Intermediate-range order in permanently densified vitreous \( \text{SiO}_2 \): A neutron-diffraction and molecular-dynamics study


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The structure of pressure-densified vitreous \( \text{SiO}_2 \) has been investigated using neutron-diffraction and molecular-dynamics techniques. After compression to 16 GPa at room temperature, recovered samples have densities 20\% higher than normal vitreous \( \text{SiO}_2 \) and show substantial changes in the first sharp diffraction peak (FSDP), an indication of modification in the intermediate-range order. The changes in the FSDP are due to increased frustration caused by the decrease in the Si—O—Si bond angle and a shift in the Si-Si and O-O correlations in the range of 4—8 Å toward lower distances.

The irreversible densification of vitreous (amorphous) silicon dioxide (\( \text{a-SiO}_2 \)) subjected to pressures above 12 GPa has been known for decades.\(^1\)–\(^11\) However, recently it has become evident that the highly densified forms of \( \text{a-SiO}_2 \) may have a very different microscopic structure than that of the “as-prepared” material and they have been termed “amorphous polymorphs”. Although Raman spectroscopy shows that the microscopic arrangement of the atoms is radically changed in the densified material,\(^12\)–\(^15\) almost no structural information is available. The reason for this is that neutron scattering, which is the most powerful tool in the study of the structure of amorphous materials, cannot be applied to the small samples of densified material which are usually produced in high-pressure experiments using diamond-anvil cells. Information obtained with x rays,\(^13\)\(^,\)\(^16\) which cover a much smaller range of wave vectors, has had limited success in unraveling the structure.

In this paper, we report the results of a combined neutron-diffraction and molecular-dynamics (MD) study of the structural changes which occur in permanently densified \( \text{a-SiO}_2 \) synthesized in a large-volume, high-pressure apparatus. The static structure factor of densified and normal \( \text{a-SiO}_2 \) determined by neutron diffraction are in good agreement with those obtained in the MD calculations. Both experiment and MD simulations show that there is no appreciable change in the short-range order (SRO), viz. the \( \text{SiO}_4^{-} \) tetrahedra, but there is a significant effect on the first sharp diffraction peak (FSDP)—the fingerprint of intermediate-range order.

The densified samples were produced at the Stony Brook High Pressure Laboratory compressing rods of normal \( \text{a-SiO}_2 \) in a uniaxial split-sphere apparatus (USSA-2000) up to pressures of 16 GPa at room temperature in 10-mm edge length MgO octahedra.\(^17\),\(^18\) A total of four densified \( \text{SiO}_2 \) rods \( \sim 4 \) mm in diameter and 7—13 mm long were produced with total weight 0.943 g. Bril-louin scattering was used to ascertain that the densification was the same in all the rods; the density homogeneities in a single rod were estimated to be 5\% and within this spread all rods were equivalent. Macroscopic density measurements yielded 2.67 g/cm\(^3\) indicating a 20\% increase over that of the undensified rods.

Neutron-diffraction experiments were carried out on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source at Argonne National Laboratory on both densified and normal \( \text{a-SiO}_2 \) obtained from the same source. Time-of-flight data were collected in six groups of time-focused detectors placed at scattering angles of \( \pm 90^\circ \), \( \pm 60^\circ \), \( -30^\circ \), and \( +15^\circ \) with respect to the incident beam. The agreement in the overlap regions between data collected with different detector banks shows that the results are not due to an experimental artifact. These data were combined by weighting with the incident neutron spectrum over the range \( \lambda = 0.3—4.0 \) Å. Both the densified and undensified cylindrical samples were mounted within thin-walled vanadium tubes 0.5 cm in diameter by 5 cm long. Corrections were made for container scattering, beam attenuation by sample and container, multiple scattering, and inelastic effects.\(^19\) The detectors were normalized by means of a separate run with a vanadium standard.

Molecular-dynamics calculations were performed with effective interparticle potentials consisting of two- and three-body covalent interactions. Similar effective interactions were used previously to successfully describe the structural properties of molten and vitreous \( \text{GeSe}_2 \).\(^20\)\(^,\)\(^21\) In the case of vitreous \( \text{GeSe}_2 \), the MD results for the phonon density of states (DOS) are also in good agreement with those obtained from inelastic neutron-scattering measurements.\(^22\) Using the same interatomic-interaction scheme, we have also performed MD simulations for molten and vitreous \( \text{SiSe}_2 \).\(^23\) Again the MD results for the structure and phonon DOS are in good agreement with neutron-scattering experiments.\(^24\)

Details of the two- and three-body potentials used for \( \text{a-SiO}_2 \) are described in Ref. 25. The two-body interactions comprise Coulomb interactions due to charge transfer between Si and O, steric repulsion due to the
finite sizes of Si and O, and charge-dipole interactions to include electronic polarizability effects. The three-body
covalent interactions involve the variations of Si—O
bond lengths and Si—O—Si and O—Si—O bond angles.

The present calculations were carried out for a system of 648 (216 Si + 432 O) particles in a box of volume
9.788 × 10^{-21} cm^3 for normal a-SiO_2 and 8.161 × 10^{-21}
from the case of densified a-SiO_2. Periodic boundary
conditions were used and the long-range Coulomb
interaction was treated with Ewald’s summation. A time
step of 0.5 × 10^{-15} sec was used in the Beeman^26 algorithm
with the total energy conserved to 1 part in 10^4
over several thousand time steps.

In the MD studies, a-SiO_2 at normal density was ob-
tained as follows: starting with a melt thermalized for
60,000 time steps at 3000 K, the system was cooled to
2500 K and thermalized for 30,000 time steps, then fur-
ther cooled to 2000 K and thermalized for another 30,000
time steps. The melt at 2000 K was quenched at a rate of
0.1% every 10 time steps until it reached ~1500 K; at this
point the system underwent thermal arrest. It was
subsequently thermalized for 60,000 time steps. From
this system glasses at 600, 300, and 10 K were obtained
by cooling and thermalizing. The higher density glasses
were obtained by increasing the density at 3000 K and
repeating the above procedure.

Figure 1 shows the experimentally determined neutron
structure factor, S_N(q), of normal and densified a-SiO_2.
Our results in the normal state agree well with previous
reports.27 Very little change can be seen in the range of
large q. The FSDP, on the other hand, undergoes sub-
stantial changes in both position and intensity. Since
features at small q correspond to a large range in r space,
the observed changes are a qualitative indication that,
while the short-range order is not changing appreciably,
the intermediate-range order is substantially modified.

Information in r space can be obtained by performing
the appropriate Fourier transform on S_N(q); one such
function is T(r) which is related to the weighted (concen-
tration and scattering cross section) pair distribution
function g_N(r) through

\[ T(r) = 4\pi pr \, g_N(r) \]

where

\[ g_N(r) = 1 + \frac{1}{4\pi r} \int_0^\infty [S_N(q) - 1] \frac{q^2 \sin(qr)}{qr} dq \]

and

\[ g_N(r) = \left( \sum_{\alpha, \beta} c_\alpha b_\alpha c_\beta b_\beta g_{\alpha\beta}(r) \right)^2 \sum_\alpha c_\alpha b_\alpha \]

The result of such a transformation is shown in Fig. 2.
The peaks at 1.6 and 2.6 Å are unambiguously as-
signed to the Si-O and O-O distances, respectively, and,
as argued in the preceding paragraph, show only nominal
changes in position upon densification. Additional exper-
imental details and peak-fit parameters are presented else-
where (see Note added in proof).

The experimental T(r) is the composite of all nearest-
neighbor, next-nearest-neighbor, and higher correlations.
Where there is complete separation of a peak, as in the
first Si-O coordination shell, a Gaussian deconvolution
procedure serves to fit the peak. This works well for the
next O-O peak in undensified ν-SiO_2 but fails for the
permanently densified material. At 3.0 Å there is a broaden-
ing of the O-O peak and a change in the sloping back-
ground. This results in an apparent shift of the Si-Si peak
to larger distances. Depending on how the background is
introduced, one can obtain an increase, a decrease, or no
change in position of the deconvoluted peaks. We con-
clude that there is no unique deconvolution of the experi-
mental T(r) for distances greater than 3.0 Å. We also
point out that in the region 1.9–2.3 Å in Fig. 2, there is a
small increase in T(r) for the densified material; although
small, this increase is larger than our estimated error.
This feature could be due to a few additional Si—O bonds
arising as a result of densification.

Figure 3 shows the neutron (solid circles) and MD re-
sults (solid line) for S_N(q) under normal and densified
conditions. In both normal and densified systems, the
MD calculations for the peak positions are in very good
agreement with the experimental results. In the normal
system the MD results for the amplitudes of all the peaks
except the FSDP are also in accord with the neutron
measurements. The observed discrepancy between the
simulation and experiment for the height of the FSDP is
a result of different quench rates used in the preparation of the computer glass and the real system.28

After densification, all high-\(q\) peaks remain unchanged while the FSDP shifts to larger \(q\). The MD simulations also reveal that the amplitude of the first peak decreases on densification. These changes in the position and amplitude29 of the FSDP are in accord with the neutron-scattering experiments. In addition, the simulation and experiment also agree on the absence of any changes in the higher-\(q\) peaks.

Molecular-dynamics results can also be used to obtain a microscopic picture of the changes occurring on densification. Figure 4 shows the MD partial pair distribution functions \(g_{\text{oO}}(r)\). In agreement with the conclusions drawn from the experimental \(T(r)\) in Fig. 2, the first peaks in Si-O and O-O correlations show only minimal changes upon densification. In the region around 3.2 Å, the partial pair distribution functions show a contribution from Si-Si as well as O-O. Since \(T(r)\) is weighted by concentrations and scattering lengths, the O-O contributions in this region are comparable to those of Si-Si.

On densification, the first peak in the Si-Si distribution shifts to lower distances, implying a reduction in the nearest-neighbor Si-Si distance. In all the three distributions, Si-Si, Si-O, and O-O (see insets on Fig. 4), second peaks are shifted to lower distances upon densification implying a reduction in the second-neighbor distances Si-Si2, Si-O2, and O-O2; changes in Si-Si2 are the largest and most noticeable. A slight discrepancy between experimental and MD results should be noted in the range 1.9–2.3 Å. Recall that the experimental \(T(r)\) increases slightly on densification. The MD results for partial pair distribution functions do not.

Using MD configurations, microscopic structural changes upon densification can be further analyzed in terms of angular correlations between atoms. The bond-angle distributions for O—Si—O and Si—O—Si for normal and densified systems are shown in Fig. 5. In both systems the distribution of O—Si—O bond angles peaks around 109°; however, for the densified case the distribu-

![FIG. 4. MD results for partial pair distribution functions \(g_{\text{oO}}(r)\) for normal (dashed line) and densified (solid line) vitreous SiO\(_2\). Inset shows \(g_{\text{oO}}(r)\) on an expanded scale in the range 4–8 Å.](image)

![FIG. 5. Bond-angle distributions O—Si—O and Si—O—Si for normal and densified (20%) vitreous SiO\(_2\) from MD calculations.](image)
in other bond-angle distributions, O—O—O, O—O—Si, and Si—Si—Si (not illustrated) are also consistent: O—O—O shows a broadening of the peak at 60°, consistent with slight distortion of the SiO1/24 tetrahedra, and changes in the angles around 140° are in accord with the changes in oxygen second neighbors observed in gO-O(r). Changes in O—O—Si at larger angles are also in accord with the above observations. Another manifestation of the connectivity changes due to densification is the increase of the 60° peak in the Si—Si—Si bond-angle distribution. The decrease in the Si—O—Si bond angle and the shorter nearest-neighbor Si—Si distance, combined with the fact that the volume of individual SiO1/24 tetrahedra remains essentially unaltered on densification, results in the increased frustration in the packing of SiO1/24 tetrahedra. In light of the preceding analysis which provides a microscopic picture of the changes occurring upon densification, it is interesting to establish a connection between the atomic rearrangements and the observed change of the first sharp diffraction peak. As can be seen in the inset in Fig. 4, in the range 4–8 Å, the Si-O correlations do not change appreciably; however, the Si-Si and, to a lesser extent, the O-O correlations shift towards lower distances. This shift in r space moves the position of the FSDP to a larger-q value upon densification, as seen in Figs. 1 and 3. The contribution to the FSDP comes from all three correlations, Si-O, O-O, and Si-Si, and each correlation is shifted to lower distances by a different amount (the shift in Si-O being the smallest and Si-Si being the largest) resulting in broadening of the FSDP upon densification. In summary, the changes in the FSDP—shift in the position to a larger-q value, reduction in its height, and increased width—are due to increased frustration caused by the decrease in the Si—O—Si bond angle and different shifts in the Si-O, O-O, and Si-Si correlations toward lower distances in the range of 4–8 Å.


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3The basis for using similar effective potentials is that SiO4 and binary chalcogenide glasses have several common structural features. These include tetrahedral units comprising short-range order and the medium-range order manifested in the form of FSDP.
4U. Walter et al., Phys. Rev. B 37, 4232 (1988). Even a subtle feature such as the companion line of the symmetric breathing mode is found present in the MD results. The energy of the companion line is also in accord with the Raman scattering measurements.
10Different quench rates do not affect the peak positions or the amplitudes of the second-, third-, and higher-order peaks in the structure factor. As regards the FSDP, its position is unaffected but its amplitude diminishes with an increase in the rate of quenching. The larger the quench rate, the higher the frustration of tetrahedral packing. This diminishes medium-range correlations, causing a decrease in the amplitude.
11In light of much higher quench rates in simulation, the excellent agreement on the amplitude of the FSDP may be fortuitous.