Pressure-Amorphized SiO$_2$ α-Quartz: An Anisotropic Amorphous Solid

L. E. McNeil

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255

M. Grimsditch

Materials Science Division, Building 223, Argonne National Laboratory, Argonne, Illinois 60439

Recent experiments [Kruger and Jeanloz, Science **249**, 647 (1990)] have shown that the pressure-induced amorphous form of AlPO$_4$ reverts to its original "single-crystal" form on release of pressure. Here we present the results of a Brillouin scattering study of the sister compound α-quartz, SiO$_2$ (which can also be pressure amorphized but retains its amorphous structure on release of pressure), which shows that the recovered material is not elastically isotropic but retains a "memory" of its original crystallographic orientation.

Amorphous solids are typically made by rapid cooling of a liquid and thereby retain the disordered structure of the liquid state together with its isotropy. Amorphous solids can also be produced from crystalline solids in disordering transitions induced by the application of pressure [1–12]. Samples produced in this fashion have been found to have x-ray-diffraction patterns and vibrational spectra which are typical of amorphous structures, including the melt-quenched forms of the same compounds. Although never explicitly stated, it appears that it is often assumed that the pressure-amorphized solid, like the melt-quenched one, should also be isotropic and therefore display no directional dependence in its properties. We report here the surprising result that pressure-amorphized SiO$_2$ retains a "memory" of its crystal orientation—the velocity of longitudinal acoustic waves in the amorphous material is different for propagation parallel and perpendicular to the direction defined by the original [001] direction of the starting crystal. Thus the structure produced by hydrostatic pressure, while amorphous in the sense that it lacks long-range order, is *not* isotropic.

Pressure-induced amorphization has been observed in a variety of materials, including SiO$_2$ [4,6,7], AlPO$_4$ [5,10], H$_2$O [1], SnI$_4$ [2,3], LiKSO$_4$ [8], CaAl$_2$Si$_2$O$_8$ [9], Ca(OH)$_2$ [11], and Pb$_2$Nb$_2$O$_7$ [12]. In some cases (SiO$_2$, H$_2$O, CaAl$_2$Si$_2$O$_8$) the amorphous phase is retained on reducing the pressure to 1 atm, while in others [AlPO$_4$, SnI$_4$, LiKSO$_4$, Ca(OH)$_2$ Pb$_2$Nb$_2$O$_7$] the amorphous solid reverts to the crystalline form when the pressure is lowered. In the case of AlPO$_4$ recent experiments by Kruger and Jeanloz [10] indicate that not only does the sample recrystallize when the pressure is released, but it reverts to a single crystal of the same crystallographic orientation as the starting material. From this they inferred that a "memory" of the crystal orientation was retained in the amorphous material. A comparison of the transformations in SiO$_2$ (quartz) and AlPO$_4$ (berlinite) is of particular interest, as the crystalline forms of the two

compounds are isomorphic (although the unit cell of AlPO$_4$ is doubled compared to that of SiO$_2$ due to the alternating substitution of Al and P on Si lattice sites) and yet they differ in their transformation pressures and in the stability of the amorphized phase at low pressure.

Crystalline SiO$_2$ can be amorphized by hydrostatic compression whether the starting crystal is trigonal α-quartz (the low-pressure form) or monoclinic coesite (the stable crystal form at room temperature in the pressure range 3–8 GPa). In either case the x-ray-diffraction pattern [6,7] and Raman spectrum [4] of the transformed material show weak broad peaks characteristic of an amorphous material and are indistinguishable from the corresponding measurements on densified fused silica [13,14]. In this work we have used Brillouin scattering to measure the pressure dependence of the sound velocity in SiO$_2$ in both the crystalline quartz and pressure-amorphized states.

We performed Brillouin scattering experiments in the backscattering geometry using a (5+4)-pass tandem scanning Fabry-Pérot interferometer. In this scattering geometry only longitudinal acoustic waves are observable. The incident light was provided by the 514.5-nm line from a single-moded Ar$^+$ laser. We achieved pressures of up to 25 GPa at room temperature using a diamond-anvil cell of the NBS design with argon as a pressure medium (in one run we used a 4:1 methanol-ethanol mixture as the pressure-transmitting medium; we observed no significant difference between spectra taken at the same pressure in the two different media). We determined the pressure from ruby fluorescence using the λ^5 scale [15]. The samples were single crystals of α-quartz cut and polished into thin platelets approximately $75 \times 75 \times 30$ μm. They were prepared in two orientations, with the smallest dimension (and, thus, in the diamond-anvil cell in backscattering geometry, the direction of phonon propagation) either parallel or perpendicular to the [001] axis of the crystal.

The measured frequency shifts (Δv) are related to the sound velocity (v) through

$$v = 7.7175 \times 10^5 \frac{\Delta v}{n} \text{ cm/sec}, \qquad (1)$$

where n is the refractive index and Δv is expressed in cm^{-1}. Although the pressure dependence of n is likely to be small, we have chosen to present our results in terms of Δv to avoid introducing any unnecessary assumptions. The frequency shifts for propagation along and perpendicular to the c axis are shown in Figs. 1(a) and 1(b), respectively. Solid (open) symbols are taken with increasing (decreasing) pressure. At pressures above 15 GPa the peaks in the spectra became rather indistinct, a fact which is reflected in the spread in the data points in Fig. 1. On decreasing the pressure sharp Brillouin peaks reappeared below ≈ 10 GPa.

For propagation along the c axis [Fig. 1(a)] the frequency shift (1.3 cm^{-1}) of the recovered sample is the same as that of the starting material, but is lower than the value of $\approx 1.4 \text{ cm}^{-1}$ measured in recovered densified a-SiO$_2$ [16,17]. For propagation perpendicular to the c axis [Fig. 1(b)] the frequency shift starts out lower (1.15 cm^{-1}) than for propagation along the c axis. The difference is in agreement with the known values of C_{11} and C_{33}. After the pressure has been raised above ≈ 17 GPa and then decreased, the measured frequencies are consistently higher than both the values recorded at increasing pressure and those recorded for the other orientation after compression. At 1 atm the Brillouin frequency is 1.45 cm^{-1} for $q \perp c$, substantially different from the starting value. Not only is it higher than the starting value but it is also higher than the value for the $q \| c$ sample, and it is even higher than that for a-SiO$_2$ densified at these pressures. From Eq. (1) it is clear that the anisotropy observed in the measured frequency shift implies an anisotropy in either the sound velocity or the refractive index, or both. An anisotropy in either one is sufficient to show that the material itself is anisotropic; however, the magnitude of the effect is so large that it is highly unlikely that it could be primarily caused by refractive-index changes. The fractional birefringence $2(n_e - n_0)/(n_e + n_0)$ of unmodified α-quartz is less than 6%, considerably smaller than the anisotropy in Δv observed in the amorphized samples. The reversal in the sign of the elastic anisotropy between the crystalline and the amorphous state is a clear indication that the observed behavior cannot be explained on the basis of incomplete amorphization since the presence of any remaining ordered portions would not lead to a change in the sign of the elastic anisotropy.

Changes in the nature of the recovered samples were also monitored by Raman scattering as shown in Fig. 2. This spectrum is identical (within the noise) to that obtained on a densified a-SiO$_2$ sample [14]. The size and geometry of the recovered sample used for our Raman
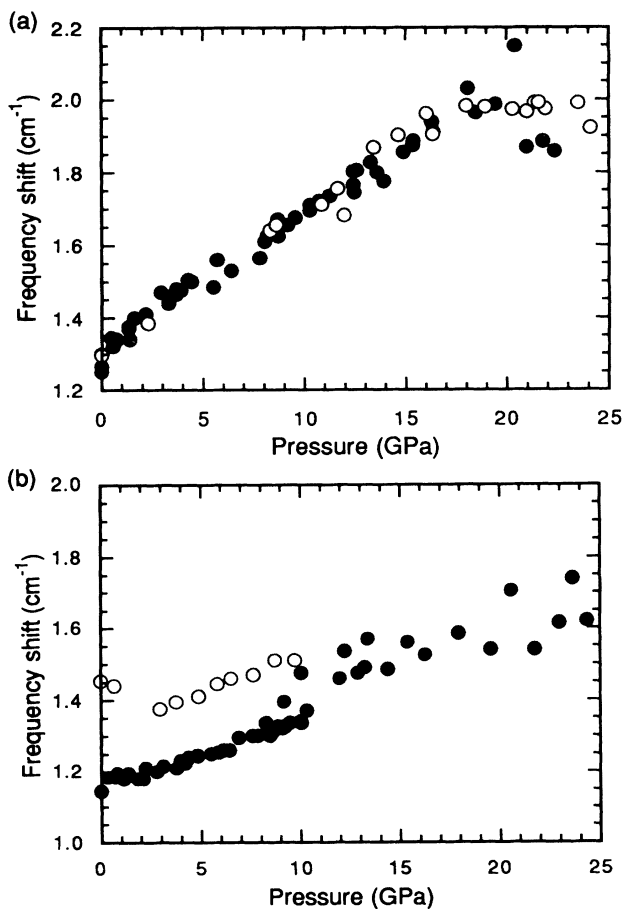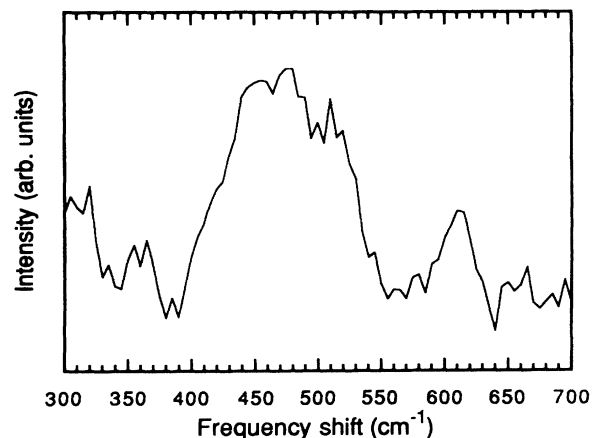
FIG. 1. Brillouin frequency shift of longitudinal waves in SiO$_2$ vs pressure. Solid and open symbols correspond to increasing and decreasing pressure. (a) and (b) correspond to propagation parallel and perpendicular to the original c axis of the α-quartz crystal.

FIG. 2. Raman spectrum of a recovered sample of pressure-amorphized α-quartz. Maximum pressure to which the sample was subjected was 24.5 GPa.

measurement did not allow us to determine if our Raman spectrum measured the α_{zz} or the α_{xx} element of the Raman tensor. In principle, based on the anisotropy exhibited by the Brillouin results, it may be possible to detect differences between the α_{zz} and α_{xx} Raman spectra. Such experiments are planned if larger recovered samples can be produced.

A detailed microscopic interpretation of our data requires considerably more structural data than presently available. At a purely speculative level, however, if we view the structure of quartz as consisting of interconnected helical chains of corner-shared SiO_4 tetrahedra with the helix axis along the c direction, then our results imply that the amorphization corresponds mainly to changes in the stacking of the helices and less to changes in the chains themselves. This results in little change in the acoustic wave velocity for q∥c but a substantial change for q⊥c. If furthermore we were to postulate a random but dense packing of chains analogous to the nematic phase of a liquid crystal, it could account for the amorphous nature of the x-ray-diffraction pattern and the Raman spectrum while retaining the elastic anisotropy exhibited in the Brillouin scattering results. The increase in the velocity for **q** perpendicular to the chains suggests that the closer packing of the chains results in decreased compressibility in that direction, perhaps due to unfavorable orientations of neighboring SiO_4 tetrahedra.

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