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Annealing and relaxation in the high-pressure phase of amorphous SiO_2

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In a recent article [Phys. Rev. Lett. **52**, 2379 (1984)] it was reported that irreversible changes occur in the Brillouin spectra of a-SiO_2 that has been subjected to pressures above ~9 GPa. Based on Raman spectra from the recovered samples it was concluded that the new "polymorph" was also amorphous. Here we report on relaxation and annealing effects in this high-pressure form which leave no doubt as to its amorphous nature.

In a recent article[1] certain irreversible changes which occur in the Brillouin and Raman spectra of a-SiO_2 as a function of pressure were interpreted as an indication of a new polymorph of a-SiO_2. Regrettably, the number of labels used for a-SiO_2 (variously described as the amorphous, glassy, vitreous, or fused phase of silica, quartz, or SiO_2) led to very serious omissions in the literature cited in Ref. 1. Regarding the general aspects of compaction of a-SiO_2 by various techniques, a review is given in Ref. 2. None of this earlier work, however, gave any strong indication that a material with a substantially different structure was being produced. A number of Raman investigations of compacted a-SiO_2 have also been previously reported in the literature.[3-8] In most of these, the reported changes in the Raman spectra are small, and the general features of the spectra remain unchanged. In Ref. 3, on the other hand, the reported Raman spectra are very similar to that presented in Ref. 1. A more recent report of Raman scattering from densified a-SiO_2,[9] which includes spectra with different polarizations, also agrees with Refs. 1 and 3. Furthermore, x-ray results[10] (quoted in Ref. 9) show that the modification in the structure arises from changes in the average Si-O-Si angles, while the Si-O and O-O distances remain essentially unchanged. The analysis of their x-ray and Raman results is found to be consistent with a reduction of the average ring size, which has also been suggested from an investigation of the refractive index.[11]

In Ref. 1 it was stated that a study of the Raman spectrum as a function of pressure was not undertaken because fluorescence and second-order Raman scattering from the diamonds occlude the signal from a-SiO_2. Very recent results,[12] using a diamond anvil cell that allows scattering geometries other than backscattering, have overcome the above problems and show the evolution of the spectrum as a function of pressure. They find that at pressures above those reported in Ref. 1 no further dramatic changes occur.

Brillouin scattering from both longitudinal and shear waves has also been previously reported[13] up to 13 GPa, but no mention is made regarding irreversible changes. As they state, however, from these results the density as a function of pressure can be calculated; at 13 GPa the density increase is ~35%.

Here we present Brillouin scattering results that deal with (i) the fact that the irreversible changes have not saturated at the maximum pressure reported in Ref. 1, (ii) relaxation phenomena related to the time scale on which densification takes place, and (iii) annealing temperatures necessary to revert the compacted state to its original state.

In Fig. 1 the Brillouin frequency shift as a function of pressure is shown . The crosses are data points taken with increasing pressure. The dots, squares, and triangles are for decreasing pressure where the maximum pressure attained was 16.5, 18, and 18.2 GPa, respectively. The first two were kept at the highest pressure for less than an hour, the last one was kept at 18.2 GPa for 15 days. This will be discussed in further detail below. It is clear from the figure that the irreversible changes occurring in this material have not yet saturated at these pressures.

The spread in experimental points at high pressures can be traced to the long times involved in the densification process. In Fig. 2 we plot the Brillouin frequency shift as a function of time after the pressure was applied. The pressure was taken from 0.8 to 18.2 GPa in about 1 min and then the frequency shift measured (~1 min per spectrum) after certain times had elapsed. The arrow on the right is

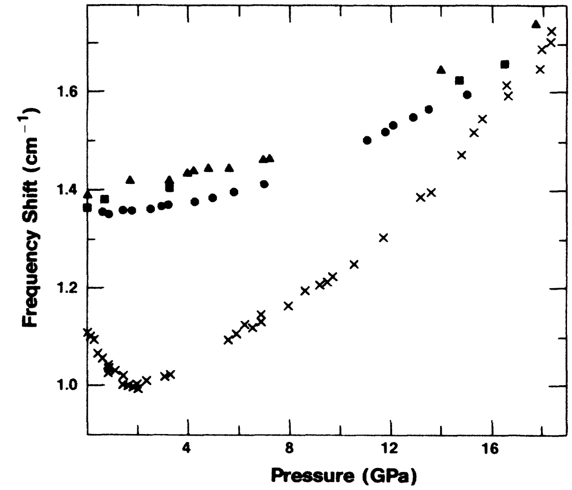

FIG. 1. Brillouin frequency shift from a-SiO_2 as a function of pressure. Crosses are for increasing pressure. Dots, squares, and triangles are for decreasing pressure for samples that had been compressed to 16.5, 18, and 18.2 GPa, respectively.

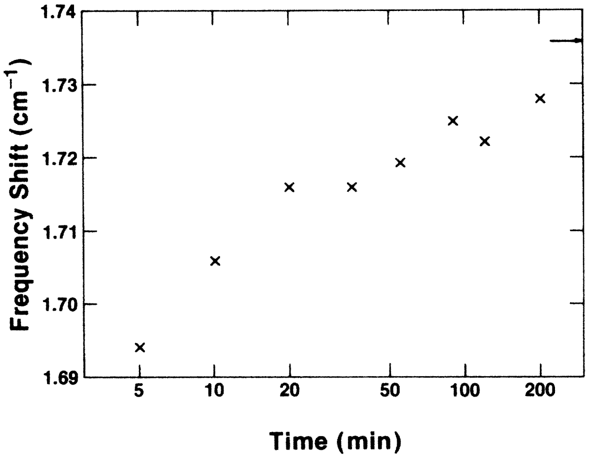

FIG. 2. Brillouin frequency shift for a-SiO$_2$ as a function of time after a pressure of 18.2 GPa was applied. The arrow is the shift measured after 15 days at that pressure.

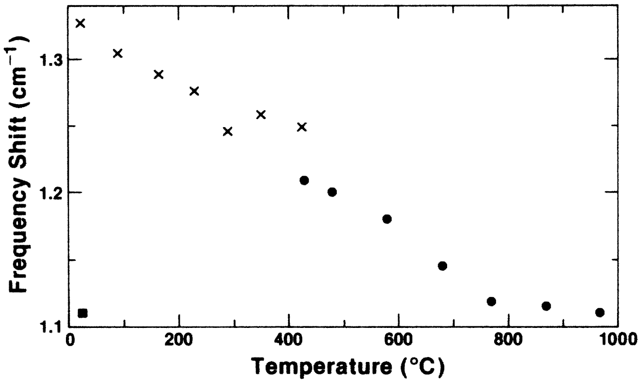

FIG. 3. Temperature dependence of the Brillouin frequency shift from a recovered sample that had been compressed to 18 GPa. Crosses are data points taken at the specified tempeature, dots are taken at room temperature after the sample was annealed for one hour at the temperature shown, and the square is from the sample prior to compression.

the frequency shift measured after 15 days at 18.2 GPa. The long times requied to reach equilibrium are surprising but consistent with the times reported in densification studies.[14]

It is also known from previous investigations[2] that heating the sample releases the compaction of a-SiO$_2$. In Fig. 3 we present temperature dependence of the Brillouin frequency shift measured at one atmosphere from a sample that had been compressed to 18 GPa. The crosses are data points taken with the sample at the specified temperature, the dots are data points taken at room temperature after the sample has been annealed at the specified temperature for one hour, and the square is the measured frequency before the sample had been compressed. Here again the behavior is similar to that found for the density of samples compressed by other means.[2] We note that the results in Fig. 3 provide further proof that the high-pressure phase is indeed amorphous since if crystallization had occurred it would be impossible to reverse the process by annealing.

We mention here that similar experiments have been tried on a-GeO$_2$ and even though there is some evidence for similar irreversible changes under pressure, the results depend on the fluid used to generate the hydrostatic environment. We attribute this behavior to chemical reactions in the cell as is dramatically illustrated when H$_2$O is used: The sample completely dissolves when pressure is applied.

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