Kinetics of Amorphous-to-Amorphous Transformations in SiO₂ and GeO₂ Glasses under High Pressure

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The kinetics of amorphous-amorphous transformation in GeO₂ glass and initial stage of densification in SiO₂ have been studied up to 9 GPa by direct volumetric measurements using the resistivity strain-gauge technique. A number of anomalous features, such as the logarithmic law of densification at a fixed pressure and the overlap of pressure ranges of the direct and reverse coordination changes in the GeO₂ network (negative hysteresis), were found to distinguish the observed transformation kinetics from that of ordinary first order transitions.

[vitreous silica, GeO₂ glass, high pressure, amorphous-to-amorphous transformation, logarithmic relaxation]

I. Introduction

The nature of phase transformations in topologically disordered systems, such as liquids and amorphous solids, has not been adequately studied as yet, and the possibility of a first order phase transition in a disordered condensed matter is still under discussion [1-9]. An amorphous solid can be well described by the traditional thermodynamics at relatively low temperatures, although it is a metastable and nonergodic system. No thermodynamic principles are violated by the first-order transition in disordered substances [1], although there are some difficulties for the introduction of order parameter in this case. The sharp transformation between the low density and high density forms of amorphous ice is considered now as a first-order transition [4,5]. The change of short range order (SRO) and existence of different polymorphs were well documented for the pressure-induced transformations in amorphous H₂O [4,5], SiO₂ [6,7,10-12], and GeO₂ [8,9,13,14]. However, experiments show a very wide pressure range of transformations in silica and germania glasses under pressure [6-17], and there is practically no information about the kinetics of these transformations.

Silica is an important glass-forming material. Vitreous silica g-SiO₂ is known to exhibit the anomalous minimum of bulk modulus at ~2 GPa [15,18-20] and irreversible densification [16]. The structural transformation of g-SiO₂ was studied by x-ray diffraction [7] and optical spectroscopic techniques [6,10-12], and was found to occur in the range 10--25 GPa. The quasistatic equation of state for silica glass was directly measured only up to 10 GPa [15], and no time-dependent variation of the sample size at a fixed pressure have been found in this study by the optic method. Vitreous germania g-GeO₂ is a chemical and structural analog of silica glass. Its high-pressure elastic properties and fourfold- to sixfold-coordination transformation were studied by different techniques [8,9,13,14,17,19,20]. The structural transformation in g-GeO₂ was observed between 4 and 13 GPa, and the equation of state was measured by the optical method in the range $P \leq 7.1$ GPa [9]. The two-domain model was found to describe quantitatively both the quasistatic and ultrasound equations of state for g-GeO₂ [9].

In this paper we present the kinetic study of amorphous-amorphous transformation in g-GeO₂ and relaxation volume measurements in g-SiO₂ up to 9 GPa. The continuous control

of volume variation during the experiment by the strain-gauge technique allowed us to perform very precise measurements and exactly detect the anelastic behavior in the glasses. The study of time-dependent volume changes at fixed pressures has given the unambiguous evidence of logarithmic glass densification at the beginning of transformation in silica glass and during the major part of transformation in g-GeO₂. Other anomalous features have been also found for the amorphous-amorphous transformation in g-GeO₂. The results obtained obviously show a significant difference between the amorphous-amorphous transformations and ordinary first-order transitions in crystals.

II. Experimental

The samples of amorphous silica were prepared by high-temperature oxidation of SiCl₄. GeO₂ glass was quenched from the melt with the subsequent annealing. We studied the samples of cubic form with the edge size 3 mm. SiO₂ and GeO₂ glasses were tested by x-ray diffraction before and after high-pressure experiments. The bulk and shear elastic moduli were determined at ambient conditions from the measured values of transverse and longitudinal sound velocities.

All the high-pressure experiments were carried out in the "toroid" device [21] capable to generate hydrostatic pressure up to 9 GPa [22]. The samples were placed in the teflon ampoule filled with methanol-ethanol (4:1) pressure transmitting medium. Pressure was measured by the calibrated manganin gauge and could be held at a set value with an accuracy of about 0.002 GPa. The precise volumetric studies were accomplished using the strain gauge technique. All details concerning the high-pressure experiments and preparation of gauges are presented in Ref. 22. The glass samples with the cemented gauges were coated by thin elastic soft films to avoid their reaction with the methanol-ethanol medium. The calibration experiments [22] allowed to estimate the absolute accuracy of volume measurements by the strain gauge technique to be about 0.3 %. At the same time, the relative sensitivity of this method, which is particularly important for time dependent relaxation measurements, is much better, $\Delta V/V \sim 10^{-5}$.

III. Results

Fig. 1 shows the equations of state, obtained by the strain gauge technique, for g-SiO₂ and g-GeO₂. The initial density

was determined by the Archimedes method as $\rho_0 = 2.20 \pm 0.03$ g/cm³ for g-SiO₂ and $\rho_0 = 3.7 \pm 0.1$ g/cm³ for g-GeO₂. Our data for vitreous silica are in good accordance with previous studies [18,19]. The main features of high-pressure volume behavior of GeO₂ glass are similar to those from Ref. 9.

Fig. 1. The equations of state: (a) for g-SiO₂ in comparison with the Brillouin scattering data of Schroeder et al. [19] (solid circles) and pressure-corrected data of Bridgman [18] from Ref. 19 (open circles); (b) for g-GeO₂ in comparison with the volumetric data of Smith et al. [9] (circles) and the Brillouin [14] (dashed and dotted lines) and ultrasonic [20] (dotted lines) equations of state.

The pressure dependence of bulk modulus for g-SiO₂ (Fig. 2) was directly calculated from the equation of state. The initial bulk modulus $B = 40 \pm 3$ GPa is in good accordance with the ultrasonic data for the same sample, $B_{us} = 37 \pm 1$ GPa. The main features of $B(P)$ curve, including the anomalous minimum at $P \approx 2$ GPa, are the same as those from the Brillouin scattering [19] and ultrasonic [20] studies. The room-pressure bulk modulus for g-GeO₂, $B = 30 \pm 2$ GPa, is slightly higher than those obtained in the previous studies. The high-pressure behaviour of GeO₂ glass compressibility in the transformation region we will consider in Discussion.

The all above data have been obtained for slow continuous increase or decrease of pressure ($dP/dt \sim 0.1$ GPa/min). After pressurization the sample of g-SiO₂ was kept at $P = 9.0$ GPa during one hour. We have found an irreversible densification of the sample, which can be described by the logarithmic law, $\Delta V/V \propto \log t$, with a high accuracy (Fig. 3). The density vs pressure curve for decompression is evidently shifted toward higher densities [Fig. 1 (a)]. The residual densification of silica glass sample was equal to 1.5 %.

Fig. 2. Pressure dependence of bulk modulus for compression (solid circles) and decompression (open circles) in comparison with the data of Schroeder et al. [19] and Suito et al. [20].

Fig. 3. Time dependence of relative volume for g-SiO₂ under pressure.

Fig. 4. Comparison of relative volume vs pressure dependence for continuous pressure increase (dashed) and intermittent compression in relaxation study (solid) in the whole experimental pressure interval (a) and in the region of intensive coordination change (b).

In the case of GeO_2 glass we used another sample. For this sample the pressure increase was interrupted by the volume vs time measurements at fixed pressures during 100 min or longer. The volume vs pressure curves for the continuous and intermittent pressure increase experiments are very close to each other [Fig. 4 (a)], because after fixed-pressure relaxation the $\Delta V/V(P)$ curve returned to the dependence observed for a continuous pressure increase (Fig. 4). The residual densification of samples after depressurizing was equal to $\approx 6\%$ from both the strain gauge and direct Archimedes measurements. The results of volume vs time measurements are shown in Fig. 5. We have found the first direct evidence of irreversible relaxation at $P=3$ GPa. In the same region the quasistatic equation of state begins to deviate from the experimental ultrasonic [20] and Brillouin [14] equations. However, the relaxed compressibility begins to increase (Fig. 6) at $P=2$ GPa. The time dependence of densification (Fig. 5) is represented by the curves, which are nearly linear at sufficiently long time interval in the $\Delta V/V$ vs $\log t$ coordinates, although there are some deviations from linearity on the logarithmic time scale, especially for short times. From the compressibility curve (Fig. 6) the reverse transformation begins at $P=4$ GPa, where we have directly found the irreversible volume relaxation with time.

Fig. 5. Time dependence of relative volume for g- GeO_2 at the different pressures.

Fig. 6. Variation of compressibility of g- GeO_2 for different experimental conditions.

IV. Discussion

A number of anomalous features distinguishes the observed transformation kinetics from that of an ordinary first order

transition. At first, the observed logarithmic kinetics of the amorphous-amorphous transformation in g- GeO_2 and initial densification in g- SiO_2 contradicts to the conception of ordinary first-order crystal-crystal transitions. The transformation kinetics of the latter can be usually described by the rate equation for a transformed volume fraction, $x(t)$, which has the Avrami form $x(t)=1-\exp(-kt^n)$ (t^n is for the initial stage). This functional form is determined by the microscopic process of nucleation and growth of a new crystalline phase. In particular, the α -quartz $\rightarrow$ rutile transition in crystalline GeO_2 was found to obey this relation with the Avrami exponent $n \sim 1$ [23]. The data of Brar and Schloessin [23] are remarkably nonlinear for the transformed fraction vs $\log t$ coordinates. The kinetic parameter k increases significantly with pressure for pressure-induced first-order transformations. The pressure-induced kinetic intensification of first order transition is connected with the decrease of corresponding activation energies for nucleation and growth. For glasses the amplitudes of kinetic variations are evidently comparable along the complete transformation region (Fig. 5). Moreover, these amplitudes are much smaller than the characteristic amplitude of kinetic changes for the α -quartz $\rightarrow$ rutile transition in crystalline GeO_2 [23].

Another very unusual feature, the overlap of regions of the direct (started at least at $P=3$ GPa) and reverse (started at $P=4$ GPa) coordination changes. The negative hysteresis can take place for the first-order transition as a result of non-hydrostaticity of a pressure medium, for example, for the α - ϵ transition in iron (see the systematic study in Ref. 24). However, in the present study we deal with the hydrostatic methanol-ethanol conditions.

A pressure increase enhances, as a rule, the transition kinetics of first-order phase transformations. This is in no agreement with the returning of the $V(P)$ curve after interruptions again to the curve followed at a continuous pressure increase, if we consider germania glass. This phenomenon is also illustrated by Fig. 6, where the compressibility varies between the relaxed and unrelaxed values for compression of glass, when pressure increases between the relaxation expositions at fixed pressures. Here, the compressibility calculated from the quasistatic equation of state is considered to relax with respect to the coordination change, in contrast to the unrelaxed compressibility from the Brillouin or ultrasonic experiments [9,14]. Just after the expositions at fixed pressures (~ 1 hour) glass becomes unrelaxed (like for the high-frequency response) and "forgets" its own prehistory and previous changes. Only an additional large enough pressure increase stimulates the further coordination change.

Thus, the precise kinetic measurements cannot allow us to treat the amorphous-amorphous transformation in g- GeO_2 and g- SiO_2 as an ordinary first order transition. At the same time, the concept of different polymorphs existing in glasses is beyond doubt now. Moreover, the two-domain model correctly describes both the relaxed and unrelaxed elastic properties of g- GeO_2 in the transformation region [9]. The x-ray absorption study of Itie et al. [8] also indicated the two different sites (4-fold and 6-fold) rather than a progressive site modification for the coordination transformation in g- GeO_2 .

The understanding of the nature of amorphous-amorphous transformations should be based on the point of view, that glass is a non-ergodic system and the basic feature of an amorphous solid (glass), distinguishing it from a crystal, is a wide variation of geometric characteristics for individual atoms and small clusters. Indeed, the logarithmic kinetics is not a unique phenomenon and is inherent to various disordered systems [25-27]. Using the phenomenological model, Karpov and Grimsditch [28] have found that the physical values can depend either quadratically or linearly on $\log t$ during the relaxation in glasses. The densified g-SiO₂ samples were also found to display the approximately logarithmic time dependence of sound velocity changes [28]. The logarithmic relaxation is connected with the existence of a continuous spectrum of relaxation times having the uniform distribution of its logarithm. As far as the structural transformations are concerned, this means a wide hierarchy of structural processes with the uniform distribution of energy barriers. The latter is in turn in accordance with the extensive character of this transformation in glasses. This consideration is also based on another important feature of amorphous-amorphous transformations: such transformations are low-temperature phenomena with respect to the crystallization and occur without any long-range diffusion.

The basic mechanism of transformations in silica and germania glasses should probably involve sharp tetrahedral-to-octahedral changes occurring at different pressures for certain small clusters and atoms. However, we cannot exclude the cooperative movements of Si(O₄)_{1/2} tetrahedra and gradual coordination change for certain atoms, as alternative mechanisms of structural modification. The latter mechanisms seem to be important for relaxation, which takes place at the beginning or end of the transformation. The five-coordinated silicon or germanium states (see Ref. 29) may also play a significant role, as intermediate states, for the coordination changes in SiO₂ and GeO₂ glasses. In any case, the SRO structural parameters, averaged over the entire network, change continuously during the densification. Obviously, the pressure-induced coordination changes in glass significantly influence the shape of distributions for all microscopic parameters. In further discussion we will not touch upon this aspect.

The wide variation of geometric characteristics results in the wide distribution of atomic energies and stresses (see, for example, Refs. 30 and 31). The distribution of intertetrahedral Si-O-Si (Ge-O-Ge) angles [32] and torsional angles of adjacent tetrahedra are of particular importance for the fourfold-to-sixfold transformation in g-SiO₂ (g-GeO₂). The increase of external pressure should upset the distribution of energy barriers for the reconstruction of SRO and soften the open-packed networks of SiO₂ and GeO₂ glasses. The wide distribution of local pressure spinodals [9] with respect to the coordination change corresponds to the softening of different network parts at different pressures. More exactly, each network part has its own instability pressure in contrast to a crystal, where the lattice becomes unstable as a whole at a certain spinodal pressure.

The lattice instability approach (see, for example, Refs. 33 and 34) was very successfully applied to understand of the

nature of diffusionless crystal-to-amorphous transformations. Whereas a crystal-crystal transition is governed by the change of lattice symmetry, and the one-particle distribution function may serve as an order parameter, this approach meets natural difficulties in amorphous solids, where all structural parameters are averaged over the network functions. However, the amorphous-amorphous transformation can be described in terms of the distributions of geometrical and dynamics characteristics. The atomic level stress tensor [35] seems to be a governing parameter for the instability of local network parts. From this point of view the distribution function for this tensor directly determines the transformation kinetics in the region of network softening.

The simplest model for the amorphous-amorphous transformation may take into account the trace of atomic level stress tensor, associated with atoms, or the local compression of individual atoms, $\sigma_i = p_i/\Omega_i$ (p_i is the atomic "pressure" and Ω_i is the volume for the i -th atom). If the pressure position of spinodal for a local network part is defined by the local atomic stress σ , the distribution of atomic stresses $\xi(\sigma)$ (Fig. 7) should directly correspond to the distribution of transformation spinodals for different network parts. The increase of external pressure evidently shifts the $\xi(\sigma)$ distribution as a whole. At a particular pressure only those portions of the network take part in the transformation, which correspond to the narrow band in the spinodal distribution and, consequently, in the atomic stresses distribution (Fig. 7). Thus, a small part of the network is involved into the transformation at a fixed pressure. When this part is essentially transformed, the compressibility becomes unrelaxed because other parts are not sensitive to the current pressure or had been transformed previously. Only a subsequent significant pressure increase involves new network parts into the coordination transformations, and the compressibility becomes relaxed. In this case, the kinetics of transformation at a new pressure point is practically not sensitive to the previous history of pressure variation, which is in a good agreement with the experimental observations (Figs. 4 and 6).

Fig. 7. Model distribution for local atomic stresses at the zero ambient pressure. The selected band corresponds to the network parts becoming unstable with respect to the coordination change at the external pressure $P = P_c + \sigma_i$, where P_c is the instability pressure for unstressed network parts.

In the framework of this model the negative hysteresis for the amorphous-amorphous transformation in g-GeO₂ is obviously associated with the overlap of tails of the atomic stresses distributions for direct and reverse transformations. The very high accuracy of relative volume measurements by the strain gauge technique allowed us to adjust the initial pressures of irreversible densification. The new directly measured points of initial volume relaxation are 3 and 9 GPa in g-GeO₂ and g-SiO₂, respectively, instead of the previously reported 4 and 10 GPa (see Introduction). However, the anelastic behavior of g-GeO₂ seems to appear even below, at $P=2$ GPa, where the relaxed compressibility starts to increase (Fig. 6). The anelastic behavior of silica glass can be detected, comparing the bulk modulus obtained from a directly measured volume change with the unrelaxed modulus (for example, from the Brillouin data) or comparing the direct and reverse $B(P)$ curves. From Fig. 2 one can estimate the starting pressure of anelastic behavior as 6–7 GPa, that is in good agreement with the recent theoretical molecular-dynamic calculation [36].

Summarizing, the local instability approach allows to explain the observed anomalous features of amorphous-amorphous transformations on the basis of distributions of energy (transformation barriers) and dynamic (tensor of atomic level stresses) characteristics. However, the theoretical analysis of the problem still remains extremely difficult. Even within crystals the competition of different instability modes [34,37] creates a very complicated scenario for the kinetics of low-temperature diffusionless transformation. Nevertheless, the local instability approach shows that the increased width of amorphous-amorphous transformation is an inherent property of silica and germania glasses, rather than a pure kinetic phenomenon. Thus, the finite width of the transformation and the logarithmic kinetics of densification may be considered as macroscopic manifestations of the glass nonergodicity. Concerning the sharp transformation in amorphous H₂O ice, one should mention that there is the experimental evidence in favor of the finite width of this transformation. This question will be considered elsewhere. The characteristic energy scale for the atomic force constants also affects the atomic level stresses distribution, i.e., the transformation width.

The reason for the zero width of first-order transitions is connected with the coexistence of two macroscopic phases. In this case, both the volume and free energy are additive functions for the two-phase mixture. The infinite time limit is not applicable to metastable glasses. The division of glass into two amorphous phases in the process of transformation is also very problematic. The success of two-domain model for g-GeO₂ [9] seems to be based on the existence of distinct structural types for SRO, energetically favorable among other configurations. It is reasonable to consider the glass characteristics as approximately additive function of the fractions of differently coordinated atomic sites, but the diminishing of free energy due to the relaxation may play a remarkable role in the formation of intermediate glass states. The delicate phenomena, such as the pressure-induced relaxation or the residual densification of glass, evidently require a discussion based on the non-ergodic concepts.

The reverse transformation in g-GeO₂ is narrower than the direct one [Fig. 1 (b)]. This effect should be associated with the

narrower distribution of atomic level stresses in the high-pressure rutile-type GeO₂ glass. The origin of such narrowing in the high-pressure form seems to be connected with the increased number of topological restrictions in the rutile-type network consisting of octahedral units.

V. Conclusion

We have studied the kinetics of amorphous-to-amorphous transformations in SiO₂ and GeO₂ glasses under pressure and found a number of anomalous phenomena, particularly, the logarithmic kinetics of densification at a fixed pressure. The approach, considering glasses as non-ergodic systems with the distributed atomic level parameters, allowed us to explain the observed anomalous features. We have established that the irreversible densification of silica and germania glasses and their anelastic behavior appear below the pressure intervals reported previously. The further progress in understanding the nature of amorphous-amorphous transformations will be probably achieved as a result of comparative kinetic studies involving the transformations in g-SiO₂, g-GeO₂, and amorphous H₂O ice.

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