

Raman investigation of ring configurations in vitreous silica

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Random network models of glass structures¹ provide satisfactory qualitative descriptions of many properties of glasses (see reviews in refs 2–4). However, to obtain good quantitative agreement between theoretical analyses and experimental observations^{5–11} it is often necessary to assume that specific ring structures in the random networks have special importance. In the case of vitreous silica ($v\text{-SiO}_2$), distributions of loops of SiO_4 tetrahedra in the random network have been invoked^{5–9} to match calculated and experimental X-ray radial distribution functions (RDF). High resolution X-ray photoelectron spectra¹² of $v\text{-SiO}_2$ and quartz also provide evidence for the occurrence of four-, six- and higher-membered rings of SiO_4 tetrahedra in $v\text{-SiO}_2$. Raman spectra are also sensitive to local microstructures in vitreous solids. We have therefore examined the question of rings in the structure of $v\text{-SiO}_2$ by comparing its Raman spectrum with spectra of crystalline silica polymorphs whose shortest loops contain four (coesite) and six (for example, α -quartz) tetrahedra. This comparison indicates that the sharp shoulder at 490 cm^{-1} in the spectrum of $v\text{-SiO}_2$, previously attributed to a defect structure³ or a longitudinal optic mode¹⁴, can be assigned to four-membered ring structure. We discuss here possible basis for the stability of four-membered rings of SiO_4 tetrahedra in $v\text{-SiO}_2$ at ambient pressure. Possible reasons for the absence of the 490 cm^{-1} band in the vibrational density-of-states derived for a random network model by Bell and co-workers^{12,15} are discussed.

Figure 1 shows first-order room-temperature Raman spectra of polycrystalline samples of α -quartz and coesite and a bulk sample of high purity $v\text{-SiO}_2$. These spectra were measured in the 90° scattering configuration with a Jobin-Yvon Raman spectrometer and 488-nm line of an argon ion laser¹⁶. The positions and spectral characteristics of the bands in these spectra are given in Table 1. Examination of these spectra suggests that the very strong band at 437 cm^{-1} and the sharp shoulder at 490 cm^{-1} in the spectrum of $v\text{-SiO}_2$ are related to the strong bands at 465 and 521 cm^{-1} in the spectra of α -quartz and coesite, respectively (Table 1).

Theoretical analyses^{17–20} of the vibrational spectrum of $v\text{-SiO}_2$ have indicated that the 437 cm^{-1} band belongs to $\nu_s(\text{Si-O-Si})$, the symmetric stretch. In this mode, the bridging oxygen moves along the line bisecting the Si-O-Si bond angle. The frequency of this mode is sensitive to both the Si-O-Si bond angle and the Si-O bond length^{18,19}. A third parameter which could affect $\nu_s(\text{Si-O-Si})$ is the short-range connectivity of the network structure. Raman data for framework aluminosilicates with four-, five- and six-membered rings of TO_4 tetrahedra ($T = \text{Si}$ or Al) indicate that, among crystals of isochemical compositions, the frequency of $\nu_s(\text{T-O-T})$ increases with reduction in the ring size (Table 2). This correlation implies that the band at 437 and the shoulder at 490 cm^{-1} in $v\text{-SiO}_2$ arise from tetrahedral network structures, composed of six- and four-membered rings, respectively. That these bands occur at lower frequencies in the spectrum of $v\text{-SiO}_2$ than in the spectra of the crystalline polymorphs is probably due to differences in Si-O-Si bond angles in the rings in $v\text{-SiO}_2$ and the crystalline

Table 1 Frequencies of the bands observed from Raman spectra

α -Quartz (cm^{-1})	Coesite (cm^{-1})	Silica glass† (cm^{-1})
—	77 s	68 s, bd, wp
128 s*	116 s	—
—	151 m	—
—	176 s	—
207 s, bd	204 m	—
—	220 w	—
264 m	269 s	—
—	314 m	—
—	326 m	—
356 m	355 m	—
395 m(sh)	—	—
—	427 m	—
465 vs	466 m	437 vs, bd, p
—	521 vs	490 s(sh), p
—	—	606 w, p
696 w	—	—
795 w(sh)	785 w	—
807 w	815 w	797 w, bd, dp
—	837 w	830 w(sh)
—	1,036 w	—
1,066 w(sh)	1,065 w	1,060 w, bd, dp
1,083 w	1,144 w	—
1,161 w	1,164 w	1,190 w, bd, dp
1,231 w	—	—

Measurement accuracy in the spectra of crystalline polymorphs, $\pm 2\text{ cm}^{-1}$ for weak band and $\pm 1\text{ cm}^{-1}$ for strong bands; in the spectrum of SiO_2 glass, $\pm 4\text{ cm}^{-1}$ for sharp and strong bands and $\pm 10\text{ cm}^{-1}$ for broad and weak bands.

* w, Weak; s, strong; vs, very strong; bd, broad; sh, shoulder; p, polarized; dp, depolarized.

† The arrow indicates the presence of a strong continuum between the band maxima.

polymorphs. Raman measurements of α -quartz under high pressures have shown that the frequency of the 464 cm^{-1} band is sensitive to compression²⁶. Studies of neutron irradiated $v\text{-SiO}_2$ also show that the frequencies of these bands increase on densification of the vitreous silica²⁷.

The large halfwidth of the 437 cm^{-1} band of $v\text{-SiO}_2$ (Fig. 1) is usually attributed to the dispersion of Si-O-Si angles. However, the position of $\nu_s(\text{Si-O-Si})$ also depends strongly on ring size (see Table 2). Thus, the $\nu_s(\text{Si-O-Si})$ vibrational modes of five-, seven- and higher-membered rings of SiO_4 tetrahedra, which may also be present in the random network, may be responsible for the broadening of the 437 cm^{-1} band.

The $v\text{-SiO}_2$ band at 606 cm^{-1} , which has been attributed to defects^{13,27}, has no counterpart in the spectra of silica polymorphs (Fig. 1). Our data, therefore, support its assignment to defect structures involving partially broken Si-O bonds in the network²⁸.

The 400–600 cm^{-1} region of the Raman spectrum of $v\text{-SiO}_2$ thus suggests that at least three different types of structural configurations occur in $v\text{-SiO}_2$. Each of these configurations, of course, will be associated with a range of Si-O-Si bond angles such that the material lacks long range order. The broad and complex bands in the 700–1,200 cm^{-1} region of the $v\text{-SiO}_2$ spectrum (Fig. 1) also may be attributed to the presence of at least three different types of structural groups in metastable equilibrium in $v\text{-SiO}_2$.

The presence of three different types of structural groups in $v\text{-SiO}_2$ can be further supported by the density and Raman data²⁷ on neutron irradiated $v\text{-SiO}_2$. Both the density and intensity of the 490 cm^{-1} band of $v\text{-SiO}_2$ increase on exposure to neutrons, and both properties show maxima at 5×10^{19} neutrons cm^{-2} . Neutron irradiation increases the intensity of the 606 cm^{-1} band at an even faster rate than the intensity of the 490 cm^{-1} band, but the 606 cm^{-1} intensity does not show a maximum. In contrast, the intensity of the 437 cm^{-1} band of unirradiated SiO_2 decreases with increasing exposure to neutrons²⁷. The different responses of the 437, 490 and 606 cm^{-1}

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bands of $v\text{-SiO}_2$ to neutron irradiation clearly demonstrate that these bands belong to different species. The observed maxima in the intensity of the 490 cm^{-1} band and in the density at 5×10^{19} neutrons cm^{-2} can be attributed to the conversion of the five-, six- and higher-membered rings of SiO_4 tetrahedra into four-membered rings.

Recently, Mikkelsen and Galeener²⁹ reported that both the density and the intensity of the 606 cm^{-1} band of $v\text{-SiO}_2$ (Suprasil W1) increase with the fictive temperature. The intensity of the 490 cm^{-1} band was also enhanced as the fictive temperature of $v\text{-SiO}_2$ increased (see Fig. 1 in ref. 29), although the magnitude of the increase could not be precisely determined.

The increase of the intensity of the 606 cm^{-1} band with increasing fictive density suggests either that a higher density structure is responsible for the 606 cm^{-1} mode, or that, while most of the network relaxes to a denser than average structure, this is accompanied by an increase in the concentration of a less dense structure responsible for the 606 cm^{-1} band²⁹. The Raman data²⁷ on neutron-irradiated $v\text{-SiO}_2$ clearly show that the 606 cm^{-1} band belongs to a less dense structure. At exposures of 2×10^{22} neutrons cm^{-2} , the intensity of the 606 cm^{-1} band is 1.4 times that for $v\text{-SiO}_2$ exposed to only 5×10^{19} neutrons cm^{-2} ; but the additional irradiation decreases the density to 2.518 g cm^{-3} from 2.560 g cm^{-3} .

The intensities of the 490 and 606 cm^{-1} bands increase with increasing fictive density as well as with increasing density of $v\text{-SiO}_2$ at low neutron irradiation ($\leq 5 \times 10^{19}$ neutrons cm^{-2}); this suggests that there is a relationship between the four-membered ring structure responsible for the 490 cm^{-1} band and the defect centres responsible for the 606 cm^{-1} mode. The silicon atoms at these defects carry a formal positive charge. We suggest that the four-membered rings in $v\text{-SiO}_2$ at ambient pressure are stabilized by the excess positive charge on silicon atoms at the defect sites just as the four-membered rings of TO_4 tetrahedra in crystalline feldspar are stabilized by cations³⁰. This interpretation suggests that the intensities of both the 490 and 606 cm^{-1} bands will initially increase with the density of $v\text{-SiO}_2$ at ambient pressure. However, the extent to which defect centres can stabilize four-membered rings at ambient pressure is limited as indicated by the maxima in both the intensity of the 490 cm^{-1} band and the density of unirradiated $v\text{-SiO}_2$ at an exposure of 5×10^{19} neutrons cm^{-2} .

Bell *et al.*¹⁵ and Bell and Dean^{17,31} have computed vibrational densities-of-states and other properties of SiO_2 for large (~ 200 SiO_4 molecular unit) continuous random-network clusters of almost perfectly tetrahedral units. Within each cluster, molecular units interact through short range (nearest-neighbour) bond forces while the cluster interacts with non-bridging oxygens at its surface. Raman spectra of $v\text{-SiO}_2$ have recently been computed¹¹ in terms of the behaviour of much smaller sections (typically 10–20 molecular units) of Bell and Dean's clusters. Computations with these models have given fairly good

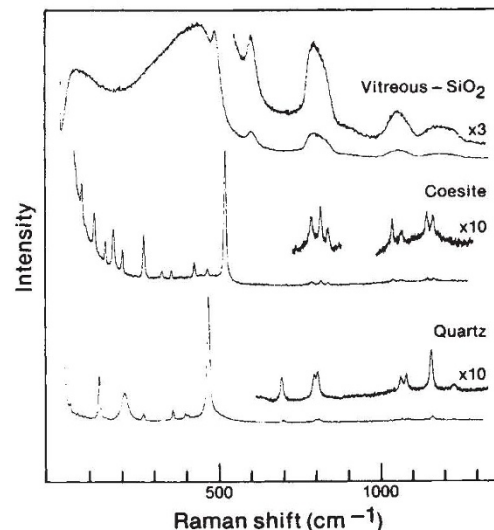


Fig. 1 Raman spectra of crystalline α -quartz, coesite and vitreous silica ($v\text{-SiO}_2$) at room temperature (laser 488.0 nm ; slit and laser power at the sample used for crystalline polymorphs were 3 cm^{-1} and 300 mW and for SiO_2 glass these were 5 cm^{-1} and 500 mW , respectively).

agreement with observed X-ray and neutron diffraction data. Calculated spectra also resemble, to a first approximation, observed Raman spectra of $v\text{-SiO}_2$. However, the sharp bands at 490 and 606 cm^{-1} and the broad band at $1,200\text{ cm}^{-1}$ do not have counterparts in the computed spectra^{14,32}. This discrepancy may result from two factors that the $v\text{-SiO}_2$ models of Bell and co-workers do not take into account: (1) the presence of defect centres involving partially broken Si–O bonds²⁸ in the interior of $v\text{-SiO}_2$ and (2) the ring statistics⁹, especially the presence of four-membered ring structures which seem to be stabilized by the defect centres. It is now possible to calculate vibrational spectra of vitreous solids on the basis of random network models containing defect centres^{10,33} and ring structures^{10,11}. The present results suggest that such calculations for $v\text{-SiO}_2$ should be attempted to extend our understanding of the Raman spectrum as well as the structure of vitreous silica.

Received 19 January; accepted 27 April 1981.

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Table 2 Relationship between $\nu_s(\text{T-O-T})$ frequency and ring structures in some tectosilicates

Minerals	$\nu_s(\text{T-O-T})$ in crystalline polymorphs	Repeat units and shortest rings of tetrahedra ²¹	Ref.
α -quartz	464 vs	6	22
β -quartz (700 °C)	464 vs	6	22
α -cristobolite	416 vs	6	23
Coesite	521 vs	4	Present work
$\text{LiAlSi}_2\text{O}_6\text{-III}$	480 vs	6	24
$\text{LiAlSi}_2\text{O}_6\text{-II}$	492 vs	5	24
Low albite ($\text{NaAlSi}_3\text{O}_8$)	506 vs	4	25
Orthoclase (KAlSi_3O_8)	513 vs	4	25
Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)	503 vs	4	25