Sound speed and refractive index of amorphous CaSiO$_3$ upon pressure cycling to 40 GPa

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Abstract

Brillouin spectroscopy at room temperature and pressure up to 40 GPa documents nearly identical elasticity and refractive index of amorphous CaSiO$_3$ created by two different methods: temperature-quenching the melt at ambient pressure, and pressure-amorphizing crystalline wollastonite at room temperature. We find reproducible hysteresis of 0 to 8% on pressure cycling that is small relative to the 30% to 60% changes in shear and longitudinal wave velocities over this pressure range. Together with observed changes in refractive index and previous results from Raman spectroscopy, these measurements reveal a continuous and reversible change in atomic-packing induced by pressure. Unlike many other silicate glasses, amorphous CaSiO$_3$ exhibits highly reproducible properties, behaving smoothly and reversibly under pressure cycling and possessing similar structure and elasticity regardless of synthesis paths for the starting material, which suggests that the amorphous solid may mimic the liquid over the pressure range investigated.
1. Introduction

Knowledge of the density and elasticity of silicate melts at high pressures is important for understanding the deep Earth, because buoyancy drives melt migration, which in turn plays a key role in the thermal-chemical evolution of our planet. Laboratory measurements of melt properties at simultaneously high temperatures and pressures are challenging, however (Sanloup et al., 2013; Ahart et al., 2014; Andrault et al., 2020). We can instead examine silicate glasses at room temperature, which provide frozen snapshots of silicate melt structure under compression and can be studied using a wide range of probes up to high pressures (Murakami and Bass, 2010, 2011; Petitgirard et al., 2017; Kono et al., 2018; Mysen and Richet, 2019). The primary concern with this approach is in establishing the degree to which the kinetically frozen structure of the glass at 300 K mimics the atomic-packing configuration of the melt, as reflected in such bulk properties as density and elasticity. Reversibility upon compression and decompression is a pre-requisite for inferring that relevant degrees of freedom remain unhindered in the glass at 300 K. For example, it is known that some properties of SiO$_2$ and MgSiO$_3$ glasses show evidence of kinetic hindrance (i.e., lack of reversibility upon compression and decompression) and are therefore not entirely representative of the properties of the corresponding melts (Grimsditch, 1984; Sanchez-Valle and Bass, 2010). In contrast, minimal hysteresis has been observed in Raman spectroscopy, IR absorption spectroscopy, x-ray diffraction, and x-ray emission spectroscopy of amorphous CaSiO$_3$, on compression and decompression (Kubicki et al., 1992; Serghiou et al., 2000; Shimoda et al., 2005; Shim and Catalli, 2009). This reversibility suggests that CaSiO$_3$ glass may reflect the physical properties (e.g., density, elasticity, structure) of the melt over a wide range of pressure.

To further compare amorphous CaSiO$_3$ samples that have experienced different pressure-temperature histories, we characterize the elasticity and refractive index of amorphous CaSiO$_3$ at ambient temperature to ~40 GPa using two different types of samples: one formed by solid-state pressure-induced amorphization, and the other formed by thermal quenching from the melt at ambient pressure. We also make measurements during multiple cycles of compression and decompression. The apparent redundancy in measurements is by design; we generate high-pressure amorphous CaSiO$_3$ from multiple starting materials and use multiple compression
cycles as a way to check both the reproducibility and reversibility of properties. To be clear, we refer to a sample lacking long-range crystalline order as being amorphous and reserve the term glass for the thermally quenched melt.

2. Experimental Method

Melt-quenched material from two different sources gave indistinguishable results and will therefore be described as the “glass” in all figures and subsequent text: the glass used by Richet et al. (1993) and the glass used by Kubicki et al. (1992). The glasses were polished on two sides to ~20 μm thickness, placed in the sample chambers of diamond-anvil cells with 350 μm culets and rhenium gaskets, and surrounded by an argon pressure medium.

Natural wollastonite crystals from Riverside, CA, with ~millimeter grain size were ground into a fine powder (< 3 μm grain size) with a mortar and pestle. The powder was loaded into the 140 μm diameter hole of a rhenium gasket pre-indentated to 30 μm thickness. The culet diameter of the diamond anvils was 350 μm.

The crystalline powder was pressure-amorphized and studied by the following procedure. The powder sample was pressure-cycled twice to ~40 GPa with no pressure medium, re-loaded into a diamond cell with a methanol-ethanol-water pressure medium (mass ratio 16:3:1), compressed to 42 GPa and decompressed to 0 GPa. The powder became mostly amorphous upon compression to 35 GPa, and was almost completely amorphous after three pressure cycles to ~40 GPa.

Amorphization was confirmed with x-ray diffraction patterns collected during the first compression and after the final decompression at beamline 12.2.2 of the ALS, using 25 keV x-rays focused to a 10 μm spot size (Yan et al., 2010). Amorphization was indicated by a nearly-complete disappearance of crystalline x-ray diffraction peaks (Fig. 1). This is consistent with the previous detection of partial amorphization between 17 and 26 GPa using energy dispersive x-ray diffraction (Serghiou and Hammack, 1993).

Note that we also attempted to study single crystal wollastonite, but sets of parallel cracks developed in the sample at pressure between 2 and 3 GPa, preventing detection of Brillouin peaks. No data for single crystal wollastonite are reported here.
Brillouin spectra were collected in 40° equal-angle forward-scattering, as well as 180°
backscattering at UC Berkeley, using the following optical path: the beam from a 532 nm Verdi
laser was expanded to 10 mm using two lenses, apertured using a 1.5 mm vertical slit, and
focused onto the sample using a 50 mm focal length achromat. Fig. 2 shows an optical image of
a sample in a diamond anvil cell with the laser focused onto it. Scattered light was collected by
an identical achromat, apertured with a 1.5 mm vertical slit, and focused onto the pinhole of a
Sandercock Tandem Fabry-Perot Interferometer using a 40 cm focal length focusing lens.

Typically, one compression-decompression cycle was completed over the course of one to
three days. The pressure was changed approximately once per hour.

Longitudinal and transverse acoustic velocities, $V_P$ and $V_S$, are determined from the
frequency shifts of Brillouin peaks in the forward scattering geometry, $\Delta f$, using the equation:

$$ V = \frac{\lambda_0 \Delta f}{2 \sin(\theta/2)} $$  \hspace{1cm} (1)

where $\lambda_0$ is the laser wavelength (532 nm), and $\theta$ is the scattering angle (40°) (Whitfield et al.,
1976). The product of refractive index, $n$, and longitudinal velocity is determined from the
frequency shift in the backscatter direction, $\Delta f_{P,b}$:

$$ nV_P = \frac{\lambda_0 \Delta f_{P,b}}{2} $$  \hspace{1cm} (2)

Dividing (2) by (1),

$$ n = \sin(\theta/2) \frac{\Delta f_{P,b}}{\Delta f_P} $$  \hspace{1cm} (3)

where the subscript $P$ refers to longitudinal wave, and $b$ refers to backscatter geometry
(Shimizu et al., 1998).

The accuracy of the system was found to be $\sim 1\%$, calibrated using the Brillouin spectra
from single crystals of quartz at ambient pressure and confirmed by measuring CaSiO$_3$ glass
between 0 and 20 GPa at GFZ in Potsdam using 60° equal angle scattering geometry. Scatter in
peak positions collected from different rotations about the diamond cell axis was 0.5 to 1%.

Pressure was measured from the fluorescence lineshift of two to four rubies spheres
placed near the edge of the gasket hole (Mao et al., 1986). All high-pressure measurements
were obtained at room temperature.
3. Results

3.1 Velocity and refractive index

The main result of the Brillouin measurements is that melt-quenched and solid-state amorphized samples exhibit identical velocities upon compression and decompression, with up to 8% hysteresis, and the results are reproducible upon multiple quasi-hydrostatic pressure-cycling to \( \sim 40 \text{ GPa} \) (Fig. 3a). In contrast, measurements under non-hydrostatic loading show a systematic reduction by \( \sim 4\% \) in velocity (see the Appendix for details); the main text describes the quasi-hydrostatic data only.

The hysteresis in \( V_P \) and \( V_S \) is a small fraction of the total change across the pressure range studied here: 7% and 8% maximum hysteresis compared to 60% and 30% changes in \( V_P \) and \( V_S \), respectively (Fig. 3a). Moreover, \( V_P \) and \( V_S \) increase smoothly with pressure, and no kinks are observed in velocity-pressure curves upon compression or decompression (Fig. 3a). As a percentage of the overall change, hysteresis is largest for the index of refraction, \( n \). During one decompression run, \( dn/dP \) is negative in the pressure range \( \sim 20 \) to \( 35 \) GPa (Fig 3b).

3.2 Lower bound on density

The bulk sound speed, \( V_\phi \), can be calculated for each data point by

\[
V_\phi = \sqrt{V_P^2 - \frac{4}{3} V_S^2}
\]  

(4)

The result, shown in Fig. 4, is fitted to a polynomial, \( V_\phi = 4.96 + 0.096P - 0.00043P^2 \), and integrated to find a lower bound on density change:

\[
\int_0^P \frac{1}{V_\phi^2} dP = \int_0^P \frac{\rho}{K_{S,\text{GHz}}} dP \leq \int_0^P \frac{\rho}{K_S} dP \leq \int_0^P \frac{\rho}{K_T} dP \leq \Delta \rho
\]  

(5)

The first inequality in equation (5) results from the fact that the adiabatic bulk modulus at GHz frequency, \( K_{S,\text{GHz}} \), which is probed with Brillouin spectroscopy, may be larger than the low frequency version, \( K_S \), due to phonon dispersion. The second inequality results from the fact that \( K_S \) is larger than the isothermal bulk modulus, \( K_T \), which controls compression in a diamond cell. Their ratio, \( K_S/K_T \), equals \( (1 + \alpha \gamma T) \), where \( \alpha \) is the coefficient of thermal expansion and \( \gamma \) is the Grüneisen parameter. The value \( \alpha \gamma T \) is of order 1% at room temperature. The third inequality is due to possible discontinuous structural changes, the analog of crystal-structural
phase transitions for crystalline materials. If they take place in the amorphous samples, these structural transitions cause $\Delta \rho/\Delta P$ at relatively large strain amplitude (i.e. compression by tightening of the diamond cell) to be larger than $\rho/K_T$ at small strain amplitude (i.e. the strain amplitudes associated with phonons and measured by Brillouin spectroscopy).

Adding $\Delta \rho$ to the density at ambient pressure, $\rho_0$, we determine a lower bound for the density at high pressure,

$$\rho \geq \rho_0 + \int_0^P \frac{1}{\nu_\phi^2} dP \quad (6)$$

The result is plotted in Fig. 5 and compared to two values for similarly low-density crystalline polymorphs, wollastonite and walstromite, as well as to the high-density polymorph perovskite. Fig. 5 shows that the density of amorphous CaSiO$_3$ increases by at least 33% from ambient pressure to 40 GPa. Amorphous CaSiO$_3$ is much more compressible than calcium perovskite over this range.

In fact, amorphous CaSiO$_3$ may be more compressible than suggested by the lower bound determined here (Fig. 5). For comparison, Petitgirard et al. (2015) argues that structural relaxation in MgSiO$_3$ causes an additional 20% density increase in the pressure range 0-35 GPa, in addition to the 20% density increase inferred by integrating the Brillouin data from Sanchez-Valle and Bass (2010).

4. Discussion

4.1 Relative stability of amorphous CaSiO$_3$

Four observations characterize the metastability of amorphous CaSiO$_3$ at room temperature and pressures from 0 to $\sim$40 GPa: (1) limited hysteresis in $V_p$ and $V_S$; (2) smooth changes in velocity vs. pressure (i.e., no kinks); (3) continuous pressure variation of Raman and infrared spectra of melt-quenched amorphous CaSiO$_3$ observed in previous studies (Kubicki et al., 1992; Shim and Catalli, 2009); and (4) the nearly identical sound speeds observed here and Raman spectra observed by Serghiou et al. (2000) for melt-quenched CaSiO$_3$ and compression-amorphized CaSiO$_3$. Table 1 and Fig. 7 show that observations (1) and (2) for amorphous CaSiO$_3$ clearly differ from the behavior observed for amorphous MgSiO$_3$ and SiO$_2$ under pressure. This
difference between CaSiO$_3$ and other silicates may be associated with the relatively small
density difference between amorphous CaSiO$_3$ and its ambient pressure crystalline polymorph,
wollastonite (Table 1). In fact, it is possible that the reproducible properties of different
amorphous CaSiO$_3$ samples, regardless of synthesis path (solid-state amorphization vs.
thermally quenched melt), and the similarity of density between amorphous solid and crystal
may both reflect a local structure that is common to liquid, crystal and solid amorphous CaSiO$_3$,
and which is energetically-favorable and accessible from many temperature routes. This
interpretation is an extension of the proposal of Ai and Lange (2008) that liquid CaSiO$_3$ has a
local structure close to that of the pyroxenoid crystal from which it melts.

To illustrate the meaning of the relative (meta)stability of amorphous CaSiO$_3$, we describe
the relevant energy landscape (Fig. 6). With compression of at least 33% up to 40 GPa, the
energies of crystalline and amorphous states increase substantially. For example, the integral of
$PdV$ from ambient pressure to 40 GPa is at least 2.8 eV/atom for amorphous CaSiO$_3$. At all
pressures from 0 to 40 GPa, potential energy barriers of at least $k_B T$ (25 meV per degree of
freedom) block the amorphous sample from finding a deeper local minimum of a significantly
different structure. Upon decompression, the sample presumably follows the same
transformational path, with a small amount of hysteresis. (Alternatively, it is possible that the
decompression path is slightly different, as suggested by the one decompression run in which
$dn/dP$ is negative in the pressure range $\sim$20 to 35 GPa.) Upon further decompression, the
sample finds its way back to the original potential energy minimum at ambient pressure.
Moreover, the same local minima of amorphous structures are reached by room temperature
compression of wollastonite powder, meaning the energy barrier between wollastonite and
amorphous CaSiO$_3$ is less than $\sim$25 meV per degree of freedom at $\sim$40 GPa and room
temperature, as shown in schematic C of Fig. 6.

Amorphous SiO$_2$, by contrast, becomes trapped in a high-pressure structure upon
decompression to ambient pressure at 300 K, with distinct intermediate-range structure (but
identical nearest-neighbor coordination) relative to the starting material. High-temperature
annealing is required to reverse the changes in structure and bulk properties (Grimsditch,
1986). The behavior of amorphous MgSiO$_3$ is in-between the behaviors exhibited by amorphous
CaSiO$_3$ and SiO$_2$. The kinks in velocity versus pressure and the reversibility of sound speed with 12% hysteresis upon pressure cycling of MgSiO$_3$ suggest the presence of a significant transition to a high-pressure amorphous structure upon compression, which is reversible upon decompression to ambient pressure.

4.2 Structural changes with pressure

Raman spectroscopy is a sensitive probe of the structure of amorphous CaSiO$_3$ (Serghiou et al., 2000; Shim and Catalli, 2009). Upon room temperature compression, Shim and Catalli (2009) document the gradual disappearance of bending modes associated with SiO$_4$ tetrahedra and appearance of a stretching mode near 800 cm$^{-1}$ in the pressure range $\sim$20 to 50 GPa. Upon decompression, the reverse occurs. This suggests a gradual and reversible structural transition from mostly 4-fold coordinated Si to a mixture of 4-fold and higher coordinated Si at high pressures (Shim and Catalli, 2009). Index of refraction measurements in the present study are consistent with this structural change. The index of refraction increases due to increasing density up to $\sim$20 GPa, but from 20 to 40 GPa the density change is countered by decreasing polarizability as silicon changes from covalent toward ionic bonding (tetrahedral to octahedral configurations) (Fig. 3b). The change in slope at 30 GPa is subtle upon compression, but more dramatic on decompression at 20 GPa. Hence, not only do amorphous CaSiO$_3$ samples synthesized by different methods exhibit the same bulk and vibrational properties at ambient conditions, but they are gradually transformed to a new, higher-coordination structure under pressure that then reverts upon return to ambient conditions. The final, recovered state of the sample is indistinguishable by Brillouin and Raman spectroscopy from the starting material.

In addition to the changes upon pressure cycling at room temperature, subtle variations in the structure of amorphous CaSiO$_3$ have been documented during pressure cycling at high-temperature. Shimoda et al. (2005) find that amorphous CaSiO$_3$ densifies by 3%, and one of its Raman modes changes by a small amount (6 cm$^{-1}$) upon cycling pressure to 7.5 GPa at 500 °C. No change is detected in x-ray emission, x-ray diffraction or IR absorption spectroscopy. Shimoda et al. (2005) suggest that the densification is due to a change in the intermediate range scale, such as a decrease in cluster size, but that any change “in Si-O-Si bond angle is very
small”. The slight changes observed upon cycling to 7.5 GPa and 500 °C suggest that high temperature can induce minor irreversible structural relaxation of amorphous CaSiO₃.

4.3 Alternate synthesis routes for amorphous CaSiO₃

A third route to synthesizing amorphous CaSiO₃ is by room-temperature decompression of the perovskite phase that is formed above 15 GPa at elevated temperatures (Ringwood and Major, 1971; Kanzaki et al., 1991). Although less is known about this decompression-amorphized material, measurements of the index of refraction and of the $^{29}$Si NMR chemical shift provide evidence that it is similar if not identical to the conventional (melt-quenched) and pressure-amorphized materials examined here (Table 2).

A fourth route to synthesizing amorphous CaSiO₃ is a variation on the conventional method: thermally quenching a high-pressure melt. While this route has only been used in one study we know of, the ambient-pressure Raman spectrum after decompressing this glass is similar to that of the conventional glass (thermally quenched from the melt at ambient pressure) and the pressure-amorphized wollastonite (Serghiou et al., 2000).

4.4 Comparison with other amorphous solids

Altogether, we find that amorphous CaSiO₃ exhibits especially reproducible properties at ambient conditions and under pressure cycling, with four synthesis routes generating amorphous CaSiO₃ having nearly identical elastic and vibrational properties (Table 1). Reproducibility upon pressure cycling and insensitivity to synthesis route has also been documented in other glasses, including H₂O (Bowron et al., 2006; Klug et al., 1989; Mishima, 1994; Mishima et al., 1984), As₂O₃ (Soignard et al., 2008), GaSe₄ (Kalkan et al., 2014), and AsSe (Ahmad et al., 2016). In addition, amorphous GeO₂ and amorphous Be₂O₃ have been pressure cycled to and from high pressure amorphous structures, but have not been pressure-amorphized from their crystalline forms to-date (Fujisawa et al., 1994; Wolf et al., 1992; Prakapenka et al., 2004; Smith et al., 1995; Grimsditch et al., 1988; Cherednichenko et al., 2016; Nicholas et al., 2004). Finally, amorphous SiO₂ can be synthesized by compression amorphization, but after pressure cycling, high-temperature annealing is required to reestablish
the low-pressure structure of silica glass (Grimsditch, 1984, 1986; Grimsditch et al., 1994; Hemley et al., 1988).

5. Implications

The structure and bulk properties of amorphous CaSiO$_3$ are reproducible and reversible under pressure, especially as compared with results for other silicate glasses. This suggests that a local structure is common to amorphous, crystalline, and liquid CaSiO$_3$. Moreover, the reproducibility of bulk properties of amorphous CaSiO$_3$ at pressures from ambient to 40 GPa suggests that the amorphous solid may mimic the liquid over this pressure range.

6. Acknowledgements

We thank Pascal Richet, Rus Hemley, and Bjorn Mysen for providing us samples of CaSiO$_3$ glass and Tim Teague for providing us with natural crystalline wollastonite. We thank Rebecca Lange, Dan Shim, David Chandler, Rus Hemley and Bjorn Mysen for helpful discussions. Work was supported by the University of California, including the Miller Institute for Basic Research in Science, and the US DOE/NNSA under award DE-NA-0002006, CDAC. The Advanced Light Source is supported by the U.S. DOE under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.

Appendix: Effect of non-hydrostatic stress

The velocities and refractive indices presented in the main text were measured in samples compressed quasi-hydrostatically during seven pressure cycles, yielding ±2% scatter in $V_p$, $V_S$, and $n$. Data were omitted from the main text from the three pressure cycles in which the sample was pressed against both diamonds without a significant layer of soft medium to distribute stress. Figs. 8-9 show these data.

Two of the previously-omitted pressure cycles were from the wollastonite powder sample that was purposefully loaded without a pressure medium. One was the second pressure cycle of a sample loaded with an argon medium. In this case, when the laser was focused on the glass sample, there was no Brillouin peak from argon (i.e. no peak at ~8 GHz in the cyan spectrum in
Fig. 9), meaning that a negligibly thin layer of argon separates the sample from the diamond anvil. Instead, the majority of the argon must have been squeezed away from the sample region during the two pressure cycles. During these three compression runs without a substantial pressure medium, Fig. 8 shows that non-hydrostatic stress (and resulting strain) cause a 4% systematic reduction of sound speed between 20 and 40 GPa.

We hypothesize that changes in atomic packing (coordination changes) during non-hydrostatic compression cause the observed sound-speed reduction; shear stresses activate rearrangements of atoms into denser packings, which cause decreases in $V_P$ and $V_S$ (Fig. 8). This hypothesis is also consistent with most of the decompression data: sound speeds during decompression following non-hydrostatic compression are slightly lower than other decompression data between 40 and 20 GPa (empty cyan squares in Fig. 8). Nonetheless, as in the case of quasi-hydrostatic compression, sound speeds return to their original values upon decompression to 0 GPa.
References


Kubicki, J.D., Hemley, R.J., Hofmeister, A.M., 1992. Raman and infrared study of pressure-induced structural changes in MgSiO$_3$, CaMgSi$_2$O$_6$, and CaSiO$_3$ glasses. American Mineralogist 77, 258–269.

Mao, H.K., Xu, J., Bell, P., 1986. Calibration of the Ruby Pressure Gauge to 800 kbar Under


Smith, K.H., Shero, E., Chizmeshya, A., Wolf, G.H., 1995. The equation of state of polyamorphic...


Yin, C.D., Okuno, M., Morikawa, H., Marumo, F., Yamanaka, T., 1986. Structural analysis of

Table 1: Comparison between compression behaviors of silicate glasses in the system CaO-MgO-SiO$_2$. Columns list maximum hysteresis and the pressures of kinks in $V_P$ or $V_S$ as functions of pressure, and the ratio of densities of glass to their crystalline polymorphs at 0 GPa. The density of CaSiO$_3$ glasses are from Shimoda et al. (2005), Taniguchi et al. (1997) and Yin et al. (1986), while those of CaMgSi$_2$O$_6$, MgSiO$_3$ and SiO$_2$ glasses are from Shimoda et al. (2005), Yamada et al. (2010), and Brückner (1970), respectively. Hysteresis and kinks are from this study for CaSiO$_3$, Sanchez-Valle and Bass (2010) for MgSiO$_3$, and Zha et al. (1994) for SiO$_2$.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Max hysteresis</th>
<th>Pressure of kinks in $V_P$ and $V_S$</th>
<th>$\rho_{\text{glass}}/\rho_{\text{crystal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSiO$_3$</td>
<td>7%</td>
<td>None</td>
<td>1, 0.99, or 0.92</td>
</tr>
<tr>
<td>CaMgSi$_2$O$_6$</td>
<td>-</td>
<td>-</td>
<td>0.87</td>
</tr>
<tr>
<td>MgSiO$_3$</td>
<td>12%</td>
<td>8 GPa</td>
<td>0.86</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>24%</td>
<td>3, 20 GPa</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 2: Properties of amorphous CaSiO$_3$ synthesized by three distinct means. All values are at room temperature, with upper and lower entries indicating measurements at ambient pressure and 41 GPa, respectively.

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_P$ (km/s)</th>
<th>$V_S$ (km/s)</th>
<th>$n$</th>
<th>$^{29}$Si NMR shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt-quenched glass</td>
<td>6.3 (±0.1)</td>
<td>3.4 (±0.1)</td>
<td>1.63 (±0.03)</td>
<td>-81.5</td>
</tr>
<tr>
<td>Compression-amorphized</td>
<td>9.3 (±0.2)</td>
<td>4.7 (±0.1)</td>
<td>1.78 (±0.05)</td>
<td>-</td>
</tr>
<tr>
<td>Decompression-amorphized</td>
<td>6.3 (±0.1)</td>
<td>3.3 (±0.2)</td>
<td>1.63 (±0.03)</td>
<td>-</td>
</tr>
<tr>
<td>References</td>
<td>This study</td>
<td>This study</td>
<td>This study and Kanzaki et al. (1991)</td>
<td>Ringwood and Major (1971)</td>
</tr>
</tbody>
</table>
Figure 1: (Top) Raw x-ray diffraction images before and after three pressure cycles to 40 GPa showing the amorphization of polycrystalline wollastonite. (Bottom) Integrated diffraction patterns showing the similarity of structure among three amorphous samples: the melt-quenched glass before compression (blue), the same glass after two pressure cycles to 40 GPa (green), and polycrystalline wollastonite after three pressure cycles to 40 GPa (red). Gaps in integrated data are shown for angles at which diffraction from diamond or gasket obscures the data from the sample. The system background has been subtracted, and the resulting uncertainty is indicated by the error bar at bottom right.
Figure 2: (a) Schematic and (b) photo of sample chamber during Brillouin experiments. A laser beam (yellow) is focused onto the CaSiO$_3$ glass sample (orange outline) inside a gasket hole compressed between diamond anvils, causing fluorescence in four rubies (red and white) located near the edge of the gasket hole. A halogen lamp illuminates the gasket (dark red). Scattered laser light illuminates the edges of the diamond facets (green). Colors in the photo have been low-pass filtered with a Kodak Wratten #22 filter, which blocks most of the elastically scattered laser light.
Figure 3: (a) Longitudinal ($V_P$) and transverse ($V_S$) wave velocities, and (b) index of refraction ($n$) of amorphous CaSiO$_3$ as a function of pressure during compression (solid symbols) and decompression (open symbols) at room temperature. Colors and shapes indicate starting material: melt-quenched CaSiO$_3$ glass (black squares), and pressure-amorphized wollastonite in a pressure-transmitting medium (red triangles). Error bars on individual data points are from scatter during rotations about the diamond-cell axis, and are approximately the same size (0.5% to 1%) as the systematic uncertainty from the Brillouin system (not shown here). Line segments connect data points during individual decompression runs in panel (b).
Figure 4: Bulk sound speed in amorphous CaSiO₃ as a function of pressure upon quasi-hydrostatic compression from 0 to 44 GPa (squares and triangles), a quadratic fit to the data (purple curve), and comparison with values for the perovskite (Shim et al., 2000) and pseudowollastonite (Yang and Prewitt, 1999) polymorphs. Colors and shapes of symbols follow Fig. 3.
Figure 5: Pressure-density equation of state constrained here. Purple curve shows lower bound on density of amorphous CaSiO$_3$ from equation 6 using $\rho_0$ from Shimoda et al. (2005), and is compared to densities of crystalline forms of CaSiO$_3$: perovskite (Shim et al., 2000), walstromite (Joswig et al., 2003), wollastonite (Ohashi, 1984), and pseudowollastonite (Yang and Prewitt, 1999).
Figure 6: Equilibrium phase diagram of CaSiO$_3$ overlain by thick arrows that show three amorphization transitions. Insets A, B, and C show schematics of the potential energy landscape at conditions of each amorphization transition: (A) Melt-quenched glass formation (Vo-Thanh et al., 1996; Kubicki et al., 1992; Ringwood and Major, 1971) and the glass used in this study; (B) amorphization by decompression of perovskite (Ringwood and Major, 1971; Kanzaki et al., 1991); (C) amorphization by compression of wollastonite (Serghiou and Hammack, 1993) and this study. Black lines mark equilibrium phase boundaries between crystalline phases, following Akaogi et al. (2004). Colors represent different structures and phases of CaSiO$_3$: amorphous (purple), wollastonite (orange), walstromite (dark yellow), larnite plus titanite (light yellow), perovskite (green), liquid (blue).
Figure 7: Comparison between sound speeds upon compression and decompression of silicate glasses in the system CaO-MgO-SiO$_2$. Experimental runs to maximum pressure are compared between this study (CaSiO$_3$, thick black curve), Sanchez-Valle and Bass (2010) (MgSiO$_3$, blue curve), and Zha et al. (1994) (SiO$_2$, thin red curve). Arrows indicate the direction of hysteresis loops. The curves for SiO$_2$ and MgSiO$_3$ were copied from figures in the corresponding publications. The curve for CaSiO$_3$ was generated from Fig. 3.
Figure 8: All sound speeds (a) and refractive indices (b) measured in the present study upon compression (solid symbols) and decompression (open symbols), as a function of pressure, including non-hydrostatically compressed samples. Black squares and red triangles represent, respectively, melt-quenched and pressure-amorphized material that is quasi-hydrostatically compressed. The powder compressed with no pressure medium is shown as blue circles, while a pressure run in which a melt-quenched glass bridged the two diamond anvils is shown in cyan squares. Sound speeds derived from the raw data of Fig. 9 are circled in pink. Line segments connect data points during individual decompression runs in panel (b).
Figure 9: Brillouin spectra at 34 (±1) GPa obtained in five different compression runs that are described to the right of the figure. Photon counts are normalized to one-minute collection time, vertically offset, and plotted versus the frequency shift of the photon. Black dashed lines mark the positions of Brillouin peaks in non-hydrostatically compressed samples (both the powdered wollastonite compressed with no pressure medium, and the glass starting material that is separated from the gasket by argon but not from the diamond anvils). Black peaks at ±8 GHz are from longitudinal phonons in argon, peaks at ±16 GHz are from shear phonons in diamond, and the apparent broadening of diamond peaks in the red spectrum is caused by longitudinal phonons in methanol-ethanol.