

Logarithmic Kinetics of the Amorphous-Amorphous Transformations in SiO_2 and GeO_2 Glasses under High Pressure

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We have studied *in situ* the kinetics of the amorphous-amorphous coordination transformation in GeO_2 glass and of the initial stage of transformation in vitreous SiO_2 up to 9 GPa by volume vs time measurements using the precise strain-gauge technique. The volume vs time dependence at all pressure points was found to obey the logarithmic law, which distinguishes the observed transformation kinetics from that of the ordinary transitions in crystals. The first evidence of anelastic behavior was found from the quasistatic equation of state at $P \approx 6\text{--}7$ GPa for SiO_2 glass and at 2–3 GPa for GeO_2 glass, i.e., at lower pressures than previously believed. [S0031-9007(97)05172-7]

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The nature of phase transformations in topologically disordered systems such as liquids and amorphous solids has not been adequately studied as yet [1–12]. Although, being a metastable and nonergodic system, the amorphous solid can be well described in many respects by the traditional thermodynamics at relatively low temperatures. The sharp transformation between the low density and high density forms of amorphous ice is considered now as a first-order transition [4–7]. However, a great number of experiments show a wide range of amorphous-amorphous transformation (AAT) or, in other words, coordination change in silica and germania glasses under pressure [8–20]. The change of short range order (SRO) and the existence of different polymorphs were well documented for the pressure-induced transformations in amorphous H_2O [5–7], SiO_2 [8–10,13,14,17], and GeO_2 [11,12,19,20]. However, there is practically no information about the kinetics of these transformations.

Silica is the most important glass-forming material. Vitreous silica $g\text{-SiO}_2$ is known to exhibit an anomalous elastic behavior under pressure, such as the minimum of bulk modulus at ~ 2 GPa [15,21–24] and irreversible densification [16,25]. The AAT in $g\text{-SiO}_2$ with the change from tetrahedral- to octahedral-Si coordination was studied *in situ* by x-ray diffraction [10] and optical spectroscopic techniques [8,9,13,14,17], 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]. No time-dependent linear change of the sample size was detected by the optic method at the peak pressure in this study. The only attempt to study time-dependent relaxation in $g\text{-SiO}_2$ at $P = 18.2$ GPa was made in Ref. [9]. No special attention was paid to determine the functional form of the time dependence in this study.

Vitreous germania $g\text{-GeO}_2$ is the excellent chemical and structural analog of silica glass. Its high-pressure elastic properties and fourfold-to-sixfold AAT were studied by different techniques [11,12,18–20,22,23]. The coordination change for $g\text{-GeO}_2$ was observed between 4 and 13 GPa, and the equation of state was directly studied by

the optical method in the range $P \leq 7.1$ GPa [12], covering approximately half of the pressure-induced AAT.

The nature of AAT's in SiO_2 and GeO_2 glasses still needs experimental and theoretical investigations to clarify the conception of “polyamorphism” [3,20,26] in these amorphous solids. In this Letter we present the kinetic study of AAT in $g\text{-GeO}_2$ and the relaxation volume measurements at the onset of AAT in $g\text{-SiO}_2$ up to 9 GPa. Continuous control of the volume change 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 law for the volume decrease at the beginning of AAT in silica glass and during the AAT in $g\text{-GeO}_2$. The results obtained obviously show a significant difference between the AAT and ordinary crystal-crystal transitions and can be considered as a macroscopic manifestation of nonergodicity in the region of glass structural modification.

The samples of amorphous silica were prepared by high-temperature oxidation of SiCl_4 . GeO_2 glass was quenched from the melt with subsequent annealing. We studied the samples of cubic form with the size 3 mm. The SiO_2 and GeO_2 glasses were tested by x-ray diffraction before and after the 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 [27] capable to generate hydrostatic pressure up to 9 GPa [28]. 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 controlled at fixed magnitude 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 elsewhere [28]. The glass samples with bonded

gauges were coated by thin elastic soft films to avoid their reaction with the methanol-ethanol medium. The calibration experiments [28] allowed one 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 critical for time-dependent relaxation measurements, is much better, $\Delta V/V \sim 10^{-5}$.

Figure 1(a) shows the equation of state for g -SiO₂, obtained by the strain-gauge technique up to 9.1 GPa. The initial density was determined by the Archimedes method, $\rho_0 = 2.20 \pm 0.03$ g/cm³. The pressure dependence of bulk modulus [Fig. 1(b)] was calculated from the direct derivative of the equation of state, $B = -V(dP/dV)$ (the application of different numerical methods has given practically equivalent results). The initial bulk modulus $B \approx 40 \pm 3$ GPa is in good accordance with the ultrasonic bulk modulus for the same sample, $B_0 \approx 37 \pm 1$ GPa (the ultrasonic shear modulus $G_0 \approx 30 \pm 1$ 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 [22] and ultrasonic [23] studies.

After pressurization the sample was kept at $P = 9.0$ GPa for one hour. We have found a time-dependent volume decrease, which can be described by the logarithmic law, $\Delta V/V \propto \log t$, with a high accuracy (Fig. 2).

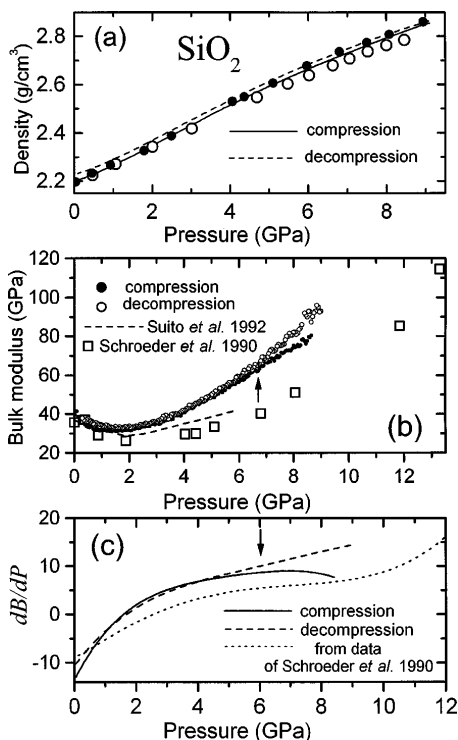


FIG. 1. High-pressure behavior of g -SiO₂: (a) The equation of state in comparison with the Brillouin scattering data of Schroeder *et al.* [22] (\bullet) and pressure-corrected data of Bridgman [21] from Ref. [22] (\circ); (b) bulk modulus; (c) pressure derivative of bulk modulus calculated using the polynomial interpolation for different data sets. The arrows indicate the starting pressure of unelastic behavior.

The $\rho(P)$ curve for decompression is obviously shifted toward higher densities [Fig. 1(a)].

Thus, the irreversible volume decrease in silica glass starts below the interval of pressure-induced AAT, 10–25 GPa, reported previously [8,10,13,14,16,17]. The anelastic behavior of glass can be detected by comparing the bulk modulus obtained from the directly measured volume change with the unrelaxed modulus (for example, from the Brillouin data) or comparing the direct and reverse $B(P)$ curves. From Figs. 1(b) and 1(c) one can estimate the starting pressure of anelastic behavior as 6–7 GPa, which is in good agreement with the recent theoretical molecular-dynamic calculation [29].

Germania glass is a more suitable object to study the AAT by the strain-gauge technique due to a lower pressure of the AAT. Two kinds of experiments were carried out for g -GeO₂ under pressure. In the first experiment, the glass sample was pressurized and depressurized under a continuous pressure change ($dP/dt \sim 0.1$ GPa/min), and in the second experiment the pressure increase was interrupted by the volume vs time measurements at fixed pressures for ~ 100 min or longer.

The direct (up to 9 GPa) and reverse equations of state are presented in Fig. 3. The samples have the initial density 3.7 ± 0.1 g/cm³ (by the Archimedes method) and the bulk modulus 30 ± 2 GPa slightly higher than those obtained in the previous studies. The main features of volume high-pressure behavior are similar to those from Ref. [12]. The difference between our data and those from Ref. [12] at high pressures can be probably due to the following reasons: first, a difference in the sample nature connected with some porosity or presence of nanocrystalline impurities, and, second, some systematic experimental error.

The results of volume vs time measurements are shown in Fig. 4. We have found the direct evidence of time-dependent irreversible relaxation at $P = 3$ GPa, in the region of divergence between the quasistatic and ultrasonic (or Brillouin) equations of state. However, the anelastic behavior seems to appear in g -GeO₂ even below, at $P \approx 2$ GPa, where the relaxed compressibility starts to increase (Fig. 5). The time dependence of volume decrease [Fig. 4(b)] is described by the curves, which are nearly

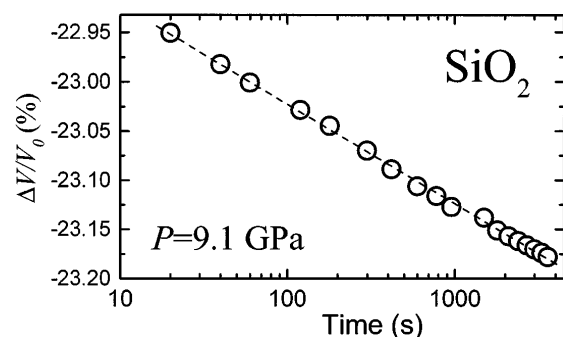


FIG. 2. Time dependence of relative volume for g -SiO₂ under pressure.

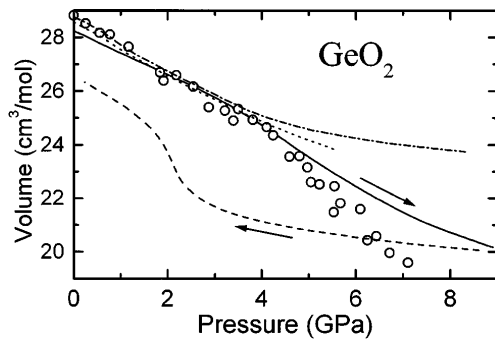


FIG. 3. The equation of state of g - GeO_2 (solid and dashed lines) in comparison with the volumetric data of Smith *et al.* [12] (\circ) and the Brillouin [20] (dash-dotted line) and ultrasonic [23] (dotted line) equations of state.

linear at a sufficiently long time interval in the $\Delta V/V$ vs $\log t$ coordinates. Another important feature is that the pressure increase between time measurement results in the returning of $V(P)$ curve to the dependence observed for a continuous pressure increase [Fig. 4(a)]. Such behavior corresponds to the variation of bulk modulus between the pauses for time-dependent volume measurements (Fig. 5). From the compressibility curve the reverse transformation begins at $P \approx 4$ GPa, where we have directly found the irreversible volume change with time.

The observed logarithmic kinetics of the AAT in g - GeO_2 and initial densification in g - SiO_2 contradict the conception about an ordinary crystal-crystal transition. The transformation kinetics of the latter can be

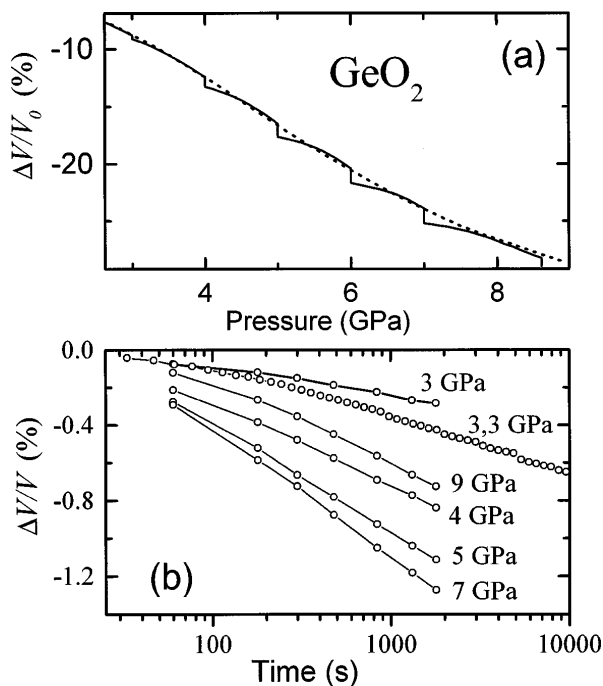


FIG. 4. Time-dependent volume study of g - GeO_2 : (a) Variation of volume with pressure in comparison with the equation of state for continuously increased pressure (dashed line); (b) time dependence of relative volume.

usually described by a rate equation for the transformed volume fraction, $x(t)$, which has the Avrami form $x(t) = 1 - \exp(-kt^n)$ ($\sim t^n$ for the initial stage). In particular, the α -quartz \rightarrow rutile transition in crystalline GeO_2 was found to obey this relation with the Avrami exponent $n \sim 1$ [30]. From the microscopic point of view, the kinetics of first-order transitions is defined by the nucleation and growth of a new crystalline phase. At low temperatures the kinetics of transitions is governed by elastic stresses and softening of definite phonon modes, rather than activation processes. Transitions in this case can be martensitic, first-order displacive, etc., but no logarithmic dependence was observed for such types of transitions [31].

The logarithmic kinetics is not a unique phenomenon and is inherent to various disordered systems [32–34]. The densified g - SiO_2 samples were also found to display the logarithmic time dependence of sound velocity change upon the room-pressure heating [35]. 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 process with the uniform distribution of energy barriers [35].

At the same time, the concept of different polymorphs in glasses is beyond doubt now. Moreover, the two-domain model correctly describes both relaxed and unrelaxed elastic properties of g - GeO_2 in the transformation region [12]. The x-ray absorption study of Itie *et al.* [11] has also indicated the two different sites (fourfold and sixfold) rather than a progressive site modification for the AAT in g - GeO_2 .

The understanding of the logarithmic kinetics in glasses should be based on both points of view mentioned above. 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 and, consequently, a wide distribution of atomic energies and stresses (see, for example, Ref. [36]). The distribution of intertetrahedral Si-O-Si (Ge-O-Ge) angles [37] and torsional angles of adjacent tetrahedra are of particular importance for the fourfold-to-sixfold

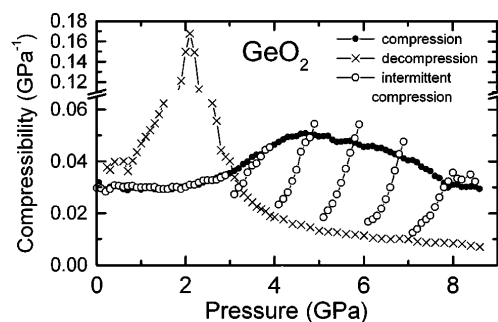


FIG. 5. Variation of compressibility of g - GeO_2 for different experimental conditions.

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 [12] with respect to the coordination change corresponds to the softening of different network parts. Considering the fourfold-to-sixfold transformation as a basic mechanism of the AAT for silica and germania glasses, we cannot exclude the contribution of cooperative movements of Si(O₄)_{1/2} tetrahedra to the logarithmic relaxation process.

From the macroscopic point of view, the logarithmic behavior results from the nonergodicity of glass. The returning of the $V(P)$ curve after pauses to the curve followed at the continuous pressure increase [Fig. 4(a)], when the glass “forgets” its own prehistory and previous changes, is another manifestation of a wide distribution of pressure spinodals for different network parts. After exposition at fixed pressures (~ 1 hour) the volume behavior of glass becomes “unrelaxed” (Fig. 5), and only an additional large enough pressure increase stimulates the further coordination change. This feature also distinguishes the transformation in glass from an ordinary crystal-crystal transition, where a pressure increase enhances, as a rule, the transition kinetics. Another very unusual feature is the overlap of regions of the direct (beginning at least at $P = 3$ GPa) and reverse (beginning at $P \approx 4$ GPa) coordination changes (negative hysteresis), obviously associated with the overlap of tails of the spinodal distributions for direct and reverse transformations.

Thus, the precise *in situ* kinetic measurements give the quantitative and qualitative information, important for theoretical interpretation of the AAT, and the direct proofs that the AAT's in g -GeO₂ and g -SiO₂ should not be treated as ordinary first-order transition. Further progress in understanding the nature of amorphous-amorphous transformations will be probably achieved as a result of the comparative kinetic study involving AAT in g -SiO₂, g -GeO₂, and amorphous ice.

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