

On the structural relaxation of chalcogenide vitreous materials

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The processes of structural relaxation of vitreous materials with different thermal history were examined using the methods of dilatometry and Raman scattering. In the glass transition interval the coefficient of linear thermal expansion of the stabilized glass samples increases rapidly, while for tempered glasses it decreases and even takes negative values. According to dilatometric measurements, the characteristic temperatures of the glass transition intervals were determined, a qualitative estimation of structural changes was made depending on the temperature and time modes of synthesis and annealing of chalcogenide glasses.

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1. Introduction

The study of physical and chemical mechanisms of relaxation processes of stabilization of the structure of vitreous materials is the subject of many multi-year and multi-faceted investigations. This topic does not lose its relevance, which is due, in particular, by the necessity of predicting changes in the properties of glasses depending on the temperature and time modes of their synthesis and cooling [1-9]. Among the methods of analyzing the structure of a substance are X-ray structural analysis, Raman spectroscopy (RS), vibrational infrared spectroscopy, differential thermal analysis (DTA), differential scanning calorimetry (DSC), dilatometry, and others. Correlation of the results obtained by different methods for inorganic glasses of different chemical composition of silicate, oxide, chalcogenide, metallic, etc., allows us to identify a number of general patterns in relation to amorphous solids. However, the complexity of solving many issues and the lack of a unified approach to the interpretation of the obtained data, determines the need for further research in this area.

Vitreous materials are metastable supercooled melts, in which changes in structure and, therefore, in physical properties of a relaxational nature occur over time. Metastability of glass in many cases is a rather conditional concept, since the duration of the transition to a more balanced state depends, first of all, from temperature and chemical composition and varies within extremely wide limits - from geological time scales ($t \rightarrow \infty$, for example, for volcanic glass), to instant changes ($t \rightarrow 0$) for disordered materials in the glass transition interval or during temperature activation of crystallization processes.

The main goal of this work was to study the features of structural relaxation of vitreous materials in the temperature range of glass transition. The publication considers chalcogenide glasses, which are characterized by different ability to glass formation, are low-melting and

therefore represent a convenient object for studying structural changes around the glass transition temperature T_g . In addition, these materials are promising for use in optoelectronics and other fields of science and technology [2], therefore, studying the stability of their physical properties is of practical importance. Features of the structure - the presence of certain structural units - were studied using RS, and structural relaxation - using the temperature dependence of the relative elongation of the samples.

2. Methods

Thermal expansion studies were carried out for As(Sb)-S glasses of binary systems, as well as for Ge-As-S-I(Br) samples of quaternary systems. As influencing factors, affecting the physical properties of samples of the same chemical composition, the change in the maximum synthesis temperature, melt cooling rates, and annealing temperature regimes were used.

The synthesis of glasses was carried out from the corresponding elementary components in vacuumed quartz containers. The maximum temperature at which synthesis can still be carried out in quartz containers was 1050 °C. The weights of the initial components were within 10 ÷ 20 g. Samples for dilatometric measurements were cut from synthesized ingots, polished in the form of a parallelepiped with a height of 10 ÷ 12 mm and an area of opposite faces of 2x2 mm².

Measurements of the temperature dependence of the relative elongation $\Delta l/l(T)$ were carried out on a quartz dilatometer with a portable capacitive sensor [10]. A feature of this automated device is a small measuring force on the sample (no more than 0.3 N), which allowed measurements at temperatures above T_g , as well as 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 voltage generator of linear-alternating voltage was used as a reference voltage source for the thermostat. This regulator has wide functionality in terms of the sweep time of the output signal. This made possible to change the speed of linear heating in the range of $0.1 \div 20$ degrees/min, to anneal the samples at a given temperature, and to cool them at given speeds.

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 $\Delta\nu \approx 1 \div 2 \text{ cm}^{-1}$. The relative error of measuring the intensity and half-width of the band did not exceed 3% [6].

3. Thermal expansion

Dilatometric studies have shown that the nature of the dependences $\Delta l/l(T)$, where Δl is the absolute elongation, l is the initial length of the sample, reveals a number of general regularities that depend on the temperature history and crystallization ability of the glasses. The criterion the last one can be the preservation of the glassy state after prolonged annealing and, conversely, crystallization at low heating rates, in particular, in the process of differential thermal analysis. Illustrative material in this work is given for glass samples tempered from the synthesis temperature, cooled at rates of $1 \div 10$ degrees/min, and annealed at temperatures close to T_g .

Fig. 1 shows the temperature dependence of the relative elongation of the glassy As_2S_3 . The elongation of annealed glasses is practically linear in the temperature range from 25°C to the glass transition temperature $T_g \approx 180^\circ\text{C}$. At temperatures above T_g , there is a jump-like increase in the linear thermal expansion coefficient (LTEC) $\alpha = \Delta l/(l \cdot \Delta T)$, and subsequently, plastic deformation of the samples under the action of the measured force of this dilatometric cell. According to the obtained results, the LTEC of As_2S_3 samples with different thermal histories in the temperature range where glass can be considered as an amorphous solid is $(21,5 \pm 0,5) \cdot 10^{-6} \text{ K}^{-1}$. During annealing, as a rule, there is a tendency to decrease α , but in this case it is insignificant and is within the measurement error. For tempered or insufficiently annealed As_2S_3 samples, a sharp decrease in relative elongation occurs already at temperatures $\sim 0,85 \cdot T_g$ (Fig. 1, curve 1).

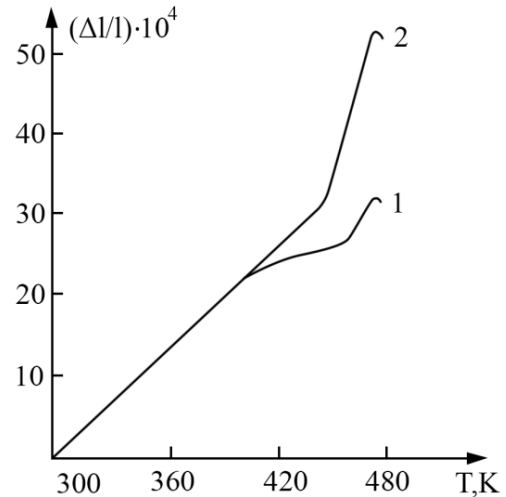


Fig. 1. Temperature dependences of the relative elongation of vitreous As_2S_3 at the linear heating rate $q = 1.0 \text{ K/min}$: 1 – the glass sample is tempered from 470 K ; 2 – the sample is cooled from 470 K at a rate of $q = 0.5 \text{ K/min}$

The interpretation of temperature dependences $\Delta l/l$ is possible within the framework of the relaxation model of vitrification, which operates, in particular, with the concept of structural temperature T_s , which is the temperature of the metastable melt, the structure of which is fixed in this glass [1]. According to this approach, the reduction in elongation of tempered glasses occurs as a result of relaxation processes of structure stabilization, provided that the relaxation time τ is proportional to the observation time. In the process of cooling of the melt, a continuous spectrum of metastable structures is formed, the stabilization of which is determined by the corresponding continuous spectrum of relaxation times [1]. Relaxation is a thermally activated process, and τ is proportional to the glass viscosity η [2]. Since structural changes in the temperature dependence of the relative elongation for As_2S_3 are identified at $\sim 0.85 \cdot T_g$ (tempering) and T_g (annealing), it should be assumed that at these temperatures the values of both the activation energy of relaxation processes and the viscosity of samples with different thermal prehistory coincide.

Atypical results were obtained for vitreous As_2S_5 (Fig. 2), for which the LTEC of the tempered sample is lower than that of the stabilized one. Perhaps this is due to the fact that when As_2S_5 is tempered, it is characterized by a statistical distribution of arsenic in the glass matrix, and during slow cooling, there is an association of structural nodes that contain arsenic. At the same time, the polymer chains of sulfur are lengthened, which leads to an increase in LTEC.

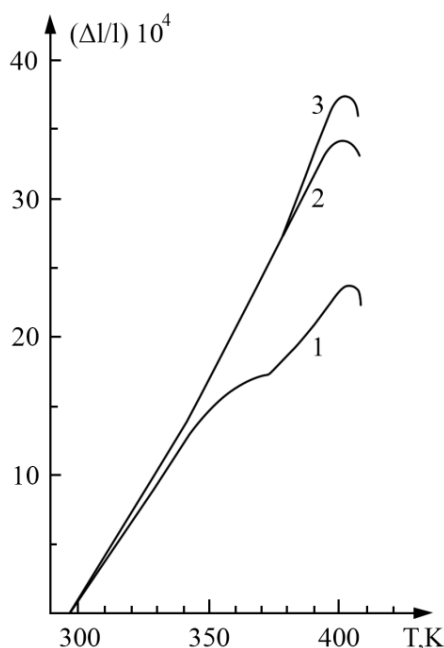


Fig. 2. Relative elongation of As_2S_5 : 1 ÷ 3 - the sample is cooled from 410 K with rates $q=10.0$; 3.0 and 0.5 K/min, respectively

The glass transition temperature should be considered as the minimum structural temperature $T_{s \text{ min}}$, which can be determined experimentally for stabilized (i.e., annealed) glasses. Temperature $T_a = k \cdot T_g$, where the coefficient $k < 1$, at which the viscosity η of the tempered glass sample decreases to the value when the relaxation processes of structural changes are activated to the same extent as it occurs for annealed samples when heated to the glass transition temperature T_g , is by the lower limit of the glass transition interval, which can be identified, in particular, on the dependences $\Delta l/l(T)$. Note that in many publications, the T_g parameter is taken as the lower limit of the glass transition interval [4], which is incorrect for glasses synthesized in the high melt cooling rates mode, since for tempered glasses the temperature of activation of structural stabilization processes is $T_a < T_g$ and depends on the achieved degree of metastability.

For vitreous samples, which can be obtained only in the tempering mode, the processes of structure stabilization in the glass transition region have a tendency to ordering, their structural temperature T_s decreases. As a result of structural relaxation, when such samples are heated, their specific volume may decrease. On the dependences $\Delta l/l(T)$ this is manifested in the form of a decrease in the relative elongation of the samples as the temperature increases. An example of similar effects for Sb_2S_3 is shown in Fig. 3.

For glasses of different compositions, a study of the influence of the maximum synthesis temperature and the cooling rate of the melt on thermal expansion was carried out. Thus, the glasses of the As-S system were cooled from temperatures in the range from 870 K to 1320 K in various modes. For samples of identical chemical composition, different LTEC values were obtained.

However, the subsequent heat treatment in the glass transition interval determined the nature of the $\Delta l/l(T)$ curves.

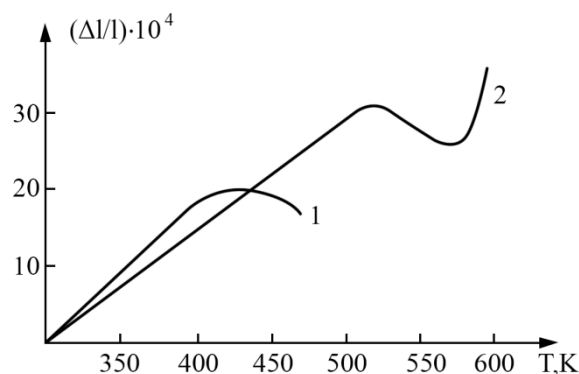


Fig. 3. Temperature dependence of the relative elongation of vitreous Sb_2S_3 ($q=1.0$ degrees/min): 1 - first measurement, 2 - repeated measurement of an identical sample

It is of interest to compare the results of dilatometric measurements of the characteristic temperatures of the glass transition interval with DTA measurements. For the annealed samples, the beginning of the endothermic effect on the DTA curves, caused by softening, correlates with T_g , determined according to the dependences $\Delta l/l(T)$ [9]. Stabilization of the structure of tempered As_2S_3 samples should be manifested by an exothermic effect at $\sim 0.85 \cdot T_g$. However, there are no corresponding deviations of the DTA curve from the baseline. Perhaps, the observation of such a phenomenon in this type of thermal analysis requires correlation of the rate heating of samples with the corresponding times of structural relaxation.

4. Raman spectra

Identification of possible structural changes depending on the conditions of synthesis was carried out by Raman spectroscopy methods for glassy As_2S_5 , As_2S_3 , As_2S_3 . As illustrative material, the Raman spectra of As_2S_5 samples obtained under the following conditions are considered below: synthesis temperature $T_1=820$ K; $T_2=1070$ K; $T_3=1320$ K; cooling rates $q_1 \sim 0.5$ deg/min, $q_2 \sim 10$ deg/min and q_3 - quenching of the melt in water.

As can be seen from the obtained results (Fig. 4), in the Raman spectra, in addition to the main peak around $\sim 340 \text{ cm}^{-1}$, a low-frequency maximum in the spectral region of $\sim 50 \text{ cm}^{-1}$ and relatively intense bands at ~ 150 , ~ 218 , ~ 233 ; ~ 474 and $\sim 520 \text{ cm}^{-1}$ are observed. All the curves of fig. 4 are normalized relative to the band of $\sim 340 \text{ cm}^{-1}$, which was chosen as a reference, what allows us to follow the changes in the relative intensity of the specified lines. The modes at 150 and 520 cm^{-1} are depolarized, while ~ 218 and $\sim 474 \text{ cm}^{-1}$ are polarized [6].

From a comparison with the Raman spectra of As_2S_3 glass and crystalline sulfur, it follows that the broad intense band (340 cm^{-1}) in glassy As_2S_5 is due to valence vibrations of arsenic and sulfur in the pyramidal structural

units of AsS_3 , and the high-frequency band (474 cm^{-1}) is caused by atomic vibrations sulfur, with which these pyramids are connected to each other. For comparison, Fig. 4 also shows the Raman spectra of $x = 0.300$ and $x = 0.260$ glasses obtained under T_2, q_2 synthesis conditions.

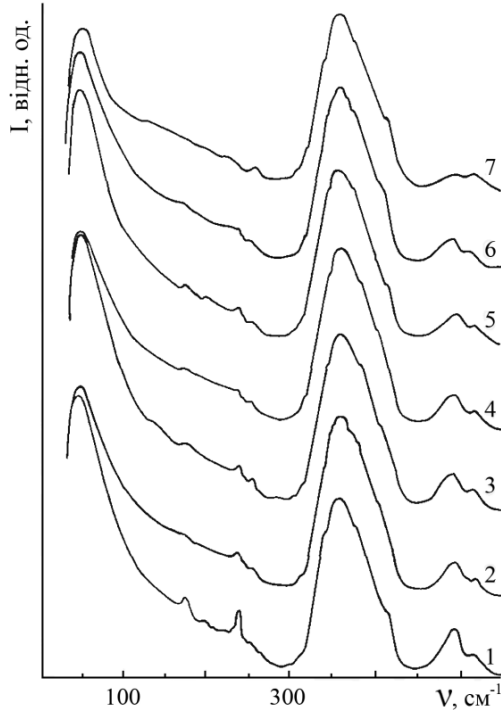


Fig. 4. Raman spectra of $\text{As}_x\text{S}_{1-x}$ glasses obtained under different synthesis conditions: 1– $x=0.260$ (T_2, q_2); 2– $x=0.286$ (T_1, q_1); 3– $x=0.286$ (T_1, q_2); 4– $x=0.286$ (T_2, q_2); 5– $x=0.286$ (T_3, q_2); 6– $x=0.286$ (T_3, q_3); 7– $x=0.300$ (T_2, q_2)

The Raman spectra in the low-frequency region of $50\text{--}100 \text{ cm}^{-1}$ is considered to be a manifestation of light scattering by acoustic phonons (bosonic peak ν_B) [11]. According to literature data [12], the presence of E_2 mode (150 cm^{-1}) and A_1 mode (220 cm^{-1}) in Raman spectra, and E_1 mode (190 cm^{-1}) and B_2 mode (240 cm^{-1}) in infrared (IR) absorption spectrum of $\text{As}_x\text{S}_{1-x}$ glasses shows the presence of S_8 sulfur rings in these materials. The band with a maximum at 233 cm^{-1} is responsible for the oscillations of the As-As bonds, and the band with a maximum at $\sim 520 \text{ cm}^{-1}$ is responsible for the oscillations of the chain sulfur S_8 .

According to Fig. 4, the position of ν_B depends on the conditions of glass production, which reflects some medium-order structural modifications, in particular, a decrease in the zone of structural correlation in As_2S_5 with an increase in the synthesis temperature [11]. However, changing the synthesis conditions practically does not affect the relative intensity of the bands associated with the oscillations of As-As and S-S homopolar bonds. The absence of a change in the nature of covalent homopolar bonds is consistent with the findings of [13], according to which the transition to the glassy state is caused by the thermal destruction of intercluster Van der Waals bonds of amorphous materials.

In the state of an amorphous solid, thermal expansion is due to the anharmonicity of the vibrations of atoms or other elementary components of the structural grid of glass. The analysis of the Raman spectra of As_2S_5 and other compositions of the As-S system indicates minor changes in the structure while preserving the main structural units for both annealed and quenching samples. However, temperature activation causes the emergence of additional degrees of freedom for these units, the minimization of the entropy of the system through the relaxation processes of structure stabilization, and the significant dependence of the results of dilatometric measurements in the vicinity of T_g on the thermal history of the samples.

5. Conclusions

Dilatometric measurements at low rates of linear heating make it possible to determine the characteristic temperatures of the glass transition interval, to draw conclusions about the thermal history and physical aging processes of the samples, and to adjust the temperature-time regimes of annealing of vitreous materials. The rate of linear heating of samples in this work did not exceed 3 degrees/min .

The glass transition temperature T_g can be defined as the minimum structural temperature of stabilized (annealed) glass. Experimentally, T_g can be measured only for annealed samples. For such glasses, T_g , determined by various methods (dilatometry, DTA, DSC), must match.

For tempered glasses, the lower temperature limit of the glass transition interval T_a decreases in proportion to the achieved degree of metastability. In particular, for glasses of the As-S system obtained in the mode of cooling with a maximum speed, the activation of structural relaxation processes is identified by the dependences $\Delta l/l(T)$ already at temperatures $T_a \approx 0,65 \div 0,85 \cdot T_g$.

The intensity of restructuring of the structural network of tempered or crystallization-prone samples leads to the appearance of temperature areas where the relative elongation of the glass decreases during the heating process, drops to zero and even takes negative values.

The Raman spectra and dependences of $\Delta l/l(T)$ for As_2S_5 confirm the thesis that the maximum synthesis temperature has an insignificant effect on the change in the physical properties of amorphous chalcogenides compared to heat treatment in the glass transition interval.

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