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Polymorphism in Amorphous SiO_2

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Brillouin scattering from a-SiO_2 up to 17 GPa shows that an irreversible change in the longitudinal sound velocity takes place between 10 and 17 GPa and that this change is stable at atmospheric pressure. Raman spectra of the retrieved sample indicate that it is also amorphous but differ noticeably from that of the original sample.

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Although the properties of glasses have been the subject of many investigations for well over fifty years, it is only relatively recently that attempts have been made to explain these properties at the microscopic level in a quantitative fashion. This interest is no doubt, at least indirectly, related to the ever-increasing technological importance of materials such as a-Si, a-Se, amorphous metals, etc.

Perhaps the system that has been most widely investigated is amorphous SiO_2, known as silica, fused quartz, or any of a number of trade names (e.g., Suprasil, Hearsil, etc.). A good overview of many of the properties of a-SiO_2 can be found in the review article by Brückner.[1] A microscopic description of some of the properties is given by Vukcevich[2] who also reviews previous theoretical work. The structure of a-SiO_2 has been shown by x-ray[3,4] and neutron scattering[5] to consist of SiO_4 tetrahedra joined at their vertices. With this model Galeener, Leadbetter, and Stringfellow[6] have recently interpreted the Raman, inelastic neutron, and infrared spectra.

Investigation of a-SiO_2 under pressure has revealed a number of interesting and anomalous properties. The bulk modulus[7-9] is found to *decrease* under pressure to a minimum at ~3 GPa and then to increase again above this pressure. These changes were found to be reversible up to the highest pressures attained, 9 GPa. Ultrasonic studies[10] up to 3 GPa also found minima in the shear and longitudinal elastic moduli between 2 and 3 GPa. Irreversible changes in the density after compression have also been reported. Under pure hydrostatic pressures[11-13] these irreversible changes only occur for pressures above ~12 GPa although shear stresses considerably lower this threshold.[1] These results have been explained on the basis of conformational changes in the glass structure.[14] However, the infrared spectra of densified and normal a-SiO_2 show no appreciable differences.[13]

The investigation of amorphous materials under the high pressures now achievable in diamond-anvil cells poses severe experimental difficulties: X-ray studies (now a well-established technique for crystals) must resolve the broad features expected for such samples from those arising from the metal gasket, the diamonds, and the pressure medium. Raman scattering, on the other hand, must contend with the fluorescence of the diamonds, which also tends to obscure the broad features expected for a glass. In a recent experiment with very-low-fluorescence diamonds, we were still not able to observe any Raman signal from an a-SiO_2 sample inside the pressure cell.

In this Letter the results of a Brillouin scattering study up to 17 GPa are reported. The spectra were recorded on a (5+2)-pass Fabry-Perot interferometer; the rest of the equipment is the same as that described by Polian and Grimsditch.[15]

In Fig. 1 the measured frequency shift is shown as a function of pressure. The large gaps in the data correspond to a crossing of the Brillouin lines from a-SiO_2 and from the methanol-ethanol mixture. The crosses are points taken with increasing pressure, the dots represent decreasing pressure, while

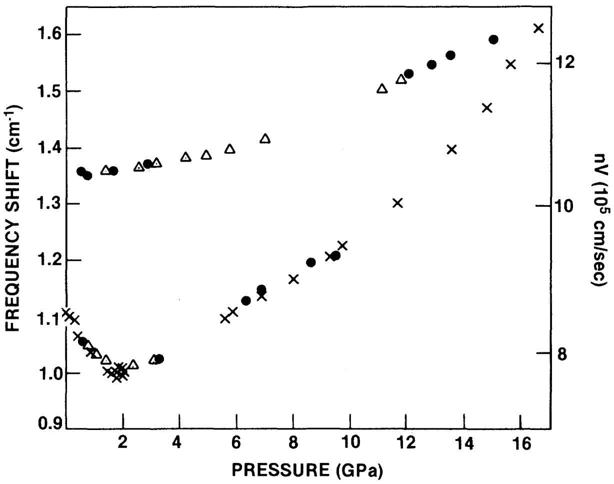

FIG. 1. Brillouin frequency shift of longitudinal waves in a-SiO_2 vs pressure. Crosses: increasing pressure, first run. Circles: decreasing pressure. Triangles: increasing pressure, second run.

the triangles are increasing pressure but after the sample has been cycled to high pressure. The measured frequency shift is related to the product of the longitudinal sound velocity V times the refractive index n which is also shown in Fig. 1. Below 3 GPa our results agree with the results of Ref. 10. The results also show that a sample taken up to 9.5 GPa showed a perfectly reversible behavior. This behavior is also consistent with the bulk-modulus results[7-9] and with the absence of irreversible changes in density at these pressures.[11-13] A sample taken to 17.5 GPa on the other hand showed a strikingly different behavior as evidenced in Fig. 1.

This "permanent" change in the elastic properties is consistent with the changes in density which were found[13] to be stable for a period of at least two years. The densification of our sample, based on a very coarse size measurement, is 20 ± 10%. We interpret our results as an indication of a new form of SiO_2. We emphasize that if the only changes were in the density, and the interactomic forces remain unchanged, we would expect a *drop* in the measured velocity. Conversely, even if the density remains unchanged, the results of Fig. 1 would indicate an increase of 50% in the longitudinal elastic modulus.

The identification of the high-pressure phase as an amorphous one is based on the following arguments: In Ref. 13, it is stated that although in most compression runs the sample remained vitreous, some runs did produce small amounts of coesite (a crystalline SiO_2 phase) which was identified by its birefringence and its infrared spectrum. Our measured value of nV in the transformed phase at 1 bar is, however, only $\sim 10.5\times10^5$ cm/sec, which must be compared with $\sim 11.7\times10^5$ cm/sec, the average value for coesite.[16] Furthermore, if the sample were crystalline, its Raman spectrum should show sharp lines characteristic of the crystalline state.[17] Although Raman spectra were not obtainable with the sample in the cell, a spectrum was obtained from the sample after it was retrieved from the cell. This spectrum is shown in Fig 2(a) together with the spectrum of the initial sample of a-SiO_2 [Fig. 2(b)]. The upper curve in Fig. 2(a) was taken under poorer resolution in order to gain intensity and observe the high-frequency lines. A number of conclusions can be drawn from the results in Fig. 2: (i) The spectra of the two samples are markedly different, indicating a different structure. (ii) The spectrum is very different from that of coesite.[17] (iii) The features are broad, which is strong evidence for a noncrystalline sample. (iv) The two strongest features in the spectrum of the compressed sample at 500 and 615 cm^{-1} are close to the two lines labeled D ("defect") in the noncompressed sample[6] (486 and 601 cm^{-1}). The identification of the main features of the Raman spectrum of the compressed sample as the defect lines in uncompressed SiO_2 is substantiated by the results of Raman scattering from irradiated a-SiO_2. It has been found[18,19] that as the density of a-SiO_2 is increased by neutron irradiation, the defect lines increase in intensity and shift to higher frequencies (500 and 608 at $\sim 2\%$ densification).

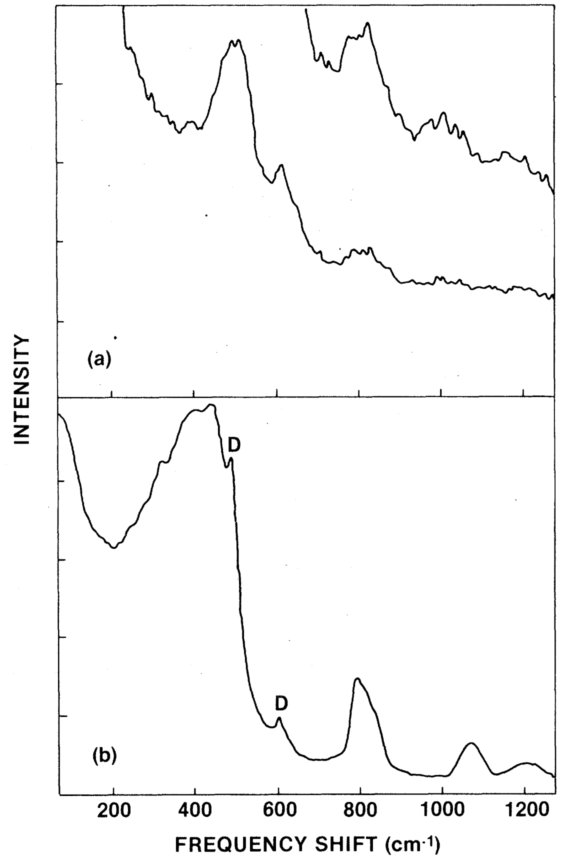

FIG. 2. Raman spectra of a-SiO_2: (a) Sample cycled to 17.5 GPa. (b) Noncompressed sample; here D labels the "defect" peaks from Ref. 6. (No analyzer was used in the scattered beam.)

Surprisingly, the origin of the defect lines in ordinary a-SiO_2 is still being debated. They have been attributed to two different mechanisms: (i) presence of threefold and fourfold rings in a random-network model,[20] and (ii) presence of nonbridging oxygens.[21] The present results can, unfortunately, also be interpreted in both schemes; either a collapse of large rings (sixfold and eightfold) to smaller ones, or a breaking of bonds to create a larger number of nonbridging oxygens. However, a structural investigation of this modified state where the defect features are dominant should allow an unambiguous assignment as to their origin. We shall refrain from speculation at this stage.

In conclusion Brillouin- and Raman-scattering results indicate the existence of a new form of amorphous SiO_2 which is stable at atmospheric pressure. This new form appears to evolve continuously from ordinary a-SiO_2, but since its Raman spectrum implies a nontrivial change in the microscopic structure, we feel that it deserves the label "amorphous polymorph." Furthermore, because the neutron-irradiation results[18,19] can be explained as simply due to a high concentration of defects, we feel that the evidence presented here is the first to show the existence of a material that can be formed in two substantially different amorphous states. Work is in progress to attempt density measurements as well as a structure determination using x rays.

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[1] R. Brückner, J. Non-Cryst. Solids **5**, 123 (1970), and **5**, 177 (1971).

[2] M. R. Vukcevich, J. Non-Cryst. Solids **11**, 25 (1972).

[3] R. L. Mozzi and B. E. Warren, J. Appl. Cryst. **2**, 164 (1969).

[4] J. H. Konnert and J. Karle, Acta. Crystallogr. **A29**, 702 (1973).

[5] R. N. Sinclair, J. A. Erwin Desa, G. Etherington, P. A. V. Johnson, and A. C. Wright, J. Non-Cryst. Solids **42**, 107 (1980); A. C. Wright and R. N. Sinclair, to be published.

[6] F. L. Galeener, A. J. Leadbetter, and M. W. Stringfellow, Phys. Rev. B **27**, 1052 (1983).

[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55, 71 (1948).

[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 9 (1945).

[9] P. W. Bridgman, Am. J. Sci. **10**, 359 (1925).

[10] Ken-ichi Kondo, Satoshi Iio, and Akira Sawaoka, J. Appl. Phys. **52**, 2826 (1981).

[11] P. W. Bridgman and J. Simon, J. Appl. Phys. **24**, 405 (1953).

[12] J. Arndt, J. Am. Ceram. Soc. **52**, 285 (1969).

[13] J. Arndt, Phys. Chem. Glasses **24**, 104 (1983).

[14] A. G. Revesz, J. Non-Cryst. Solids **7**, 77 (1972).

[15] A. Polian and M. Grimsditch, Phys. Rev. B **27**, 6409 (1983).

[16] D. J. Weidner and H. R. Carleton, J. Geophys. Res. **82**, 1334 (1977).

[17] S. K. Sharma, J. F. Mammone, and M. F. Nicol, Nature (London) **292**, 140 (1981).

[18] J. B. Bates, R. W. Hendricks, and L. B. Shaffer, J. Chem. Phys. **61**, 4163 (1974).

[19] R. H. Stolen, J. T. Krause, and C. R. Kurkjian, Discuss. Faraday Soc. **50**, 103 (1970).

[20] F. L. Galeener, Solid State Commun. **44**, 1037 (1982).

[21] J. C. Phillips, Solid State Phys. **37**, 93 (1982), and to be published.