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ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED SYSTEM

High-Precision Measurements of the Compressibility of Chalcogenide Glasses at a Hydrostatic Pressure up to 9 GPa

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Abstract—The volumes of glassy germanium chalcogenides $GeSe_2$, GeS_2, $Ge_{17}Se_{83}$, and Ge_8Se_{92} are precisely measured at a hydrostatic pressure up to 8.5 GPa. The stoichiometric $GeSe_2$ and GeS_2 glasses exhibit elastic behavior in the pressure range up to 3 GPa, and their bulk modulus decreases at pressures higher than 2–2.5 GPa. At higher pressures, inelastic relaxation processes begin and their intensity is proportional to the logarithm of time. The relaxation rate for the $GeSe_2$ glasses has a pronounced maximum at 3.5–4.5 GPa, which indicates the existence of several parallel structural transformation mechanisms. The nonstoichiometric glasses exhibit a diffuse transformation and inelastic behavior at pressures above 1–2 GPa. The maximum relaxation rate in these glasses is significantly lower than that in the stoichiometric $GeSe_2$ glasses. All glasses are characterized by the “loss of memory” of history: after relaxation at a fixed pressure, the further increase in the pressure returns the volume to the compression curve obtained without a stop for relaxation. After pressure release, the residual densification in the stoichiometric glasses is about 7% and that in the $Ge_{17}Se_{83}$ glasses is 1.5%. The volume of the Ge_8Se_{92} glass returns to its initial value within the limits of experimental error. As the pressure decreases, the effective bulk moduli of the $Ge_{17}Se_{83}$ and Ge_8Se_{92} glasses coincide with the moduli after isobaric relaxation at the stage of increasing pressure, and the bulk modulus of the stoichiometric $GeSe_2$ glass upon decreasing pressure noticeably exceeds the bulk modulus after isobaric relaxation at the stage of increasing pressure. Along with the reported data, our results can be used to draw conclusions regarding the diffuse transformations in glassy germanium chalcogenides during compression.

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1. INTRODUCTION

To study the gradual structural transformations in glasses during compression is very important to understand many aspects of the physics of disordered systems. By analogy with polymorphism in crystals, the term “polyamorphism” was introduced for the transformations in glasses and amorphous solids. The changes in the short- and medium-range orders in glasses and amorphous solids are investigated by X-ray diffraction, neutron diffraction, and EXAFS (extended X-ray absorption fine structure). However, the structural characteristics of glasses give incomplete information as compared to the structural data of crystals. Therefore, a comprehensive investigation of the physical properties, in particular, thermodynamic properties, and computer simulation play an important role in studying polyamorphism.

The glasses based on germanium selenides and sulfides are classical glassy chalcogenides [1–3]. In contrast to glassy oxides of the type SiO_2 and GeO_2, these chalcogenides glasses form in a wide composition range, including the compositions far from stoichiometric ones, and all glass compositions have a significant number of “wrong” homopolar bonds [3, 4]. The stoichiometric $GeSe_2$ and GeS_2 glasses are also characterized by the fact that a significant fraction (30–50%) of the basic structural units—$Ge(Se_4)_{1/2}$ and $Ge(S_4)_{1/2}$ tetrahedra—are corner- and edge-sharing units [1, 5]. The same is true of the corresponding crystalline modifications stable at normal pressure: half the tetrahedra are edge-sharing units and the other half consists of corner-sharing units.

All glassy germanium chalcogenides are characterized by a certain intermediate structural order. Depending on composition, Ge–Se glasses can be conventionally attributed to the regions that differ in the connection of tetrahedra [6]. Form a structural standpoint, the glasses with 10–12% germanium consist of free $Ge(Se_4)_{1/2}$ tetrahedra in a matrix of Se chains [6]. The glasses with 12–33% Ge (stoichiometric composition) have a network of connected tetrahedra with a certain degree of connectivity. At a higher germanium concentration, the fractions of edge-sharing tetrahedra and “wrong” Ge–Ge neighbors increase [6]. The region of an “unstrained rigid” state from 20 to 25% Ge, which is intermediate between the soft and rigid states of a bond network, can also be additionally distinguished [6, 7]. The recent investigations of this intermediate state [8] demonstrate that $Ge(Se_4)_{1/2}$ tetrahedra connected by Se_2 dimers are absent in the glass and that this glass separates into connected tetrahedra and selenium chains on a nanoscale. The aforesaid is also true of glassy germanium sulfides.

The numerous unusual structural and physical properties of glassy germanium chalcogenides stimulated their investigations under pressure: the structures of the short- and medium-range orders in glasses were studied by X-ray diffraction, neutron diffraction, and EXAFS; the optical properties (Raman scattering) and the elastic properties (ultrasonic methods) were also investigated. Moreover, the behavior of $GeSe_2$ and GeS_2 glasses under pressure was actively examined by computer simulation. The $GeSe_2$ glasses have been studied most extensively [2, 3, 9]. The GeS_2 [3, 10, 11], nonstoichiometric $GeSe_4$ [6], and Ge–Se glasses over a wide concentration range [7] have received little attention. Irreversible degradation of the intermediate order was detected in all glasses, which is a common feature of the behavior of noncrystalline media during compression. The data obtained for the $GeSe_2$ glasses point to the following two processes occurring in compression: a continuous increase in the coordination number (appearance of five- and six-coordinated Ge atoms) over a wide pressure range and a change in the type of connection from edge-sharing to corner-sharing tetrahedra in the initial pressure range up to 3–4 GPa [2, 3, 9]. Note that both processes agree well with the data on the behavior of crystalline phases during compression.

At high pressures, the $GeSe_2$ II and GeS_2 II crystallographic modifications, which are based on tetrahedral structural elements with a common vertex, first become stable. As the pressure increases further, the $GeSe_2$ III phase based on six-coordinated Ge atoms becomes stable [12]. Here, the $GeSe_2$ II, GeS_2 II, and $GeSe_2$ III phases are semiconductors and the $GeSe_2$ III phase is a metal [13]. Obviously, a combination of these two glass densification mechanisms leads to anomalous behavior of the elastic characteristics of glassy $GeSe_2$ near 4 GPa, according to the data of ultrasonic measurements [9]. The baric dependences of the elastic moduli were assumed to have an inflection point at 4 GPa. As the pressure decreases, a significant hysteresis is detected, and the $GeSe_2$ glasses remain densified (by 4–5%) after pressure release despite the fact that the coordination number almost returns to the initial value [2, 3].

The densification processes that occur in the GeS_2 glasses during compression are likely to be similar, although the fractions of edge-sharing tetrahedra and wrong bonds differ significantly from those in the $GeSe_2$ glasses [3, 10, 11]. On the whole, computer simulation data support the experimental results regarding an increase in the coordination number for glasses, although fine effects, such as the connection of tetrahedra, are reproduced worse in simulation [14, 15]. Molecular dynamics data also point to gradual metallization of the $GeSe_2$ and GeS_2 glasses at a pressure well above 10 GPa, which was indirectly corroborated in experiments [14, 15]. The results [16] indicating a sharp transition into a crystalline metallic phase in glassy $GeSe_2$ at a pressure of 7–9 GPa were likely to be related to the strong nonhydrostaticity of the pressure-transferring medium.

When studying nonstoichiometric $GeSe_4$ glasses, the authors of [6] did not detect a significant increase in the coordination number during compression up to 9 GPa, unlike the situation in the $GeSe_2$ glasses. The increase in the glass density in this case was likely to be due to degradation of the intermediate order (closing of nanovoids) and to changes in far coordination shells. The hysteresis caused by a decrease in the pressure and the residual densification in these glasses were very small as compared to the $GeSe_2$ glasses.

The investigations [7] of the Raman spectra of Ge–Se glasses over a wide composition range under pressure revealed nonmonotonic behavior of the thermodynamic and dynamic properties of the glasses as a function of glass composition. The data obtained were interpreted in terms of an unstrained rigid state and a “reversibility window” for the compositions with 20–25% Ge. Moreover, based on the Raman spectra, the authors of [7] assumed that edge-sharing tetrahedra change into corner-sharing tetrahedra in the $GeSe_2$ glasses at a pressure up to 3 GPa and that this change softens the glass network.

The thermodynamic characteristic that reflects glass densification is the specific volume (reciprocal density) of a substance. The investigation of the transformations and the relaxation phenomena in glasses requires the accuracy of measuring the specific volume that is better than 0.01–0.1%. However, the compressibilities of glasses and amorphous substances cannot be precisely determined from diffraction data. The compressibilities of glasses can be relatively precisely measured by a piezoelectric method up to a pressure of 2–5 GPa [17]. Other techniques of measuring the specific volume, including density estimation from diffraction data [18], measuring the linear sample sizes by optical methods [19], and measuring the material density from X-ray absorption [20, 21], have a low accuracy (several percent). The density of glassy germanium chalcogenides under pressure was measured by an optical method for $GeSe_2$ [2] and $GeSe_4$ [6] glasses. The accuracy of measuring the density under pressure for these glasses was 5 and 2.5%, respectively.

The compressibilities of the $GeSe_2$ and GeS_2 glasses under pressure were determined from computer simulation data at an accuracy of several percent as well [14, 15]. This accuracy makes it possible to perform a qualitative analysis of the structural characteristics and cannot be used for a quantitative analysis of fine effects in the compressibility of glass. Moreover, the use of the data on the $GeSe_2$ glass density for an analysis of ultrasonic data leads to a substantial scatter of results.

The bulk compression modulus estimated from direct volume measurement data at normal pressure is $B = 14.2$ GPa, and its pressure derivative is $dB/dP = 2.7$ [2]. However, the bulk compression modulus estimated from ultrasonic data is $B = 10$ GPa and its derivative is $dB/dP = 7.5$ at a pressure of 1 GPa, which corresponds to a too low (from a physical viewpoint) modulus ($B = 2.5$ GPa) at normal pressure [9]. The bulk compression modulus of $GeSe_2$ glasses estimated from the old ultrasonic data [22] is $B = 18$ GPa at a possible error of ±4 GPa. Thus, high-precision density measurements during the compression of glassy germanium chalcogenides seem to be very important to reveal the specific features of polyamorphism and relaxation in these systems.

High-precision glass density measurements at a pressure up to 10 GPa under hydrostatic conditions can be performed using the strain gauge technique [23]. This method was used earlier to study the polyamorphism of SiO_2 and GeO_2 glasses [24], B_2O_3 glass [25, 26], and amorphous $ZrSiO_4$ [27]. These measurements allowed researchers to detect the following important features of polyamorphism: logarithmic density relaxation (as a function of time) at a constant pressure in the transformation range, a huge difference between the relaxing and unrelaxing bulk compression moduli in the elastic region, a negative hysteresis of diffuse transformations in glasses (reverse transformation begins at a pressure that is higher than that of the forward transformation), and the loss of memory (after storage and density relaxation at a fixed pressure, the initial compression curve is rapidly reached upon further increase in the pressure as though storage and relaxation were absent) [24–26]. Moreover, it was found that the transformations in all glasses are gradual and the assumptions regarding the possibility of a sharp reverse transformation in B_2O_3 glasses are erroneous [26].

The purpose of this work is to measure the densities of stoichiometric $GeSe_2$ and GeS_2 glasses and selenium-rich $Ge_{17}Se_{83}$ and Ge_8Se_{92} glasses at a high accuracy and a hydrostatic pressure up to 8.5 GPa.

2. EXPERIMENTAL

High-pressure experiments were carried out on a Toroid apparatus with a central pip diameter of 15 mm [28]. The strain gauge technique [23] was used to measure the amorphous sample volume under hydrostatic pressure. The absolute error of measuring the volume in this technique is 0.2% and the relative error (measurement sensitivity) is 10^{-3}%. An important advantage of this technique is a very short measurement time as compared to, e.g., the diffraction measurement time. As a result, the strain gauge technique can be used to obtain much more comprehensive information on the behavior of the sample volume under pressure. In addition, this technique makes it possible to study the volume kinetics under pressure over a wide time range ($10–10^5$ s or more). An important advantage of this technique is the fact that baric dependences of the volume can be obtained upon both an increase and a decrease in the pressure under purely hydrostatic conditions.

A mixture methanol–ethanol (4 : 1) with a hydrostatic limit of about 10 GPa was used as a pressure-transferring medium. The pressure was measured by a manganin transducer calibrated against the transitions in bismuth (2.54 and 7.7 GPa). The reproducibility of the pressure scale was 0.01 GPa (100 bar) in all experiments, and the absolute accuracy of measuring the pressure (about 1%) was only determined by the absolute accuracy of the reference scale.

The volume V measurements were performed at a continuous change in the pressure at a rate of 0.07–0.12 GPa/min upon increasing pressure and 0.03–0.05 GPa/min upon decreasing pressure. The load applied to a chamber was controlled when the given pressure was reached in order to study the glass densification kinetics at a fixed pressure; as a result, the pressure during measurements was maintained at a constant level accurate to ±2 MPa (20 bar). The load applied to a chamber was simply fixed in some cases (e.g., GeS_2 at the maximum pressure). The pressure drift in this case was taken into account by the projection of the obtained $V(P, t)$ dependence onto line $P =$ const along the slope of the $V(P)$ curve.

Although the unique strain gauge technique of measuring the volume at a high hydrostatic pressure has an extremely high accuracy and sensitivity, it places stringent requirements upon samples: they should be sufficiently large ($3 \times 2 \times 1.5$ mm^3; the measurement accuracy decreases noticeably when the sizes decrease) and have highly homogeneous composition and properties.

The initial glasses were fabricated from pure elemental substances Ge (99.9999%), Se (99.999%), and S (99.999%) (Aldrich Chemical Ltd.). The substances were placed in preliminarily cleaned quartz tubes with an inside diameter of 8 mm, which were then pumped out and hermetically sealed. The melts were held and stirred at 950°C for 48 h. The temperature was then decreased to 800°C and the melts were additionally homogenized for 24 h and then water quenched.

The initial ingots had pores from several tens of microns to 200–300 μm in size. If additional measures were not taken, these pores made it impossible to perform measurements, since cracks appeared in samples at a pressure of 0.7–1.2 GPa. The $GeSe_2$ glass is highly transparent in the red region. Workpieces were illuminated by a powerful light beam through a diaphragm, and internal defects became visible in a microscope. Samples were cut and polished so that large defects were absent in them. This method could not be used for the alloys with 8 and 17% Ge because of their low transparency; on the other hand, these glasses had a low softening temperature. The workpieces were situated in a hydrostatic chamber (cylinder–piston) preliminarily heated to 450 K for Ge_8Se_{92} and to 475 K for $Ge_{17}Se_{83}$ and held for 2 min to be heated, and the pressure in the chamber was then increased rapidly to 0.2 GPa. The chamber was water cooled under pressure and was unloaded after cooling.

The samples for compressibility measurements had a rectangular shape and were from $1.3 \times 0.8 \times 0.6$ mm^3 ($GeSe_2$, GeS_2) to $3 \times 2 \times 1.7$ mm^3 (alloys with 8 and 17% Ge) in size.

It was important that the standard technique [23] of bonding strain gages upon cement polymerization at a high temperature turned out to be unsuitable because of the low softening temperature of the Ge_8Se_{92} and $Ge_{17}Se_{83}$ glasses. Strain gages were glued with epoxy adhesive, which resulted in a large adhesive joint thickness and, hence, a possible systematic error in experimental results. Three experiments per glass were performed for all glasses except for GeS_2 and good reproducibility of the results was observed. Nevertheless, the results of measuring $V(P)$ dependence could have a systematic error of 0.5% for the relative change in the volume at the maximum pressure because of the small sample sizes ($GeSe_2$, GeS_2) and the nonstandard technique of bonding strain gages (Ge_8Se_{92}, $Ge_{17}Se_{83}$). The possible maximum systematic error in determining the bulk modulus was estimated at ±2%.

3. EXPERIMENTAL RESULTS

Figure 1 shows the baric dependences of the volume of the stoichiometric glasses ($GeSe_2$, GeS_2). The measurements were carried out at a pressure step of 0.02–0.03 GPa upon both increasing and decreasing pressure, which allowed us to obtain an almost continuous curve without interpolation. It is seen that the compression curves of both glasses cannot be approximated by a general simple equation of state: at least two different segments, to a pressure of 2 GPa and at particles higher then 4.5 GPa, with an intermediate region between them are present. Both glasses exhibit a significant hysteresis between the compression and unloading curves, and the glasses are retained in a densified state (by 6–7% for $GeSe_2$, by 7–8% for GeS_2) after pressure release. The inset to Fig. 1a shows the baric dependences of the $GeSe_2$ glass obtained on different samples in two independent experiments. Relaxation measurements at a fixed pressure were carried out on one of the samples. The baric dependences are seen to coincide at a high accuracy (better than 0.1%), and the compression curve after isobaric relaxation merges asymptotically with the compression curve without relaxation measurements when the pressure increases. For comparison, we also present the results obtained for $GeSe_2$ by optical methods.

At a pressure above 3 GPa, the volume of the $GeSe_2$ glass depends on time at a fixed pressure (relaxation), and the volume change is proportional to the logarithm of time (Fig. 2). The deviation from the logarithmic dependence at short times is related to the finite rate of increase of pressure in the experiment. The processes with relaxation times shorter than 100–300 s are partly or fully completed at the stage of increasing pressure before holding. Similarly to SiO_2 and GeO_2 glasses, $GeSe_2$ density relaxation is not detected in the initial pressure range up to 2.5 GPa, where the system exhibits fully elastic behavior. When the pressure increases further, relaxation processes appear at a certain threshold and their intensity grows sharply. The relaxation rate is maximal at 4.5 GPa and decreases gradually at higher pressures. The relaxation processes in the $GeSe_2$ glasses were not systematically studied and were semiquantitatively measured only in the maximum pressure range (see Fig. 2).

The high sensitivity of the strain gauge technique makes it possible to determine the bulk moduli of the glasses by numerical differentiation without additional processing. Figure 3 depicts the bulk moduli of the $GeSe_2$ and GeS_2 glasses as functions of pressure. A conventional linear increase of bulk modulus with pressure is observed only up to 1 GPa for both glasses. The bulk modulus of the $GeSe_2$ glass at normal pressure is $B = 13.9$ GPa and that of the GeS_2 glass is $B = 11.7$ GPa. The pressure derivative of the bulk modulus in the initial segment is $dB/dP = 5$ for both glasses, which is well below the estimate from the ultrasonic data in [9, 22] (according to which this derivative in the range 7.5–8.5 for all Se–Ge glasses falls). As the pressure increases further, derivative dB/dP decreases for both glasses and becomes negative (modulus “softening”). This anomalous behavior of compressibility is observed in the elasticity region up to 3 GPa. Similar softening of the bulk modulus during compression in the elastic region was observed earlier only for quartz glass [24, 29].

As the pressure increases further, intense volume relaxation begins and continues up to the highest pressures, and the bulk modulus obtained by direct differentiation corresponds to the effective relaxation values. Thus, the fitting of the baric dependence of volume by a general equation of state for these glasses is ungrounded. After long-term isobaric relaxation, the effective bulk modulus first corresponds high unrelaxing values when pressure increases further and then decreases to the effective “relaxing” values that corre-

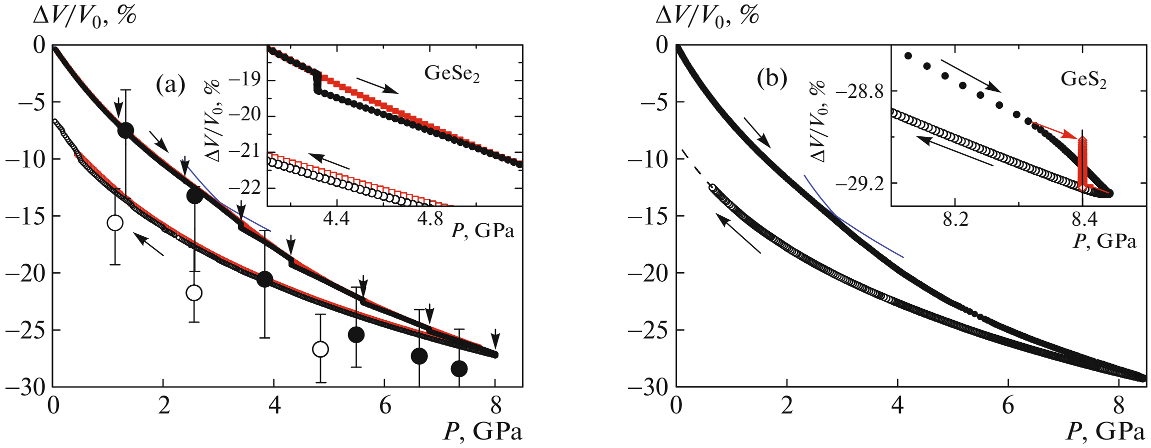

Fig. 1. (Color online) Baric dependences of volume on pressure for (a) GeSe$_2$ and (b) GeS$_2$ glasses for increasing and decreasing pressure. The thin lines indicating two-stage densification were obtained by fitting the initial segments in the $V(P)$ dependences by the Murnaghan equation and fitting the high-pressure regions by a similar equation with free parameter V_0. (a) Results of two experiments in one of which the glass densification kinetics was studied at fixed pressures (indicated by vertical arrows): (circles) data of optical measurements of the volume obtained upon (solid circles) increasing and (open circles) decreasing pressure (half the experimental points are shown) [2]. (insets) Enlarged pressure regions where the glass densification kinetics was studied at fixed pressures. (inset to (b)) Explanation of the extraction of "pure" $V(t)$ dependence (at P = const) from the real $V(P, t)$ data for the case where pressure drifted noticeably upon holding. The procedure consists in the projection of the $V(P, t)$ data on vertical P = const along the "relaxed" slope of the $V(P)$ curve obtained from the reverse pressure curve.

spond to curves at a constant rate of loading (bulk modulus "forgets" its history; see Fig. 3a). The small irregularities in the relaxing moduli of all glasses are related to the differences in the rate of increase of pressure. The behavior of the effective modulus clearly reproduces the variations of the rate of change of pressure in the region where relaxation takes place. The effective modulus does not depend on the rate of change of pressure in the elasticity region (below 3 GPa when pressure increases and above 3 GPa when pressure decreases).

For systems with elastic behavior, the bulk moduli determined by various measurement methods coincide. The bulk moduli measured by different methods can be strongly different is inelastic relaxation processes or phase transformations occur in a substance. The elementary act of phase transformation on a microlevel consists in regrouping a certain number of atoms, which requires the overcoming of an energy barrier and takes some time. In direct volume measurements, the times of all fast processes are usually shorter than the time is takes for pressure to change or volume to be measured (several hundred seconds). In this case, phase transformations can "trace" pressure changes to a certain extent, which leads to a decrease in the effective relaxing bulk modulus [26]. When the bulk modulus is obtained from the sound velocity determined in ultrasonic measurements or from Brillouin spectroscopy data, the times of pressure change in a traveling wave in a sample are very short, namely, several fractions of a microsecond for ultrasonic measurements and several fractions of a picosecond for Brillouin spectroscopy. These times are too short for the number of transformation acts to be significant. In this case, the substance behaves almost elastically and the bulk modulus to be measured corresponds to "unrelaxing" values. The difference between the relaxing and unrelaxing bulk moduli points to the existence of activation processes and diffuse transformations in glasses [26].

Upon pressure release, both glasses behave elastically up to 3 GPa. Their bulk moduli correspond to unrelaxing values, and the pressure derivatives for the

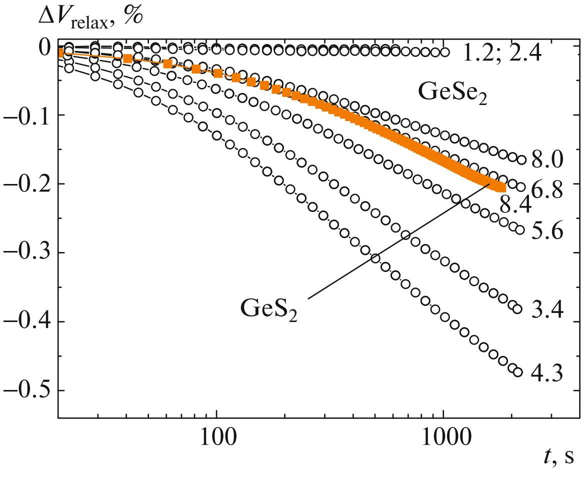

Fig. 2. (Color online) Change in the volume during the relaxation of GeSe$_2$ glass at a fixed pressure. The numerals at the curves correspond to the pressures in GPa. (squares) Relaxation of the GeS$_2$ volume at a pressure of 8.30–8.44 GPa (projected to 8.4 GPa).

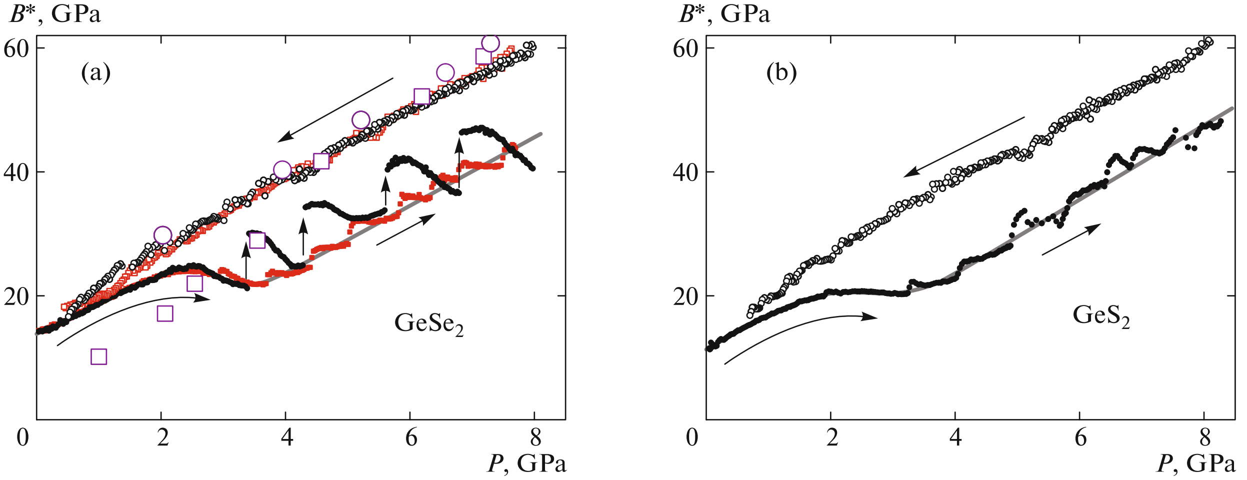

Fig. 3. (Color online) Effective bulk moduli $B^* = -VdP/dV$ of glassy (a) GeSe$_2$ and (b) GeS$_2$ obtained from the initial $V(P)$ data upon increasing and decreasing pressure: (squares) results from [9], (large circles) bulk modulus calculation for decreasing pressure from the sound velocity determined in [9] and from the density determined in this work.

reverse pressure run for both glasses almost coincide with those in the initial loading segment, $dB/dP = 5$. At pressures below 3 GPa, the bulk moduli of the GeSe$_2$ and GeS$_2$ glasses change more intensely due to relaxation during the reverse transformation. Relaxation takes place at the lowest pressures down to atmospheric pressure. Note that, in the range from 3 to 8 GPa, the bulk moduli of the GeSe$_2$ glass for the reverse run noticeably exceed the moduli after isobaric relaxation at the stage of growing pressure (see Fig. 3a). This finding indicates substantial differences between the short-range orders and densities of the glasses corresponding to the forward and reverse curves in this pressure range.

For comparison, Fig. 3a shows the results of ultrasonic measurements of unrelaxing bulk modulus [9]. The forward curve was taken from [9]. The data upon decreasing pressure were obtained from the sound velocities from [9] and the densities measured in this work. It is seen that the ultrasonic data corresponding to the reverse curve agree well with the results of our measurements in the elastic region when pressure decreases from 8 to 3 GPa. However, the ultrasonic measurements give too low (by a factor of 2–4) bulk moduli for the forward curve, which is likely to be related to the strong nonhydrostaticity of the pressure-transferring solid medium (which is always more significant when pressure grows). All baric dependences are smooth upon both increasing and decreasing pressure. Obviously, the conclusion [9] about an inflection point in the elastic modulus curve at 4 GPa is associated with a small number of experimental points and a significant measurement error. The too high baric derivatives of the moduli obtained in [22] are likely to be related to the very short pressure range used for measurements (up to 0.1 GPa).

Figure 4 depicts the baric dependences of the volume of the nonstoichiometric Ge$_{17}$Se$_{83}$ and Ge$_8$Se$_{92}$ glasses. The data obtained for different samples coincide accurate to 0.2%. The inset to Fig. 4a presents enlarged curves at the maximum pressures. For comparison, we also present the densities of the GeSe$_4$ glass (similar composition) measured by an optical method. These curves cannot be approximated by simple equations of state. In particular, the equation of state for the Ge$_{17}$Se$_{83}$ glasses is well described by the Murnaghan equation only up to 1 GPa ($B = 11$ GPa, $dB/dP = 6.7$). The hysteresis between the forward and reverse curves for both nonstoichiometric glasses is significantly smaller than for the stoichiometric glasses (about 2% for Ge$_{17}$Se$_{83}$ and 1.5% for Ge$_8$Se$_{92}$). After pressure release, the residual densification of *a*-Ge$_{17}$Se$_{83}$ is about 1.5%, and residual densification is absent for *a*-Ge$_8$Se$_{92}$ at the experimental accuracy.

The volume relaxation at a fixed pressure was studied for both nonstoichiometric glasses (Fig. 5). Weak logarithmic relaxation was found to occur in these glasses beginning from relatively low pressures. No sharp threshold “turning on” of intense relaxation, as in the GeSe$_2$ glasses, is detected for the selenium-rich glasses. At the same time, the Ge$_{17}$Se$_{83}$ glasses exhibit a weak relaxation rate maximum at a pressure near 4.5 GPa, and the relaxation rate in the Ge$_8$Se$_{92}$ glasses at pressures above 2 GPa is almost constant. On the whole, relaxation in these glasses is less pronounced than in the GeSe$_2$ glasses, especially in the intermediate pressure range 3–6 GPa. In Fig. 6, we compare the relaxation rates under pressure for various glasses.

Figure 7 depicts the baric dependences of the effective bulk moduli of the Ge$_{17}$Se$_{83}$ and Ge$_8$Se$_{92}$ glasses. In the initial compression range, the bulk modulus of *a*-Ge$_{17}$Se$_{83}$ is $B = 11$ GPa and the pressure derivative of

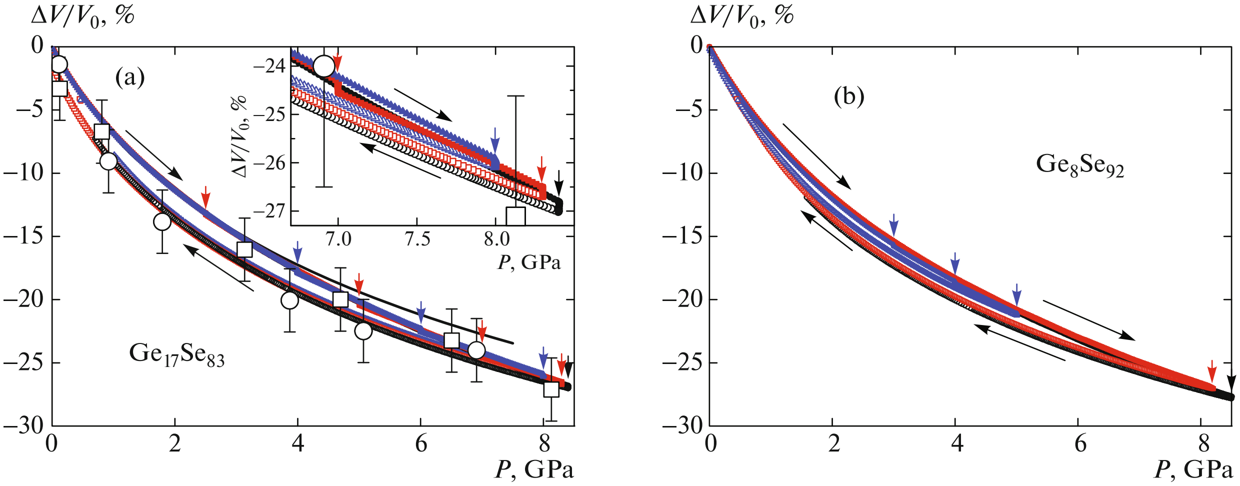

Fig. 4. (Color online) Baric dependences of volume on pressure for (a) $Ge_{17}Se_{83}$ and (b) Ge_8Se_{92} glasses upon increasing and decreasing pressure. The glass densification kinetics was studied at the pressures indicated by arrows. (a): (squares and circles) data of optical measurements of the volume obtained upon increasing and decreasing pressure, respectively (half the experimental points are shown) [6], and (solid line) fitting of the initial (0–2.5 GPa) segment of the $V(P)$ curves by the Murnaghan equation. (inset) Region near the maximum pressure.

the modulus is $dB/dP = 6.5$. For a-Ge_8Se_{92}, we have $B = 11.5$ GPa ad $dB/dP = 5$. It is interesting that the composition that is closest to the unstrained rigid state has the lowest bulk modulus and the highest pressure derivative. The estimates made for $GeSe_4$ glasses in [6] also give a low bulk modulus and a high pressure derivative of the modulus, $B = 10.4$ GPa and $dB/dP = 6$. The regions of a linear increase in the bulk moduli of both glasses do not exceed 1.5–2 GPa. Along with the data on the relaxation of these glasses, we assume that the region of almost elastic behavior also corresponds to the initial pressure range up to 1.5 GPa.

At higher pressures, the baric derivative of the bulk modulus begins to decrease, which is obviously associated with the beginning of inelastic relaxation processes. This decrease in the derivative is most pronounced for the $Ge_{17}Se_{83}$ glasses and begins at lower pressures. The noticeable irregularities in the relaxing modulus for both glasses are related to the fact that the rate of increase of pressure is not constant. The behavior of the bulk modulus exactly reproduces the variation of the rate of change of pressure in the region where relaxation occurs. As in the stoichiometric glasses, the effective bulk modulus after isobaric relaxation decreases to the relaxing values corresponding to the curves with a constant rate of loading (loss of memory of history) when the pressure increases further, Upon pressure release, both glasses behave almost elastically up to a pressure of 2.5–3 GPa. Here, the bulk modulus corresponds to unrelaxing values and the pr derivatives for the reverse curves are $dB/dP = 5$ for both glasses. At pressures below 2.5 GPa, the bulk moduli of the $Ge_{17}Se_{83}$ and Ge_8Se_{92} glasses begin to decrease rapidly, which is obviously related to relaxation during the reverse transformation. In the range from 2.5 to 8 GPa, the bulk moduli of the $Ge_{17}Se_{83}$ glasses in the reverse curve almost coincide with the bulk moduli after isobaric relaxation at the stage of increasing pressure (see Fig. 6). Obviously, this finding evidences the same short-range order structures of these glasses for the forward and reverse curves. The bulk modulus of the Ge_8Se_{92} glasses in the reverse curves also coincides with the modulus after relaxation in the forward curve at a pressure of 3 and 4 GPa.

4. DISCUSSION AND CONCLUSIONS

A phenomenological analysis of our results (without using the reported structural data) makes it possible to distinguish the following two processes. The first, “low-barrier,” process is clearly observed in the Ge_8Se_{92} glass. It consists in reversible but lagging behind (relaxing) adjustment of the volume to the current pressure. The second, “high-barrier,” process is most pronounced the stoichiometric glasses. It consists in irreversible volume changes and has two stages during compression. In terms of “crystalline prototypes,” it corresponds to an irreversible phase transition between the glasses the structures of which are close to the structures of the low- and high-pressure phases. It is difficult to unambiguously identify these processes in terms of structural changes because of the significant disagreements and contradictions existing in the literature. Nevertheless, the results obtained suggest that the low-barrier process corresponds to reversible changes in the short- and intermediate-orders in the structure (correspondingly, the coordination numbers) and does not influence the topology of connection between the structural elements in an

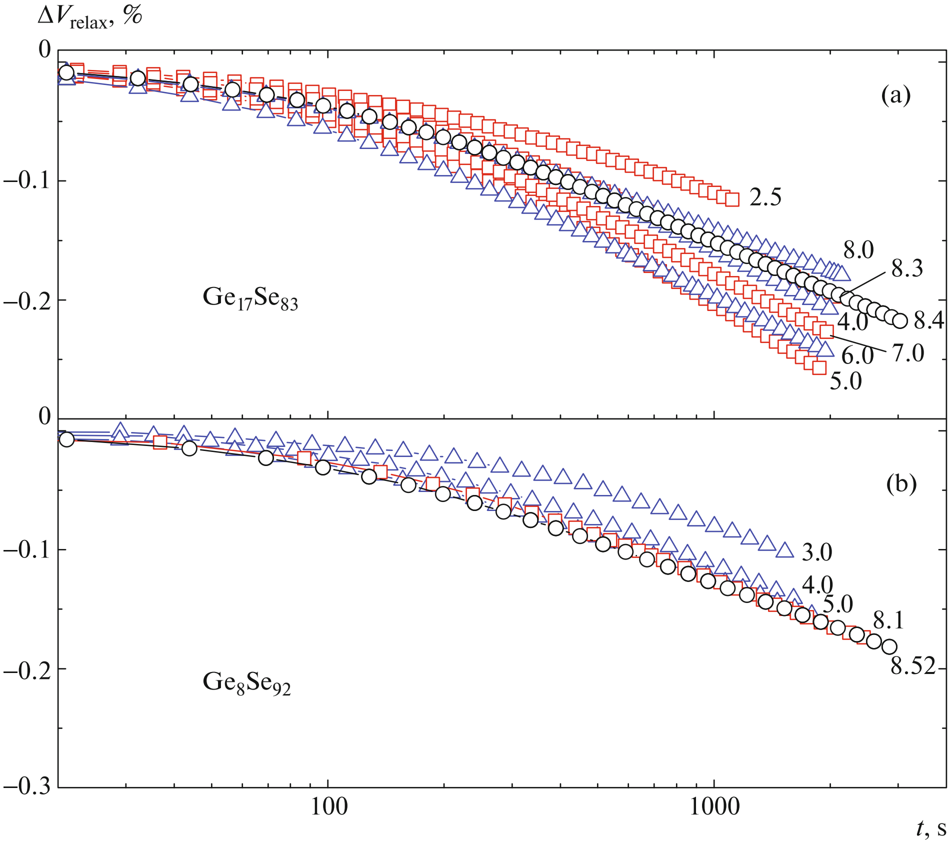

Fig. 5. (Color online) Change in the volume during the relaxation of glassy (a) $Ge_{17}Se_{83}$ and (b) Ge_8Se_{92} at a fixed pressure. The numerals at the curves correspond to the pressures in GPa.

amorphous network. In essence, these are self-consistent diffusion atomic displacements at distances that are smaller that the interatomic distances and are not related to breaking and "switching" of covalent bonds. The high-barrier process is associated with the restructuring of the network topology: this is a break in the edge-sharing connection between the network structural elements ($GeSe_4$ tetrahedra) and the switching of the corresponding covalent bonds to the corner-sharing connection of the structural tetrahedra. Of course, topology restructuring is to be accompanied by the diffusion low-barrier process.

Along with the reported data on structural changes, our results can be used to draw some conclusions regarding the behavior of the $GeSe_2$ and GeS_2 glasses during compression. Elastic behavior is observed at pressures up to 2.5–3 GPa. No substantial structural changes, including changes in the type of connection of tetrahedra (as structural units) and the coordination number, are likely to occur here. In this pressure range, the softening of both the shear modulus [9] and the bulk modulus takes place, which increases the instability of the amorphous network. This instability is likely to be associated with the softening of local elastic constants for the edge-sharing tetrahedra. The assumption that the change from edge-sharing tetrahedra to corner-sharing tetrahedra in the $GeSe_2$ glasses occurs before 3 GPa [2], which was based on the Raman data from [7], is likely to be wrong.

Obviously, the intense relaxation processes in the $GeSe_2$ glasses that take place in the pressure range 3–5 GPa are caused by structural changes, mainly by the change from edge-sharing tetrahedra to corner-sharing tetrahedra. Note that this pressure range corresponds to the region of the stable crystalline $GeSe_2$ II and GeS_2 II phases, which are also based on corner-sharing tetrahedral structural elements [12]. Simultaneously, some tetrahedra are broken and the coordination number begins to grow gradually up to the maximum pressure. As in oxide glass, logarithmic kinetics, which is related to a wide relaxation time spectrum, is observed. According to the diffraction data in [2], a noticeable increase in the coordination number (the number of neighbors in the first coordination shell) in a-$GeSe_2$ takes place at 3.9 GPa. The $GeSe_2$ and GeS_2 glasses remain dielectric up to the maximum pressure of 8.5 GPa, and the detected elastic glass softening is not related to their metallization. After pressure release, the coordination in both glasses is high up to 3 GPa and elastic behavior is observed in this pressure

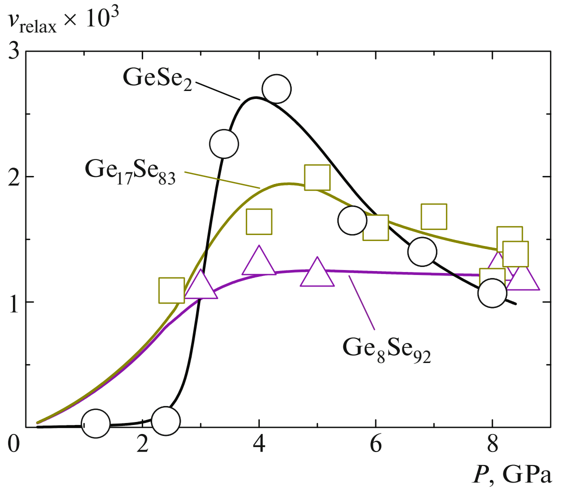

Fig. 6. (Color online) Steady relaxation rate $v_{relax} = -d(V/V_0)/d(\log t)$ vs. pressure for glasses (circles) $GeSe_2$, (squares) $Ge_{17}Se_{83}$, and (triangles) Ge_8Se_{92}. The relaxation rate was determined in the linear segments of the time dependences shown in Figs. 2 and 5.

range. In the pressure range from 3 GPa to atmospheric pressure, both glasses undergo the reverse transformation, which is obviously associated with full restoration of the coordination numbers to the initial values. The residual densification is caused by modification of the intermediate order and partial irreversibility of the type of tetrahedron connection.

The nonstoichiometric glasses undergo a diffuse transformation over a wide pressure range. Relaxation processes also occur at almost all pressures but are weak. We assume that the average coordination number in both glasses in this pressure range changes weakly and the transformation is mainly caused by changes in far coordination shells and the degradation of the intermediate order. These changes are almost fully reversible after pressure release. The results obtained agree well with the data of structural studies of $GeSe_4$ glasses [6]. However, the $Ge_{17}Se_{83}$ glasses exhibit small residual densification and a weak relaxation rate maximum at 4–5 GPa. The type of connection of tetrahedra in certain regions in the amorphous network is assumed to change in these glasses, although this change is much less pronounced than in the stoichiometric glasses. The nonmonotonic composition dependences of the bulk modulus and its derivative are likely to be caused by the existence of a "reversibility window" near the $GeSe_4$ composition.

Thus, high-precision volume measurements under pressure under hydrostatic conditions allowed us to reveal the main features of the transformations in glassy germanium chalcogenides. The stoichiometric glasses are characterized by the following pronounced pressure ranges: up to 1.5 GPa, normal elastic behavior; from 1.5 to 3 GPa, elastic behavior, where the elastic moduli cease to increase and begin to decrease; from 3 to 5 GPa, inelastic behavior, which is likely to be related to a change in the type of connection of tetrahedra (as structural units) and the beginning of increasing the coordination number (break of tetrahedra); and from 5 to 8 GPa, inelastic behavior associated with a continuing increase in the coordination number. The diffuse transformation in these glasses is partly reversible. The diffuse transformation and inelastic behavior are detected in the nonstoichiometric glasses at pressures above 1–2 GPa and are associated with changes in far coordination shells. These transformations are almost fully reversible. The $Ge_{17}Se_{83}$ glasses exhibit anomalies in the bulk modulus and its derivative, which are likely to be caused by the existence of the concentration region of the reversibil-

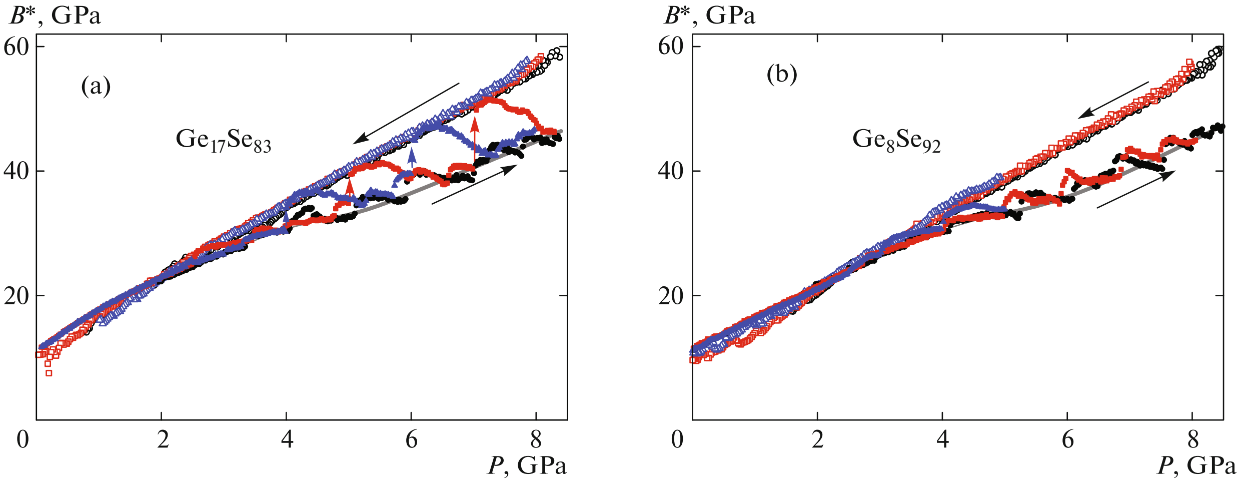

Fig. 7. (Color online) Effective bulk moduli of (a) $Ge_{17}Se_{83}$ and (b) Ge_8Se_{92} glasses obtained from the initial $V(P)$ data upon increasing and decreasing pressure. The gray line is drawn for clarity.

ity window in these glasses. The diffuse transformations in all glasses have logarithmic kinetics. Note that all (forward, reverse) transformations in the glasses are gradual, although an anomalously high rate of the forward transformation is detected in the stoichiometric glasses in a rather narrow pressure range (3.5–4.5 GPa).

Thus, during compression, the chalcogenides glasses exhibit the features that are universal for all glasses (elastic softening before transformation, diffuse transformation, logarithmic relaxation, loss of memory of history after isobaric holding, residual densification after pressure release) and specific features, which are related to the structure of the chalcogenides glasses and the possibility of existence of wrong homopolar bonds. These specific features are simultaneous existence of several structural modification mechanisms and anomalous behavior of the glasses with the compositions near the reversibility window.

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