

Room-temperature densification of α -SiO₂ versus pressure

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(Received 19 October 1989)

Using Brillouin scattering, we have investigated the room-temperature densification of hydrostatically compressed α -SiO₂. Irreversible densification occurs in the range 10–25 GPa; at higher pressures (25–40 GPa) no further densification is observed. The densified state is found to be metastable and decreases in density over time spans of the order of years. The presence of large uniaxial stresses *during* compression is found to lead to a densified state which relaxes much more rapidly (\sim hours) towards the undensified state.

In spite of the very substantial literature^{1–11} which exists on the densified forms of amorphous SiO₂, it is only relatively recently^{12–16} that it has become clear that the high-density forms are substantially different on a microscopic scale. The first experiments on densification² found a 6% density increase at 20 GPa while subsequent experiments^{3,4} achieved 16% densification at 14 GPa; these differences were attributed to differences in the shear component of the applied stress. Experiments in which hydrostatic pressures were applied^{5–8} were limited to pressures below 8 GPa but succeeded in achieving densifications of \sim 18% by pressurizing at temperatures up to 800 °C. None of the preceding experiments showed evidence of a saturation of the densification process.

The advent of diamond anvil cells¹⁷ (DAC) has now made it possible to routinely reach pressures well above 30 GPa. The samples which can be investigated by this technique are typically only $100 \times 100 \times 20 \mu\text{m}^3$ and hence make the determination of many physical properties nontrivial. Two recent articles^{14,16} have investigated the densification process in α -SiO₂ using Brillouin scattering. It was found that samples recovered after compression to \sim 18 GPa at room temperature exhibit substantially different elastic properties than those of the starting material. Raman spectra of the recovered samples^{12–15} were also interpreted as a clear indication of substantial changes at the microscopic level.

Not much is known about the structure of the dense forms: in Refs. 13 and 18, x-ray studies were performed on 16% densified material and in Ref. 19 neutron scattering from a 20% densified material. The conclusion from these studies is that most of the structural changes are associated mainly with changes in the Si-Si nearest-neighbor distances, while the Si(O_{1/2})₄ tetrahedra remain essentially unchanged.

Here we report the results of a study of the room-temperature densification of α -SiO₂ in a quasihydrostatic environment of a DAC. Using Brillouin scattering we monitor irreversible changes in sound velocity in samples

recovered after pressurization. The Brillouin-scattering apparatus and the experimental conditions are the same as those used in Refs. 14 and 16. The α -SiO₂ (Suprasil) samples were loaded into the cell, held at the required pressure for \sim 20 h, and then removed from the cell and measured at 1 atm. The solid squares in Fig. 1 show the measured Brillouin frequency shift as a function of the maximum pressure to which the sample was compressed. The frequency shift (in units of cm^{-1}) can be converted to a longitudinal sound velocity (in units of km/sec) by multiplying by $7.718/n$, where n is the refractive index for 514.5-nm radiation; since n for the recovered sample is not known we leave the results in frequency units. It can be seen from Fig. 1 that the irreversible densification process is completed at \sim 25 GPa. The measurement er-

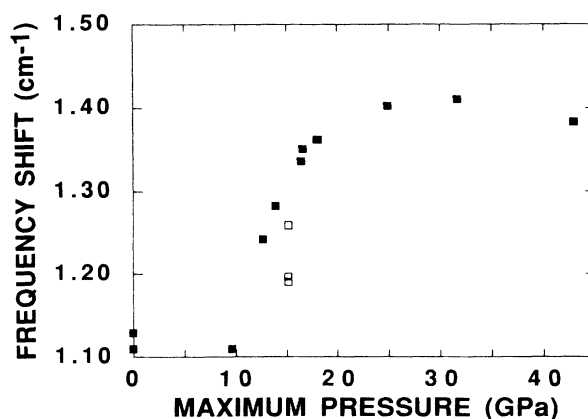


FIG. 1. Brillouin frequency shift measured in samples recovered after compression to the indicated pressure. Solid squares are for hydrostatic compression; open symbols are for a sample subjected to a large uniaxial stress as explained in the text. The errors in frequency and pressure are roughly equal to the size of the symbols used.

rors in frequency are typically 0.01 cm^{-1} while the error in the maximum pressure is always less than 0.4 GPa. The size of the data points in Fig. 1 is therefore a good indication of the experimental accuracy. We attribute the spread in our results to variations in sample characterization due either to quenching rates during fabrication or uniaxial stresses during compression. The density of the most compacted material can be roughly estimated using the results of Ref. 19; there it has been reported that a sample prepared in a large press at a pressure of $\sim 15 \text{ GPa}$ had a density 20% higher than the starting material. The Brillouin shift from this sample was 1.26 cm^{-1} (compared with 1.11 cm^{-1} in the undensified material); assuming a Murnaghan²⁰ equation of state the densification corresponding to the maximum measured frequency shift (1.40 cm^{-1} , Fig. 1) is then close to 40%—considerably higher than in previous reports.

The details of the microscopic structural changes occurring during densification are at present not known. In $\alpha\text{-GeO}_2$ it has been shown²¹ that although Ge increases its coordination number from 4 to 6 under pressure this change is reversible when pressure is released. A Brillouin and Raman study, on the other hand,²² show that the recovered samples of $\alpha\text{-GeO}_2$ are different from the starting materials. The possibility of densification without a coordination change is consistent with the findings of Ref. 19, where a neutron-scattering study of densified $\alpha\text{-SiO}_2$ showed that, although there is no appreciable change in the short-range order, substantial modification occurs in the intermediate-range order.

The long-term stability of the densified material was

also investigated. The Brillouin shift in a sample pressurized to 18 GPa was 1.36 cm^{-1} measured just after pressure release, 1.33 cm^{-1} after two months, and 1.28 and 1.25 cm^{-1} in two samples stored for five years. These results clearly show the metastable nature of the highly densified form.

All the preceding results refer to samples which were pressurized in an ethanol-methanol mixture in a DAC, and are therefore expected to have undergone almost hydrostatic compression. An anomalous pressure run to 15 GPa is shown by the open symbols in Fig. 1; the frequency shifts measured in a sample 10, 20, and 60 min after decompression were 1.26, 1.20, and 1.19 indicating a very rapid "undensification." A careful examination of this sample showed that its thickness (after recovery) was greater than that of the recovered gasket used in that run. It appears therefore from this very limited information that the densification which takes place under uniaxial stress is not the same as that occurring if the pressure is hydrostatic. This finding may be related to the optical anisotropy found in recovered chalcogenide glasses after uniaxial compression.²³

Laboratoire de Physique des Milieux Condensés is Unité de Recherche Associé No. 782 du Centre National de Recherche Scientifique, France. This work was supported by the U.S. Department of Energy (Division of Materials Sciences of the Office of Basic Energy Sciences), under Contract No. W-31-109-ENG-38, and by a travel grant (No. 0082/89) from the North Atlantic Treaty Organization.

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