Raman Spectroscopy of SiO_2 Glass at High Pressure

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A new technique has been developed for optical studies of amorphous solids to very high pressures. Raman spectra of SiO_2 glass measured at 8 GPa indicate a significant reduction in the width of the Si-O-Si angle distribution, which has been associated with a number of anomalous properties of silica glass under ambient conditions. Between 8 and ~ 30 GPa irreversible changes in the Raman spectrum occur that are consistent with a shift in ring statistics in densified glass. The spectra suggest a breakdown in intermediate-range order at higher pressure.

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The structure and properties of amorphous solids are of widespread interest because of their obvious importance in the design and synthesis of new materials.[1] The structure of these materials, including the degree of short-range and intermediate order and the dependence of these quantities on pressure and temperature, are also of fundamental concern. The detailed structure of vitreous silica, a tetrahedral oxide glass, has in fact been the subject of much recent controversy.[2-7] In the case of crystalline solids, the application of diffraction and spectroscopic techniques at high pressure for determining the effect of pressure on structure and for constraining assignments for phonon spectra has long been recognized.[8] Similar studies of amorphous materials at high pressure, however, have been unsuccessful.[9] The problem with such measurements arises from limited access to samples in high-pressure devices, strong spurious scattering from the apparatus which interferes with the signal from the sample, and the generally weak and/or broad absorption or scattering cross sections of amorphous solids in comparison to those of crystals. In the present study we show that high-quality Raman spectra of weakly scattering amorphous solids at pressures of >30 GPa (>300 kbar) can be obtained with a sensitive micro-optical technique. We report the first Raman spectra of SiO_2 glass measured *in situ* at high pressure and find dramatic effects of pressure on its structure and vibrational properties.

In addition to the controversy surrounding the structure of silica glass, there is fundamental interest in this material because it has a number of unusual properties, including anomalous behavior at high pressure.[9-11] On compression, the bulk and longitudinal moduli of silica glass decrease, in contrast to the increase which is observed in most solids, and pass through a minimum at ~ 2 GPa.[9,10] In addition, silica glass can be densified or compacted by static high pressures (i.e., >10 GPa), shock loading, and neutron irradiation.[11] On the basis of Brillouin scattering measurements performed at high pressure and Raman measurements of the material *quenched* from high pressure, Grimsditch[9] proposed that a new type of polymorphism between amorphous states occurs on static compression. However, the structural basis of such a transformation is unknown, as Raman spectra could not be measured *in situ* at high pressure because of strong interference from fluorescence from the diamond anvils of the high-pressure cell. It is not clear, therefore, whether the structure formed at high pressure was in fact quenched.

In the present study the problem of interference from the diamonds has been circumvented by the use of a sensitive micro-optical spectrometer system especially designed for the measurement of weak Raman spectra of samples contained in a diamond-anvil cell at very high pressures. A 135° light-scattering configuration was used along with spatial filtering of the spurious diamond signal and imaging of the Raman signal from micron-sized excitation volumes of the sample.[12] The experiments were performed on polished plates (10–35-μm thickness) of Herasil type II SiO_2 glass[13] loaded in a gasketed Mao-Bell–type diamond-anvil cell along with the pressure-transmitting medium. Because of the sensitivity of silica to nonhydrostatic stresses at high pressure, a soft (quasihydrostatic) medium is required. In addition, for weak scatterers no spurious signal from the medium can be tolerated. These criteria are met with solid argon, which remains quasihydrostatic and lacks a first-order Raman spectrum (i.e., face-centered-cubic structure) to 80 GPa.[14] The thickness of the glass plates was always less than the final thickness of the gasket (30–80 μm) to prevent bridging. The pressure was determined by the standard ruby-fluorescence method.[15]

The Raman spectrum of normal silica glass at 0.1 MPa (1 bar) is characterized by a relatively strong, diffuse band at 440 cm^{-1}, with weaker features near 800, 1060, and 1190 cm^{-1}. In addition, there are two relatively sharp bands at 492 and 605 cm^{-1}, the "defect" bands denoted D_1 and D_2, respectively.[3-7] An entirely different pattern evolves on compression, as shown in

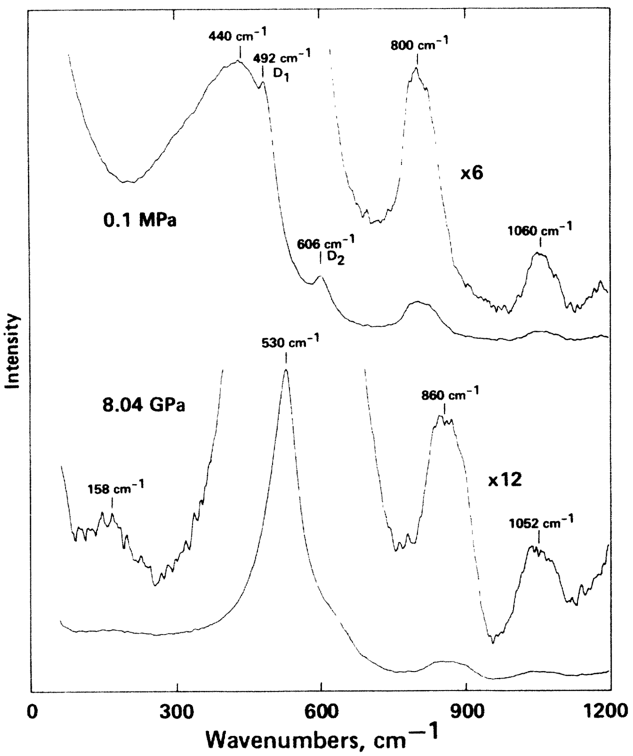

FIG. 1. Spontaneous room-temperature Raman spectra of SiO_2 glass at 0.1 MPa (1 bar) and 8.04 GPa (80.4 kbar). The two spectra were measured with use of the same scattering configuration (135°) with the sample contained in the diamond-anvil cell. The spectra are unpolarized [hence the predominance of *HH* scattering (Ref. 3)], and the intensity scales are arbitrary.

Fig. 1. At a pressure of 8 GPa there is a collapse of scattering intensity at low frequency (below ~ 400 cm^{-1}). This decrease in intensity is accompanied by a nearly threefold enhancement of scattering intensity at higher frequencies such that a pronounced peak at 530 cm^{-1} is observed at 8 GPa. Both positive and negative frequency shifts are found for the weaker bands, as detailed in Fig. 1. These changes in the room-temperature spectrum are found to be reversible in the argon medium.

A quantitative interpretation of the observed changes in the spectrum requires a detailed treatment of the short-range and long-range forces, as well as an assessment of the relative contribution of density-of-state and matrix-element terms.[3,4] Nevertheless, a number of important structural constraints are provided by the present spectra. An important question that arises is whether or not the material has crystallized (devitrified) on compression. The spectrum of the glass is distinct from that of any of the known crystalline phases of SiO_2 at 0.1 MPa, as well as from the spectrum of quartz, coesite, or stishovite at high pressure.[12] Coesite can be produced on static compression of silica glass, but only at *high temperature* ($>400\,°C$).[16] It is interesting that the position of the principal feature in the 8-GPa spectrum at 530 cm^{-1} is close to that of the strongest band in coesite at 0.1 MPa (521 cm^{-1}), but the high-pressure spectra lack the characteristic low-frequency bands of coesite.[5] In addition, the strong band in coesite is much narrower and shifts to higher frequencies at these pressures.[12] Thus, there is no evidence for crystallization, in agreement with the previous room-temperature compression studies.[9,17]

X-ray and neutron diffraction studies[2] of SiO_2 glass at 0.1 MPa indicate that the structure is characterized by corner-sharing SiO_4 tetrahedra with well-defined Si—O bond lengths R and O-Si-O angles ψ (e.g., $R \approx 1.62$ Å and $\psi \approx 109°$), but with a broad range of intertetrahedral Si-O-Si angles θ (from $\sim 120°$ to $180°$, with a most probable value θ_M of $144°$). It has been proposed that a wide distribution of Si-O-Si angles is associated with the excess low-temperature heat capacity, ultrasonic attenuation, and negative thermal expansion at 0.1 MPa found for silica glass (see Vukcevich[18]). Previous studies of the Raman spectrum indicate that the relatively strong, diffuse band at ~ 440 cm^{-1} arises from symmetrical Si-O-Si stretching modes principally involving motion of the oxygen atom.[3-6] According to central-force-field calculations with a continuous random network model,[4] the broadness of this feature (denoted W_1 in Ref. 4) is associated with the wide θ(Si-O-Si) distribution. The decrease in bandwidth thus indicates that the width of the angle distribution $\langle \theta^2 \rangle$ narrows significantly to 8 GPa. This change is therefore expected to result in a substantial decrease in the magnitude of the anomalous thermodynamic properties of SiO_2 at these pressures.

The central-force-model calculations also permit the determination of the principal compression mechanism in this pressure region. The calculations indicate that the frequencies of the 440- and 800-cm^{-1} bands (W_1 and W_2) should increase and that of the 1060-cm^{-1} band (W_4) decrease with decreasing angle θ. As shown in Fig. 1, this is indeed the case, with the position of the former moving to 850 cm^{-1} and the latter (less strongly) to 1052 cm^{-1} at 8 GPa. Similar structural changes for the crystalline phases quartz and coesite in this pressure range have been determined by x-ray diffraction.[19] The value of θ in quartz, for example, decreases from 143° at 0.1 MPa to 134° at 6 GPa, with negligible change in the Si-O bond length. In this regard, it is important to note that the spectrum at 8 GPa has a pattern similar to that of the 0.1 MPa spectrum of GeO_2 glass, a material in which the maximum in the intertetrahedral angle distribution is significantly smaller ($\theta_M \approx 133°$; Ref. 4) than in SiO_2 glass.

The series of spectra shown in Fig. 2 illustrates the continuous nature of these changes and shows the behavior observed at higher pressures. Above ~ 8

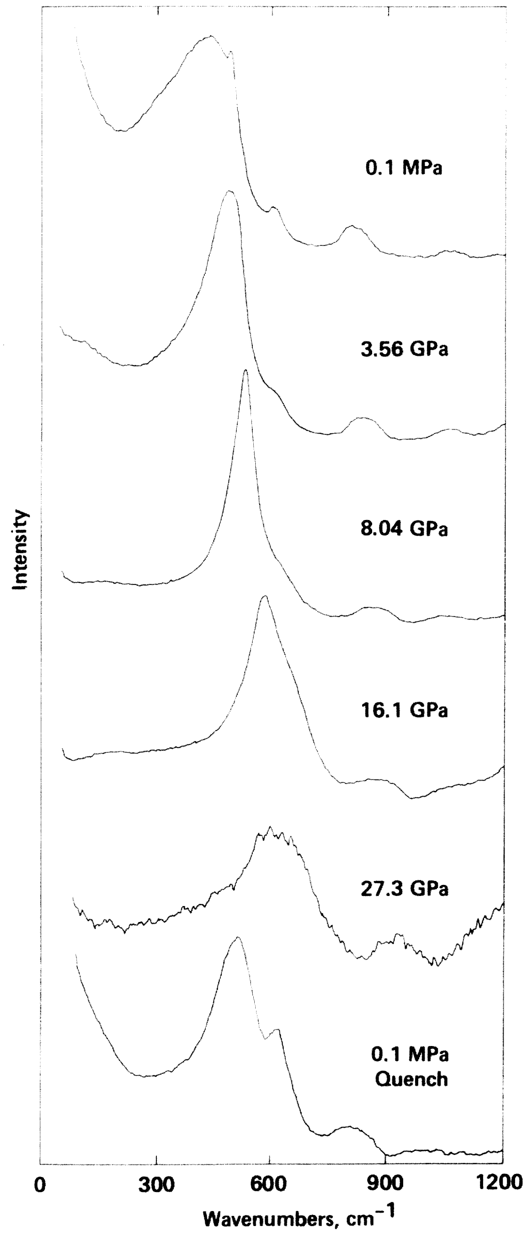

FIG. 2. Raman spectra of SiO_2 glass as a function of pressure, including the spectrum of the sample quenched from ~ 30 GPa. Above 8 GPa the spectra weaken, and no peaks could be detected above ~ 40 GPa.

GPa, the bandwidth begins to increase and the overall intensity decreases. The position of the broadened band continues to increase with pressure to a maximum of ~ 620 cm^{-1} at ~ 30 GPa. The spectrum of the material quenched from high pressure (30 GPa) is also shown in Fig. 2. It is characterized by a relatively strong band at 520 cm^{-1} and a second feature at 620 cm^{-1}, with weaker bands at high frequency (850 and ~ 1000 cm^{-1}). This spectrum is similar to those measured previously by Grimsditch[9] (sample quenched from 17 GPa) and by Mochizuki and Kawai[17] (from ~ 34 GPa). Note that the spectrum of the quenched material differs markedly from *any measured at high pressure.*

Because the changes in the spectrum are reversible below 8 GPa, reconstruction (i.e., bond breaking) seems unlikely at these pressures. There appears to be a continuous shift of the 440-cm^{-1} feature with at most a small change in the 492-cm^{-1} band. Such a change in the spectrum would be consistent with an elastic collapse of open-ring configurations (i.e., six-membered rings and larger), a mechanism by which the angle distribution is altered without bond breaking. In contrast, at higher pressures reconstructive changes are evident. An enhancement of the ~ 620-cm^{-1} band relative to other features occurs, together with a minor increase in the intensity at ~ 500 cm^{-1}. These changes are most clearly evident in the character of the 0.1-MPa spectrum of the sample quenched from high pressure (Fig. 2). In spectra measured at high pressure (e.g., 16 GPa), this change is evident as an enhancement of the shoulder on the high-frequency edge of the stronger band. It appears, therefore, that the intensities of the D_2 and (to a lesser degree) D_1 bands are enhanced on compression above 8 GPa.

This behavior sheds light on the recent controversy concerning the origin of the "defect" bands, which were originally assigned to defects but more recently have been interpreted in terms of more general structural features in the glass.[5-7] The present data indicate that such configurations are stabilized by pressure; i.e., they are high-density structures, with the density of the D_2 component larger than that of the D_1. Recent proposals[5,6] that these bands arise from symmetric stretching modes of small-ring configurations in the three-dimensional random network are consistent with the present data. The observed enhancement in the region of the D_1 and D_2 bands above 8 GPa would indicate a shift in ring statistics toward smaller (e.g., four- and three-membered) rings of tetrahedra in the structure. This analysis is discussed in detail elsewhere, along with a comparative study of the high-pressure Raman spectra of the crystalline polymorphs.[12]

There appears to be a maximum pressure shift in the higher-frequency band to 620 cm^{-1}, and above ~ 30 GPa the band rapidly broadens and loses intensity. The formation of very-small-ring configurations (e.g., two-membered or edge-sharing tetrahedra) is possible at high compression. The results of quantum-mechanical calculations of isolated molecular units[20] indicate that such configurations have high strain energy and thus would have to be stabilized by the dense surrounding medium. It is also possible that small rings (e.g., planar three-membered rings[6]) may pucker or distort at these pressures. The individual SiO_4

tetrahedra, although rigid at lower pressures,[19] may also become deformed at the very highest pressures to accommodate more efficient packing of ions. Under these conditions the coordination may in fact be ill defined, an effect that would give rise to the observed loss of intensity in the spectrum at ~40 GPa.

Finally, the present measurements provide a basis for analysis of previously reported 0.1 MPa spectra of quenched densified samples. In contrast to the behavior of silica glass quenched from higher pressures[9,17] and consistent with the present results, Raman spectra of the samples recovered from compression below ~9 GPa show comparatively small shifts in band frequencies and intensities, effects which also depend on temperature, impurities, and sample history.[13,21,22] In addition, there are similarities between the spectra of the quenched material reported here (Fig. 2) and that of silica glass densified by neutron irradiation. Enhancement of scattering intensity in the region of the D_2 band (and to a lesser degree D_1) is observed in both experiments. That such changes may arise from a shift in ring statistics is supported by the measured reduction in the Si-Si separation in both neutrino-irradiated and pressure-densified glass, corresponding to a decrease in θ_M by 4° and 6°, respectively.[22,23]

In conclusion, *in situ* Raman measurements of silica glass at high pressure detail the evolution of structural changes associated with its high-pressure polymorphism.[9] The following sequence is evident: (1) The continuous sharpening of the spectrum and reduction in density of states of low-frequency modes to 8 GPa indicate a significant increase in intermediate-range order, and specifically, a narrowing and shift of the broad θ(Si-O-Si) distribution that is characteristic of the structure of the material at 0.1 MPa. (2) Irreversible changes in the two strongest bands begin at ~8 GPa, effects that are fully consistent with a pressure-dependent shift in ring statistics. (3) At higher pressures (>30 GPa), the broadening and loss of Raman intensity suggest a gradual breakdown in intermediate-range (and perhaps short-range) order. Although changes in the spectrum at low pressures are qualitatively consistent with the central-force-model results, quantitative interpretation will require more elaborate force fields and, ideally, constant-pressure dynamics simulations. The application of the present technique for structural and vibrational studies of a variety of other amorphous systems at high pressure now appears possible.

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[1] *The Structure of Non-Crystalline Materials,* edited by P. H. Gaskell (Taylor and Francis, London, 1977).

[2] R. L. Mozzi and B. E. Warren, J. Appl. Crystallogr. **2**, 164 (1969); R. N. Sinclair, J. A. E. Desa, G. Etherington, P. A. V. Johnson, and A. C. Wright, J. Non-Cryst. Solids **42**, 107 (1980); P. C. Coombs, J. F. DeNatale, P. J. Hood, D. K. McElfresh, R. S. Wortman, and J. F. Shackelford, Philos. Mag. **B51**, L39 (1985).

[3] R. J. Bell, N. F. Bird, and P. Dean, J. Phys. C **1**, 299 (1968); F. L. Galeener, A. J. Leadbetter, and M. W. Stringfellow, Phys. Rev. B **27**, 1052 (1983).

[4] F. L. Galeener, Phys. Rev. B **19**, 4292 (1979); P. N. Sen and M. F. Thorpe, Phys. Rev. B **15**, 4030 (1977).

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

[6] F. L. Galeener, Solid State Commun. **44**, 1037 (1982); F. L. Galeener and A. E. Geissberger, Phys. Rev. B **27**, 6199 (1983); F. L. Galeener, R. A. Barrio, E. Martinez, and R. J. Elliott, Phys. Rev. Lett. **53**, 2429 (1984); F. L. Galeener and A. C. Wright, Solid State Commun. **57**, 677 (1986).

[7] J. C. Phillips, Solid State Phys. **37**, 93 (1982), and J. Non-Cryst. Solids **63**, 347 (1984).

[8] A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).

[9] M. Grimsditch, Phys. Rev. Lett. **52**, 2379 (1984).

[10] K.-i. Kondo, S. Ito, and A. Sawaoka, J. Appl. Phys. **52**, 2826 (1981).

[11] S. Sakka and J. D. Mackenzie, J. Non-Cryst. Solids **1**, 107 (1969); W. Primak, *Compacted States of Vitreous Silica, Studies in Radiation Effects in Solids* (Gordon and Breach, New York, 1975).

[12] R. J. Hemley, to be published.

[13] F. Seifert, B. O. Mysen, and D. Virgo, Phys. Chem. Glasses **24**, 141 (1983).

[14] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[15] H. K. Mao, P. M. Bell, J. Shaner, and D. Steinberg, J. Appl. Phys. **49**, 3279 (1978).

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

[17] S. Mochizuki and N. Kawai, Solid State Commun. **11**, 763 (1972).

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

[19] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral. **65**, 920 (1980); L. Levien and C. T. Prewitt, Am. Mineral. **66**, 324 (1981).

[20] M. O'Keeffe and G. V. Gibbs, J. Chem. Phys. **81**, 876 (1984).

[21] G. E. Walrafen and P. N. Krishnan, J. Chem. Phys. **74**, 5328 (1981).

[22] P. McMillan, B. Piriou, and R. Couty, J. Chem. Phys. **81**, 4234 (1984).

[23] R. H. Stolen, J. T. Krause, and C. R. Kurkjian, Discuss. Faraday Soc. **50**, 103 (1970); J. B. Bates, R. W. Hendricks, and L. B. Shaffer, J. Chem. Phys. **61**, 4163 (1974).