusters of a molecular nature. Features at 188, 218 and 360 cm^{-1} against the background of the continuous continuum of the Raman spectra of $Ge_X(As_2S_3)_{1-X}$ glasses (x≥0.02) are very close to the positions of the bands of crystalline β–As_4S_4 in the Raman spectra of As_XS_{1-X} glasses at $x \geq 0.44$ [16]. The shift of the high-frequency band from 340 to 345 cm^{-1} suggests that the germanium present in the glass is primarily surrounded by sulfur atoms. This can be explained by the stronger bond of Ge–S compared to As–S. We assume that the structure of glassy As_2S_3 preserves three non-equivalent As–S interatomic distances, which are realized in AsS_3 pyramids. The weakest bound sulfur atoms in the AsS_3 asymmetric pyramid first come into contact with germanium.

As mentioned above, the high-frequency bands of Raman spectra of vitreous GeS2 have an asymmetric shape, which is due to the presence of non-equivalent Ge–S interatomic distances realized in GeS4 tetrahedra. Therefore, the shift of the maximum from 342 to 344 cm^{-1} and the decrease in the intensity of the band in the region of 342 cm^{-1} in comparison with the intensity of the band with a maximum at 344 cm^{-1} indicates an increase in the concentration of stronger (stronger) Ge–S bonds with increasing temperature synthesis of germanium disulfide.

Conclusions

Thus, the change in the relative intensity of the high-frequency bands, the decrease in the degree of polarization of the high-frequency band, and the increase in the half-width of the dominant Raman band correspond to the increase in bond angle disorder and the formation of stronger Ge–S bonds in the tetrahedral structure depending on the increase in the synthesis temperature of glassy GeS2. According to dilatometric measurements, significant changes in the structural mesh of the glass also occur depending on the thermal history of the samples in the vitrification interval.

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Вплив температурних режимів синтезу на структуру скловидного GeS_2

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Методами дилатометрії та комбінаційного розсіювання світла розглянуто вплив температурних режимів синтезу на структуру і деякі фізичні властивості скловидного дисульфіду германію. Зроблено висновок про збільшення невпорядкованості кута зв’язку і утворенню більш міцних зв’язків Ge–S у тетраедричній структурі в залежності від збільшення температури синтезу скловидного GeS_2. Суттєві зміни структурної сітки скла відбуваються також при варіації термічної передісторії зразків в інтервалі склування.

Ключові слова*:* дисульфід германію, лінійне розширення, комбінаційне розсіювання, структурні одиниці.