Spectroscopic Evidence for Ultrahigh-Pressure Polymorphism in SiO_2 Glass

Motohiko Murakami[1] and Jay D. Bass[2]
[1]Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[2]Department of Geology, University of Illinois, 245, 1301 W. Green Street, Urbana, Illinois 61801, USA

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Acoustic wave velocities of SiO_2 glass were measured up to pressures of 207 GPa using newly developed Brillouin scattering spectroscopic techniques to address the nature of pressure-induced structural changes. The acoustic wave velocity data suggests three distinct pressure regimes, two of which correspond to changes in the Si-O coordination number with pressure, and one of which indicates the stability of sixfold-coordinated Si over a broad pressure interval from ~40–140 GPa. An anomalous increase in the effect of pressure on velocity at 140 GPa most likely corresponds to the onset of structural densification associated with an increase in coordination number from sixfold to a higher coordination state.

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Atomic rearrangements and phase transformations in glasses at high pressure and temperature (polyamorphism) are one of the most intriguing and puzzling topics in condensed matter physics. Anomalous properties, such as permanent densification of glasses subjected to high pressures, has attracted much attention to understanding the compression mechanisms of glasses. At low pressures the highly compressibility of oxide glasses is attributed to its network structure. At higher pressures, transitions to much denser amorphous states are due to changes in short-range order and coordination numbers. In this regard, SiO_2 glass is of fundamental interest as the prototype network-forming glass. The structural transitions of glassy materials under high-pressure conditions can lead to the development of new, technologically useful families of glasses that are chemically identical to currently known materials but with quite different thermodynamic, rheological, and other physical properties [1]. In the Earth sciences, dense, gravitationally stable melts (magmas) deep within the Earth have been proposed as a possible consequence of formation processes in the early Earth [2–11]. Knowledge of the physical properties of silicate glasses and melts under extreme pressure conditions is therefore also essential to modeling the thermal, chemical, and dynamical states of the Earth. SiO_2 glass is in fact the main analogue for all geologically relevant melts, in addition to being a material of enormous technological relevance. SiO_2 glass has therefore been extensively studied, and is considered to show polyamorphism [12], which closely resembles behavior associated with first-order phase transitions.

Previous studies on SiO_2 glass demonstrate anomalous behavior under pressure, such as permanent densification at <20 GPa (at room temperature). This densification is thought to result from an amorphous-amorphous transition primarily involving changes in intermediate-range order rather than a change in the coordination number of Si (the number of nearest-neighbor oxygen ions around silicon ions). A gradual change in the Si-O coordination number from fourfold (tetrahedrally-coordinated SiO_4) to sixfold (octahedrally-coordinated SiO_6), likely begins at about 10–20 GPa [13–18], with the sixfold-coordinated structure dominant by 40–45 GPa [17], as inferred by Raman scattering [13], infrared absorption [14], x-ray diffraction/absorption [15–17], Brillouin scattering [18,19], and x-ray Raman scattering [20]. Little is known of further densification trends and structural changes above ~50 GPa due to experimental challenges [21] and the lack of suitable *in situ* structural probes. Previous computational studies on SiO_2 glass have also provided critical information but have, however, focused primarily on lower pressures [22,23].

An experimental hurdle in studying the structures of glasses arises from the significant signal weakening and broadening in comparison to spectroscopy on crystals, thus making experiments at extremely high pressure especially difficult. Brillouin scattering has proven to be highly suitable for characterizing glasses under a range of pressure-temperature conditions. It is highly sensitive to the structural changes accompanying first-order phase transitions, and for detecting second-order transitions in the absence of a density jump, regardless of the state of the sample (glass, liquid or crystal). Although the available Brillouin data on SiO_2 glass have thus far been limited to moderate pressures [19], recent progress in Brillouin scattering measurements optimized for extreme high-pressure conditions enables us to measure acoustic velocities above 170 GPa [24] from samples compressed in a diamond anvil cell. Here we report the *in situ* Brillouin scattering results for SiO_2 glass up to 207 GPa, revealing a precisely determined systematic change in the velocity-pressure trajectory starting at ~140 GPa. We infer this to be a new amorphous-amorphous transition that is likely associated with the onset of a change in the coordination number to higher than sixfold.

In situ high-pressure Brillouin scattering measurements of acoustic wave velocities were carried out at room temperature in a symmetric diamond anvil cell [24]. An Ar laser with a wavelength of 514.5 nm was used as the probe beam. The incident laser beam was focused to a spot size of ~20 μm. The scattered light was analyzed by a 6-pass tandem Fabry-Perot interferometer. In all Brillouin experiments, we used a symmetric scattering geometry with a 50° external scattering angle. A prepressed plate of SiO_2 glass powder (Suprasil-P) was loaded into a 50 μm hole drilled in a rhenium gasket without a pressure-transmitting medium. The sample was compressed with 150 μm culet beveled diamond anvils (Fig. 1). Pressure was determined using the Raman T_{2g} mode of the diamond anvil [25] by measuring several points adjacent to the sample, yielding uncertainties typically within 1 GPa. Brillouin spectra were collected on the compressed SiO_2 glass at forty pressures from 13 to 207 GPa in 2–7 GPa increments. The collecting time for a single Brillouin scattering measurement was from 30 min to 24 h. At each pressure, the raw Brillouin spectra of Stokes and anti-Stokes peaks were fitted with Gaussian functions to obtain the peak positions.

As shown in Fig. 2, we obtained very sharp peaks from the acoustic modes of SiO_2 glass over the entire pressure range explored up to 207 GPa. At lower pressures up to 32 GPa, both longitudinal and transverse acoustic modes of SiO_2 glass were observed [Fig. 2(a)]. The peaks from longitudinal acoustic modes were masked by those of the diamond transverse acoustic modes under higher-pressure conditions [Fig. 2(b)]. The full width at half maximum (FWHM) of the transverse acoustic peaks at lower pressure [Fig. 2(a)] and higher pressure [Fig. 2(b)] were identical within the uncertainties [0.29(3) and 0.30(5) GHz, respectively]. Thus, no significant peak broadening was observed with pressure, indicating that the hydrostaticity in the sample chamber did not drastically change with increasing pressure. The high-quality Brillouin scattering signals under extreme pressure conditions resulted in velocity errors of 0.8% on average throughout the pressure range we explored. Figure 3 shows the results for the transverse acoustic wave velocities for SiO_2 glass as a function of pressure.

The transverse acoustic wave velocity of SiO_2 glass increases dramatically from 13 to 40 GPa in an exponential fashion, with no discontinuous changes that would indicate a first-order structural transition in this pressure range. The velocity increase with pressure is more gradual above ~40 GPa, in stark contrast to the behavior at lower pressure. The velocity data are remarkably well described by least-square fitting of a concave logarithmic function at least up to approximately 140 GPa, with an adjusted R-squared value of 0.9978. Over the pressure range from ~40 GPa to 140 GPa, the derivative of the transverse acoustic velocity (dV_S/dP) decreases gradually by an order of magnitude, from 35.9 to 2.5 (m/ sec)/GPa. In contrast, we found a significantly steeper velocity trajectory upon subsequent pressure increase from ~140 to 207 GPa compared to the lower pressure trend. This velocity profile exhibits an almost linear gradient with (dV_S/dP) of 6.0 (m/ sec)/GPa, an increase of more than a factor of 2 compared to the lower pressure trend below 140 GPa [2.5 (m/ sec)/GPa].

The pronounced changes in the pressure dependence of acoustic velocities of SiO_2 glass suggest the presence of amorphous-amorphous transitions that occur during compression [18,19]. Based upon our results and those of previous studies, we find that the variation in acoustic

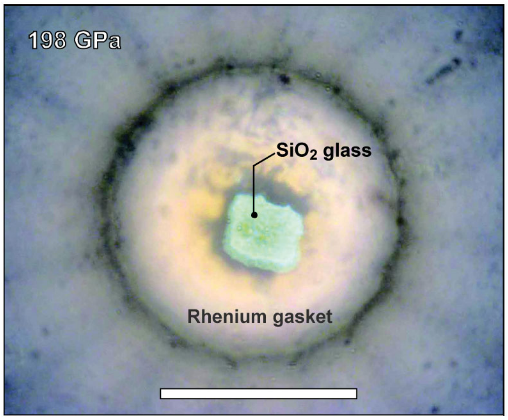

FIG. 1 (color). Microscopic image of the SiO_2 sample at 198 GPa as viewed through the diamond anvil. Scale bar indicates 100 μm. Outer ring shows the indentation of the rhenium gasket by the diamond anvil with 150 μm culet. The compressed SiO_2 glass is located in the inner hole.

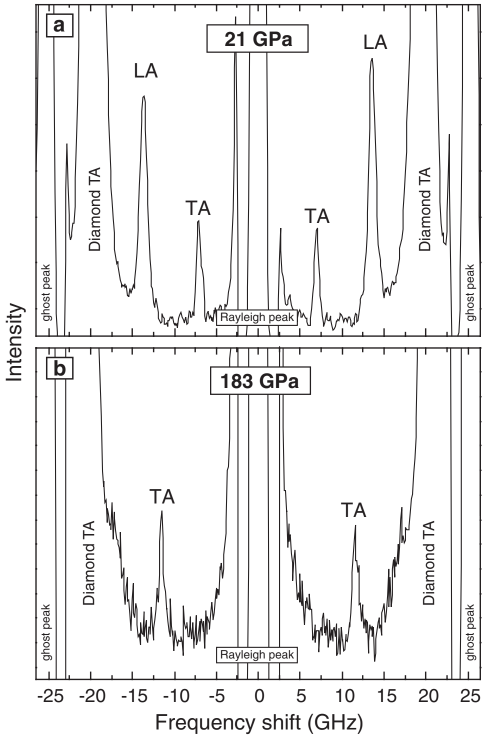

FIG. 2. High-pressure Brillouin spectra at 21 GPa (a) and 183 GPa (b). TA, transverse acoustic mode; LA, longitudinal acoustic mode of SiO_2 glass.

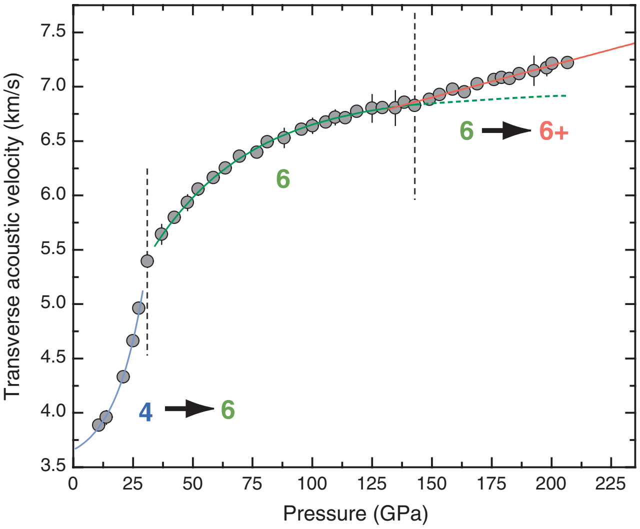

FIG. 3 (color). Transverse acoustic wave velocities of SiO_2 glass as a function of pressure up to 207 GPa at ambient temperature. The velocity trajectories for three distinct high-pressure regimes are shown as blue, green and orange lines, respectively. Numbers indicate the potential Si-O coordination number within each pressure regime. Approximate pressure boundaries for each Si-O coordinated structure are shown as the vertical dotted lines.

wave velocities with pressure fall into four distinct pressure regimes: (i) the lowest pressure region of rapid, permanent densification to perhaps ~20 GPa; (ii) a low-pressure regime up to ~40 GPa showing exponential growth; (iii) a high-pressure regime from ~40–140 GPa with a gentle gradient along a progressively flattening trend, and (iv) an ultrahigh-pressure regime above ~140 GPa, with an anomalously steep linear trend. Because region (i) does not involve changes in short-range order or coordination number, and has been discussed extensively in the literature (e.g., [26]), it will not be considered further here. The behavior in the low-pressure regime (ii) is in good agreement with previous studies of sound velocities[18,19], and with other independent optical measurements [13–17,20], all of which indicate that this velocity trajectory corresponds to a gradual change in Si-O coordination number from fourfold to sixfold in this pressure regime. Although there has been some controversy among previous studies regarding the onset pressure for coordination changes (ranging from ~5 to 20 GPa), our results indicate that the rapid velocity change starts by 13 GPa, if not lower. The amorphous-amorphous transition in region (i) without Si-O coordination change [26] may overlap with this transition at room temperature while being distinct at elevated temperature [27].

The gentle increase in velocity, following the convex-upward trend and without any discontinuous feature above ~40 GPa, can be interpreted as due to completion of the change in the Si-O coordination number from fourfold to sixfold, and subsequent compression of the sixfold-coordinated structure. That is, SiO_2 glass behaves as a single amorphous phase within this pressure regime to ~140 GPa, in excellent agreement with interpretations based on recent x-ray absorption measurements up to 50 GPa [17]. Previous x-ray Raman scattering measurements indicated the absence of the sixfold-coordinated structure even at 70 GPa [28], in apparent contradiction to our observations of both low- and high-pressure regimes, as well as the results of density measurements [17]. The electronic structure of silicon/oxygen in SiO_2 glass observed by measurements of Ref. [17] is, however, not always related to the coordination number, and the comparison of the x-ray Raman spectra between SiO_2 glass and "crystalline" stishovite in that study cannot rule out the possible presence of a sixfold-coordinated structure in the glassy material.

If the sixfold-coordinated structure continues to dominate at higher pressure, SiO_2 glass should behave as a single amorphous phase and the velocity change with pressure should be gradual and gentle. The sharp increase in the velocity gradient in the ultrahigh-pressure regime above 140 GPa, which is clearly inconsistent with the velocity trend at lower pressures, indicates a further structural change of SiO_2 glass that is likely associated with a gradual change in the coordination number from sixfold to a higher coordination state. Recent molecular dynamics simulations on SiO_2 liquid to 150 GPa indicate that an abrupt increase in the fraction of seven/eightfold coordination could occur around 140–150 GPa, with the average coordination number reaching 6.5 at 150 GPa [29]. The results of this simulation and our observations are in remarkably good agreement, strongly supporting our interpretation that 140 GPa marks the onset of an increase in the coordination number above sixfold. Based on the stability of pyrite-structured SiO_2 with Si in eightfold coordination, Loerting *et al.* [26] have suggested a transformation to higher Si coordination states in SiO_2 glass between 100–200 GPa, again in agreement with our observations. While we believe that the most plausible explanation of our data at $P > 140$ GPa is the onset of a change in the coordination number to higher than sixfold, we cannot with 100% certainty discount possible alternative explanations such as the formation of nanocrystalline SiO_2 nuclei [26], or even a transition to a superviscous fluid phase. It will be important in the future to explore all possible explanations of our results using other experimental probes and theoretical models of glass structure and properties.

The identification of a new densification mechanism for SiO_2 glass in the ultrahigh-pressure regime implies that at extremely high pressures, SiO_2 glass is far more compressed and dense than inferred from observations in the fourfold- and sixfold-coordinated pressure regimes. Although the effect of temperature [15] and chemical composition [30,31] needs further experimental exploration to obtain insight on the behavior of more complex melt systems, recent computational studies on SiO_2 liquid [29] suggests that the Si-O coordination change in the ultrahigh-pressure regime is enhanced with increasing temperature; that is, the transition to a higher coordination state than sixfold has a negative temperature-pressure slope. This would imply that elevated temperatures are likely to further stabilize the highly densified structure of chemically complex melts. Significantly, the results of Stixrude and Karki [32] indicate that higher Si-O coordination states than sixfold in $MgSiO_3$ liquid are possible around 125 GPa. This pressure corresponds to the D” region at the bottom of Earth's mantle, just above the core-mantle boundary, where some have proposed the existence of dense melts to explain highly unusual seismic structure.

In summary, we have investigated the structural changes of SiO_2 glass in the previously unexplored pressure range from 60–207 GPa by Brillouin scattering, significantly expanding our ability to explore the structural states of glass under extreme pressure condition, and contributing to an improved understanding of the anomalous behavior of the glassy materials and melts under pressure. Our results reveal the onset of a new densification mechanism for SiO_2 glass at a pressure 140 GPa. High-pressure ($P > 10$ GPa) polyamorphic transitions involving coordination changes in Si are characterized by three distinct pressure regimes: a low-pressure regime up to 40 GPa, with a gradual transition from fourfold to sixfold-coordination; a high-pressure regime from 40–140 GPa dominated by sixfold-coordinated silicon; and a newly discovered ultrahigh-pressure regime above 140 GPa in which there is a transition from sixfold to a higher coordination state of Si. The identification of a new densification mechanism above 140 GPa strongly suggest that glasses and melts are probably far denser under ultrahigh-pressure conditions than previously envisioned. These results should provide a basis for evaluating the structural states of more compositionally complex silicate glasses and melts. The existence of highly densified SiO_2 glass with Si-O coordination numbers higher than 6 suggests the possible occurrence of gravitationally stable dense magmas deep within the Earth [2–11], and may have profound consequences for the compression mechanisms of network-structured glasses at ultrahigh-pressure conditions.

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