

MECHANICAL RELAXATION IN CHALCOGENIDE GLASSES OF THE Ge—As—S SYSTEM¹

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The temperature- (in the range 100 K– T_g) and frequency-related (in the range 5–50 mHz) dependences of the internal friction and the shear modulus in $\text{Ge}_x\text{As}_{40-x}\text{Se}_{60}$ glasses have been studied. The maxima of internal friction of both the relaxation and non-relaxation types have been found in the low-temperature range. A relaxation maximum has been revealed in the vitrification region, and its parameters have been determined. Possible mechanisms of these processes have been discussed.

This leads to the appearance of some features in the concentration dependences of the physical properties of glasses, and these dependences become nonmonotonic.

This work aimed at studying the relaxation phenomena in glasses of the Ge_2S_3 – As_2S_3 system, making use of the method of ultra-low-frequency mechanical spectroscopy.

1. Introduction

Chalcogenide glasses belonging to the cross-sections of the Ge—As—S ternary system with the base composition of As_2S_3 attract the keenest practical interest among scientists. Upon the formation of these glasses, the coordination numbers of Ge, As, and S amount to 4, 3, and 2, respectively. An increase of the germanium content was shown in work [1] to result in a structural phase transition from the two-dimensional structure (similar to that of As_2S_3) to a three-dimensional one (similar to that of GeS_2), when passing the coordination number of 2.67. Owing to a discrepancy between the spatial patterns of tetrahedral ($\text{GeS}_{4/2}$) and trigonal ($\text{AsS}_{3/2}$) structural units, Ge—As—S glasses are characterized by a complex structure and can be chemically non-uniform. While introducing small amounts of Ge into As_2S_3 , germanium atoms completely interact with sulfur to reduce the concentration of the latter in As_2S_3 structural sites. As a result, in addition to As_2S_3 structural units, there emerge $\text{GeS}_{4/2}$ and $\text{AsS}_{2/2}$ ones. A variation of the component percentage in the Ge—As—S system can result in the formation of the following binary compounds: As_2S_3 , As_2S_5 , GeS , GeS_2 , AsGe , and As_2Ge [2]. In the course of vitrification in the system concerned, sulfur interacts, first of all, with germanium and afterwards with arsenic. So that, while cooling the melt, the structural units $\text{GeS}_{4/2}$ and $\text{GeS}_{2/2}$ would predominantly appear, and only afterwards the structural units $\text{AsS}_{3/2}$ and $\text{As}_2\text{S}_{4/2}$, where the interaction energy is lower, would emerge.

2. Experimental Method

The internal friction coefficient Q^{-1} and the shear modulus G of $\text{Ge}_x\text{As}_{40-x}\text{Se}_{60}$ glasses were measured in a wide temperature range, using a torsion pendulum of the inverted type operating at frequencies of 10^{-3} – 10^{-1} Hz under the condition of quasi-static loading [3]. To evaluate the numerical values of Q^{-1} and G , the dependences $\varepsilon(M_{\text{tor}})$ of the relative deformation of a specimen ε on the harmonically variable torsion moment M_{tor} were recorded. For glasses, these curves had an elliptic shape. From the obtained elliptic loops of mechanical hysteresis, the values of Q^{-1} and G were calculated by the formulae

$$Q^{-1} = \text{tg } \delta = \frac{\sin \delta}{\sqrt{1 - \sin^2 \delta}}, \quad \sin \delta = \frac{\Delta \varepsilon}{\varepsilon_m}; \quad G = A \frac{M_{\text{tor.m}}}{\varepsilon_m},$$

where $\Delta \varepsilon$ is the residual deformation at the time moment, when $M_{\text{tor}} = 0$; ε_m the maximal value of deformation; $M_{\text{tor.m}}$ the maximal value of the torsion moment; and A the coefficient dependent on the geometrical parameters of the researched specimen. The temperature dependences $Q^{-1}(T)$ and $G(T)$ were measured, while heating the specimen at a constant rate of $v_h = 37.7$ K/h.

The glasses of the Ge—As—S system were prepared from elementary substances: HPLC grade arsenic, HPLC grade sulfur, and B5 grade germanium. The synthesis was carried on in quartz ampoules. First, the ampoules were heated up to 550 °C and held for 6 h. Then, the temperature was slowly raised up to 800 °C. After the

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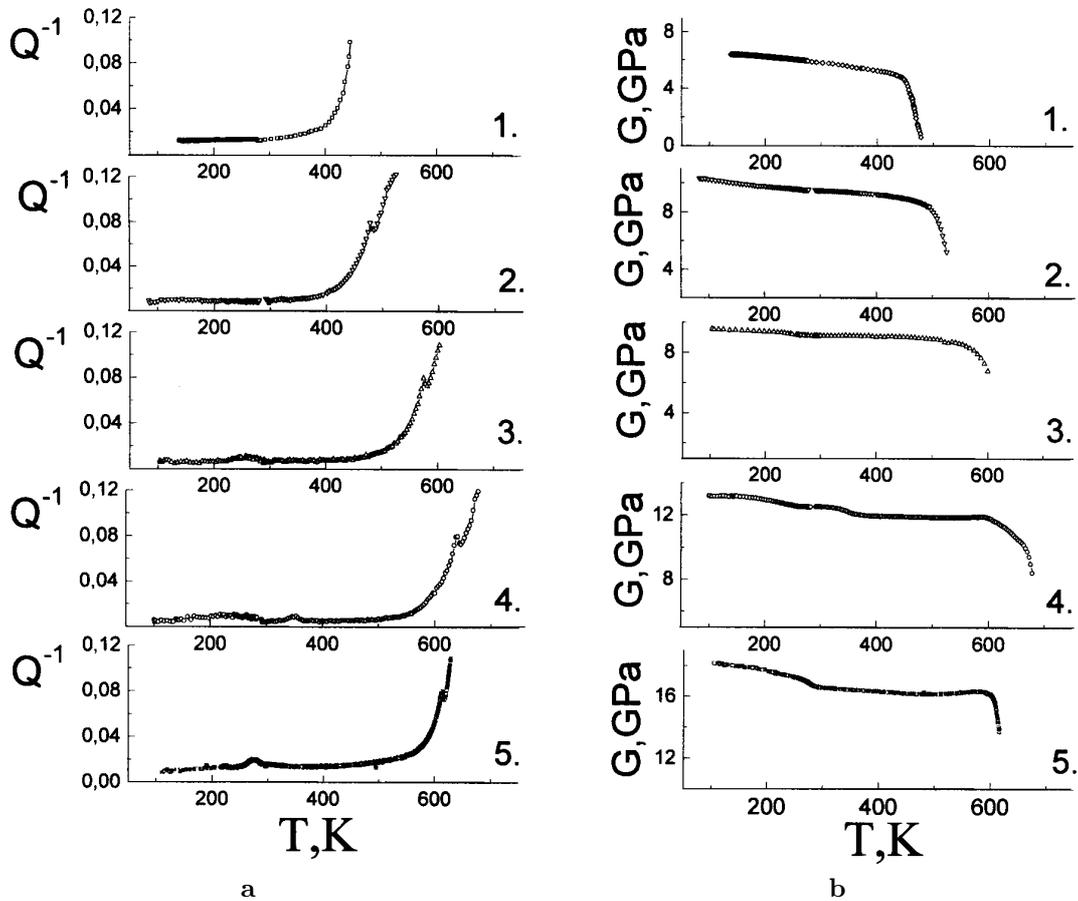


Fig. 1. Temperature dependences of the internal friction coefficient (a) and the shear modulus (b) in $Ge_xAs_{40-x}S_{60}$ glasses at a deformation frequency of 10 mHz and the amplitude of deformation oscillations of 2×10^5 : $As_{40}S_{60}$ (1), $Ge_{13}As_{27}S_{60}$ (2), $Ge_{24}As_{16}S_{60}$ (3), $Ge_{32}As_8S_{60}$ (4), and $Ge_{40}S_{60}$ (5)

prolonged homogenization, the glasses were tempered in air. The vitreous state of the alloys obtained was verified by the X-ray diffraction method. The specimens for studies were cut off from massive vitreous ingots in the form of $2 \times 2 \times 20$ -mm³ rectangular parallelepipeds. In order to determine the temperature intervals of probable relaxation processes, the dependences $Q^{-1}(T)$ and $G(T)$ were measured at one frequency. In order to establish the regularities and parameters of these processes, the measurements of the dependences indicated were carried out simultaneously at several frequencies during the same cycle of heating.

3. Experimental Results and Their Discussion

Fig. 1 exposes the dependences $Q^{-1}(T)$ and $G(T)$ for $As_{40}S_{60}$, $Ge_{13}As_{27}S_{60}$, $Ge_{24}As_{16}S_{60}$, $Ge_{32}As_8S_{60}$, and $Ge_{40}S_{60}$ glasses at a frequency of 10 mHz. From the

figure, one can see that, in certain temperature regions, the curves $Q^{-1}(T)$ manifest peculiarities either in the form of the maxima of internal friction, which possess various widths and amplitudes, or as the intervals in the high-temperature range, where $Q^{-1}(T)$ grows intensively. Those anomalies are accompanied by the respective alterations in the temperature dependences of the shear modulus.

In the low-temperature range, the dependences $Q^{-1}(T)$ for Ge_2S_3 , $Ge_{32}As_8S_{60}$, and $Ge_{24}As_{16}S_{60}$ glasses reveal the maxima of internal friction of various nature. In As_2S_3 and $Ge_{13}As_{27}S_{60}$ glasses, such maxima are absent.

In $Ge_{32}As_8S_{60}$ glass, the maximal amplitude of $Q^{-1}(T)$ is equal to 8×10^{-3} in the temperature range 150–270 K. In this case, the shear modulus is decreased by 0.5 GPa on the average. The shape of the $G(T)$ curve in the range 150–270 K is similar to that of the curves

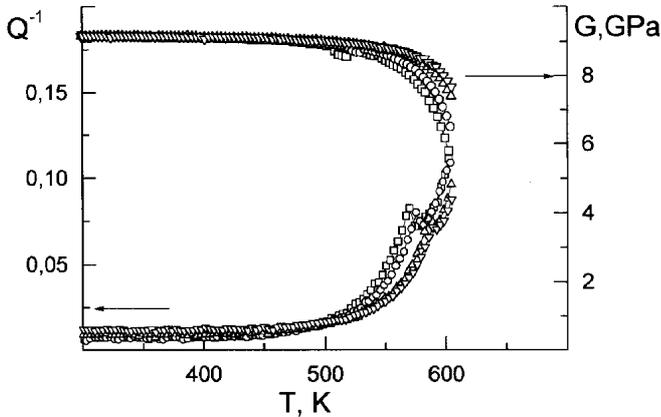


Fig. 2. Temperature dependences $Q^{-1}(T)$ and $G(T)$ for $Ge_{24}As_{16}S_{60}$ glass at various deformation frequencies: 5 (squares), 10 (circles), 30 (deltas), and 50 mHz (nablas)

which describe the changes of elastic moduli in the course of relaxation processes [4]. If the deformation frequency f decreases, the temperature of the maximum T_m is shifted towards the lower-temperature region. In particular, for $Ge_{32}As_8S_{60}$ glass, the temperature of the maximum of internal friction falls down from 237 to 216 K if the frequency is lowered from 50 to 5 mHz. Taking such a frequency shift of T_m into account, one may assert that it is a relaxation-induced maximum.

To analyze the features of this low-temperature relaxation process, the dependence of the temperature of the internal friction maximum on the deformation frequency was plotted in the coordinates $\ln f$ vs T_m^{-1} , where it can be extrapolated well by a straight line. A slope of the line is proportional to the activation energy of the relaxation process concerned. Taking into account the condition for the maximum to be observed during the relaxation process,

$$2\pi\nu\tau(T_m) = 1,$$

where $\tau(T_m)$ is the relaxation time at the temperature corresponding to the maximum of internal friction at the deformation frequency f , and the dependence

$$\tau = \tau_0 \exp\left(\frac{U}{kT}\right)$$

of the relaxation time on the temperature at thermal activation of the relaxation process, the energy of activation U and the frequency factor τ_0 were determined. For the low-temperature relaxation process under consideration, $U = 50$ kJ/mol and $\lg \tau_0 = 10.5$. These parameters depend rather weakly on the chemical composition of the researched glasses.

Another maximum in the dependence $Q^{-1}(T)$ located within a small temperature interval is observed for $Ge_{32}As_8S_{60}$ glass in the temperature range 330 – 360 K. The variation of the deformation frequency does not result in an appreciable shift of the temperature of this maximum; therefore, it is not relaxation-induced. A maximum, which is similar by the shape and character of the frequency dependence, is observed in Ge_2S_3 glass as well; however, its temperature interval is shifted to some extent towards lower temperatures and amounts to 280–300 K.

The low-temperature maxima of internal friction of the relaxation type were observed by us earlier in glasses of the As–S(Se) system with the increased content of sulfur [5], and the relaxation process was explained by the availability of structural defects of a special kind – chalcogene atoms with nonsaturated bonds.

Fig. 1 demonstrates that low-temperature relaxation maxima are observed in the range 200–300 K for compositions $Ge_{24}As_{16}S_{60}$ and $Ge_{32}As_8S_{60}$. One may admit that these relaxation processes are also related to the presence of defect atoms. Taking into account the priority of the formation of Ge–S bonds rather than As–S ones in $Ge_xAs_{40-x}S_{60}$ glasses and supposing the prevailing formation of the GeS_2 compound rather than the GeS one, it is possible to assert that, in this case, defects will be generated by As and Ge atoms. In so doing, the low-temperature maximum of internal friction in $Ge_{40}S_{60}$ glass at 330–360 K will be induced by extra germanium atoms. In compositions $Ge_{24}As_{16}S_{60}$ and $Ge_{32}As_8S_{60}$, the relaxation process at 170–270 K can be stimulated by arsenic defect atoms, while the non-relaxation maximum of internal friction at 280–300 K is related to germanium atoms, as it occurs in $Ge_{40}S_{60}$.

Fig. 1 demonstrates that the most intensive enhancement of mechanical losses occurs in the high-temperature range. In the range of softening, together with the increase of background mechanical losses, a strong reduction of G and an increase of Q^{-1} take place, as the temperature grows. If the deformation frequency becomes higher, all those effects are shifted towards higher temperatures, which evidences for their relaxation character (Fig. 2).

It is known that such behaviors of internal friction and the shear modulus are typical of the α -process of mechanical relaxation of polymers [6] and glassy materials [7], chalcogenide glasses included [8].

One can see from Fig. 1 that the interval, where internal friction in $Ge_{32}As_8S_{60}$ glass increases and its shear modulus decreases intensively, is located approximately by 30 degrees higher than the similar

interval for $\text{Ge}_{40}\text{S}_{60}$ glass. Moreover, the dependences $Q^{-1}(T)$ for $\text{Ge}_{13}\text{As}_{27}\text{S}_{60}$, $\text{Ge}_{24}\text{As}_{16}\text{S}_{60}$, $\text{Ge}_{32}\text{As}_8\text{S}_{60}$, and $\text{Ge}_{40}\text{S}_{60}$ glasses exhibit a peak of internal friction in the range 600–675 K which is superimposed onto monotonically growing mechanical losses in the range of softening. If the deformation frequency increases, the temperature of this maximum grows. Such a frequency shift of the maximum evidences for its relaxation character. In Fig. 3, the temperatures plotted in the scale $\ln f$ vs T_m^{-1} , at which the maxima are observed, are indicated for various deformation frequencies. From the figure, one can see that the dependences concerned are well extrapolated by straight lines. The frequency shifts of the maxima of internal friction, i.e. the slopes of the straight lines in Fig. 3, allowed us to determine the activation energy U and the frequency factor $\lg \tau_0$ of this relaxation processes: $U = 350$ kJ/mol and $\lg \tau_0 = 28$ for $\text{Ge}_{40}\text{S}_{60}$, $U = 272$ kJ/mol and $\lg \tau_0 = 20$ for $\text{Ge}_{32}\text{As}_8\text{S}_{60}$, $U = 320$ kJ/mol and $\lg \tau_0 = 27$ for $\text{Ge}_{24}\text{As}_{16}\text{S}_{60}$, and $U = 170$ kJ/mol and $\lg \tau_0 = 16$ for $\text{Ge}_{13}\text{As}_{27}\text{S}_{60}$.

An additional maximum of internal friction in the range of the α -process of relaxation indicates a complicated character of the softening of the compounds considered. The features in the behavior of internal friction, which were revealed in the high-temperature range, can be explained, if one considers the structure of those glasses as a set of two structural subsystems formed by GeS_2 (curve 1) and GeS (curve 2) structural units.

Taking into account the features of vitrification in the Ge–As–S system [2], one may admit that the basic structural units, which govern the softening of $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses, are complexes $\text{GeS}_{2/2}$ and $\text{GeS}_{4/2}$. If so, since the temperature range of the GeS softening is located lower than that for GeS_2 , one may admit that the maximum of $Q^{-1}(T)$ against its background can be related to the thermal activation of the mobility of the structure generated by $\text{GeS}_{2/2}$ complexes. The softening of the structural subsystem generated by $\text{GeS}_{4/2}$ complexes occurs at higher temperatures and determines the main maximum of internal friction under the α -relaxation of the chalcogenide glasses under consideration.

4. Conclusions

The temperature dependences of internal friction and the shear modulus of $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses have been studied at super-low frequencies. In the range 160–290 K, a relaxation process with an activation energy of 50 kJ/mol has been revealed. It has been shown that

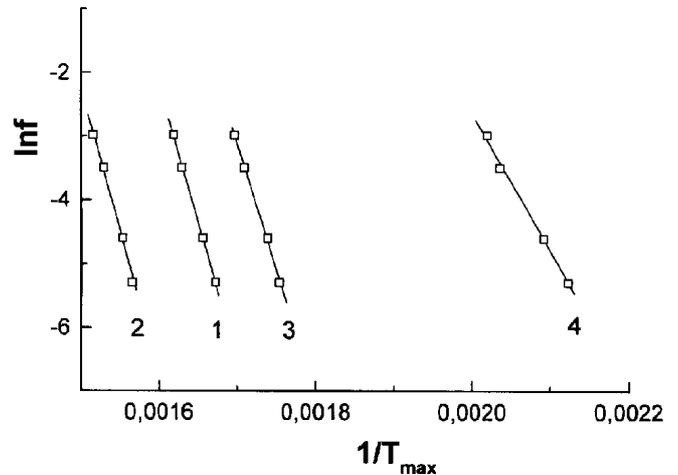


Fig. 3. Dependences of the temperature of the high-temperature maximum of the internal friction coefficient on the deformation frequency for various $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses: $\text{Ge}_{40}\text{S}_{60}$ (1), $\text{Ge}_{32}\text{As}_8\text{S}_{60}$ (2), $\text{Ge}_{24}\text{As}_{16}\text{S}_{60}$ (3), and $\text{Ge}_{13}\text{As}_{27}\text{S}_{60}$ (4)

its occurrence can be related to the presence of defect arsenic atoms in non-stoichiometric compounds $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$. The frequency-independent maximum of internal friction in the range of low temperatures can be related to the presence of defect germanium atoms in the glasses.

The internal friction has been analyzed in the range of high temperatures. It has been shown that the intensive increase of mechanical losses and the reduction of the shear modulus in this temperature range are caused by the softening of the glasses concerned. A complicated character of the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glass softening has been revealed. It manifests itself in the appearance of an additional peak of the internal friction coefficient on the growing branch of $Q^{-1}(T)$. This effect can be caused by the softening of the structural subsystem formed by $\text{GeS}_{2/2}$ complexes.

1. Tanaka K. // Phys. Rev. B. — 1989. — **39**. — P. 1270.
2. Borisova Z.U. Chalcogenide Semiconductor Glasses. — Leningrad: Leningrad University Publ. House, 1983 (in Russian).
3. Bilanich V.S. Processes of Mechanical Relaxation in Vitreous Arsenic Sulfides and Selenides: Thesis for Ph.D. degree in physics and mathematics. — Uzhgorod: Uzhgorod State University, 1993 (in Russian).
4. Physical Acoustics / Ed. by W.P. Mason. — Vol. 3, Part A. — New York: Academic Press, 1966.
5. Bilanich V.S., Gorvat A.A., Turyanitsa I.D. // Izv. RAN. Ser. Fiz. — 1993. — **57**, N 11. — P. 163–168.

6. *Bartenev G.M., Zelenev Yu.V.* Physics and Mechanics of Polymers. — Moscow: Vysshaya Shkola, 1983 (in Russian).
7. *Bartenev G.M., Sanditov D.S.* Relaxation Processes in Vitreous Systems. — Novosibirsk: Nauka, 1986 (in Russian).
8. *Bilanich V.S., Gorvat A.A.* // Fiz. Khim. Stekla. — 1998. — **24**, N 6. — P. 825–829.
9. *Mechanisms of Relaxation Phenomena in Solids* / Ed. by V.S. Postnikov. — Kaunas: Kaunas Polytechnic Institute, 1974 (in Russian).

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МЕХАНІЧНА РЕЛАКСАЦІЯ В ХАЛЬКОГЕНІДНОМУ СКЛІ СИСТЕМИ Ge–As–S

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Резюме

Досліджено температурно-частотні залежності внутрішнього тертя і модуля зсуву стекол $\text{Ge}_x\text{As}_{40-x}\text{Se}_{60}$ в інтервалі температур 100 К — T_g і частот 5–50 мГц. В області низьких температур виявлено максимуми внутрішнього тертя як релаксаційного, так і нерелаксаційного типу. В області склування виявлено релаксаційний максимум і визначено його параметри. Обговорюються можливі механізми цих процесів.