

Local structures of silica polymorphs

Silica, SiO_2 , exists in many different phases at ambient pressure, all of which form structures which are networks of corner-sharing tetrahedra with differing amounts of disorder. There is interest in the relationship between the local structures of these silica polymorphs and amorphous silica; neutron scattering measurements on LAD are revealing the structural similarities, and these can be interpreted in terms of the extent to which the structures allow the silica tetrahedra to rotate and move.

The equilibrium sequence of silica phase transitions with increasing temperature are: α -quartz to β -quartz (at 574 °C) to HP-tridymite (867 °C) and finally to β -cristobalite (1470 °C) prior to melting at 1727 °C. In addition there are several other metastable phase formed by more rapid cooling of the high temperature phases such as silica glass (from rapid cooling of the liquid) and α -cristobalite (from cooling β -cristobalite below about 280 °C). The similarities in bonding, density and positions of the first diffraction peaks in amorphous silica and β -cristobalite have led to the suggestions that the local structures of these two phases are similar. In addition the observation of high-pressure amorphisation in silica makes the relationship between the structures of the crystalline and amorphous silica polymorphs more topical.

Total scattering neutron scattering measurements on polycrystalline samples of a number of silica phases have been made using the LAD diffractometer at ISIS. Rietveld refinement of the Bragg peaks yields the time-average periodic structure, whereas the total scattering gives information about the instantaneous structure through pair correlation functions. When a structure is dynamically disordered the time-average periodic structure and the instantaneous local structures may be very different. In these silica phases, the average structures show an apparent contraction of the SiO_4 tetrahedra with increased temperature and, in HP-tridymite and β -cristobalite, linear Si-O-Si bonds. In contrast, the peak positions in the pair correlation functions give a direct measure of the bond lengths and show no tetrahedral contraction or anomalous Si-O-Si bond angles. The high-temperature phases have dynamically disordered orientations of the tetrahedra and the refined anisotropic thermal parameters for the

oxygen atoms are large and elongated in the plane that bisects the Si-Si vector.

Three-dimensional local structures that are fully consistent with the average and instantaneous structures have been produced using the reverse Monte Carlo technique modified to refine an initial model produced from the average structure. The models were required to

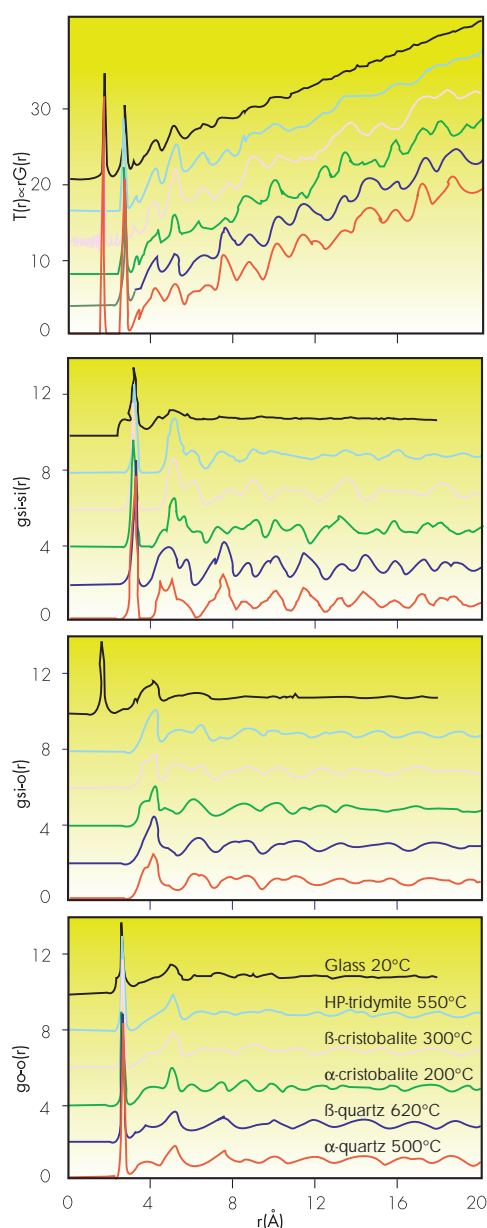


Figure F3.1. Total ($T(r)$) and partial ($g_{ij}(r)$) radial distribution functions obtained from the RMC models (successive functions offset by 2 for clarity). The direct transformed 'experimental' $T(r)$ for β -cristobalite and the calculated $T(r)$ for amorphous silica are both shown superimposed on their respective RMC generated $T(r)$.

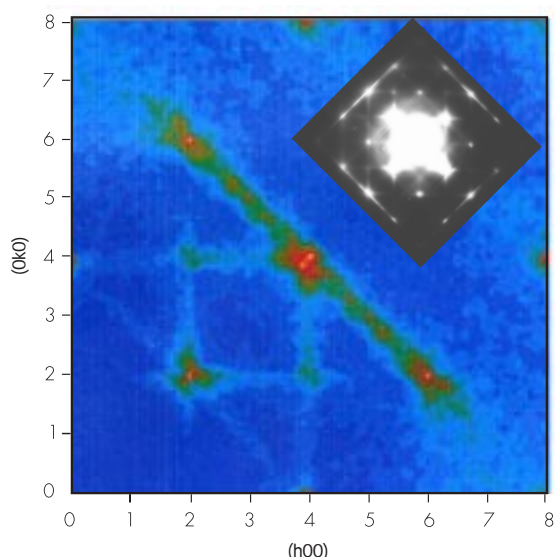


Figure F3.2. Diffuse scattering from β -cristobalite calculated from the RMC configurations. The lines of diffuse scattering correspond to the predictions of the RUM model and to those found in experimental TEM data (inset - c/o R L Withers and T R Welberry).

maintain regular, fully connected SiO_4 tetrahedra and to fit the experimental total scattering structure factor. Figure F3.1 shows the radial distribution functions calculated from the refined models. Three results are immediately evident from the models. First, α - and β -cristobalite have different local structures with different pair correlation functions. Contrary to previous suggestions, β -cristobalite does not contain domains of the lower symmetry α -phase. Secondly, domains of α -quartz are not found in β -quartz and thirdly there is a remarkable correspondence between the radial distribution functions from HP-tridymite, β -cristobalite and glass with the oscillations remaining in phase until well above 10 Å. Assuming that the correlation between the local structures of the disordered crystal and amorphous phases decays exponentially with distance, then a typical correlation length of $\xi \sim 7.5$ Å is found. Figure F3.1 shows a comparison between the glass radial distribution function and that which has been calculated from a sum of radial distribution functions from HP-tridymite and a random arrangement with $\xi = 7.5$ Å. This is too short to admit a microcrystalline interpretation of glass structure but does show that up to distances of ξ , which is typically slightly larger than a ring of six linked SiO_4 tetrahedra, there are regions of the glass that have structural elements of the crystal and beyond this the glass and crystal structures diverge.

The structural similarities between HP-tridymite, β -cristobalite and amorphous silica over the length scale 0-

10 Å can now be interpreted in terms of their internal flexibility as deduced by the Rigid Unit Mode model which is concerned with ways a structure can distort by rotations and displacements of undeformed rigid units. This model, confirmed by inelastic neutron scattering measurements, diffuse electron scattering and also by our local structure models (see figure F3.2) shows that there is far more flexibility in the HP-tridymite and β -cristobalite structures than in any of their lower temperature phases or the quartz phases. Since the disordered glass structure needs considerable flexibility of the shapes of the rings of linked tetrahedra in order to form a continuous random network, it is not surprising that the glass structure uses structural elements of these flexible phases which are unlike their ideal structures or the more ordered crystalline phases. By inverting this comparison, the internal flexibility will distort the local structures of the crystalline phases to give disorder similar to that found in the glass. The linear Si-O-Si bonds achieve a more favourable value locally when the tetrahedra rotate within the allowed RUM flexibility. This is illustrated in figure F3.3 which shows how the local disorder in the RMC models is accommodated within the average structure of HP-tridymite with displaced and rotated SiO_4 tetrahedra on a regular lattice. The wide distribution of ring shapes is strongly reminiscent of the glass structure and can be seen in simulations of the dynamics of HP-tridymite and amorphous silica using the RUM approach.

Finally we note that although similarities in the local *instantaneous* structures are found, in the crystalline phases this disorder is *dynamic*, arising from the RUM phonons supported by the underlying periodic structure and driven by the need to avoid local configurations with linear Si-O-Si bonds, whereas in the glass the disorder is *static*, forced by the topological disorder which does not change over short time scales.

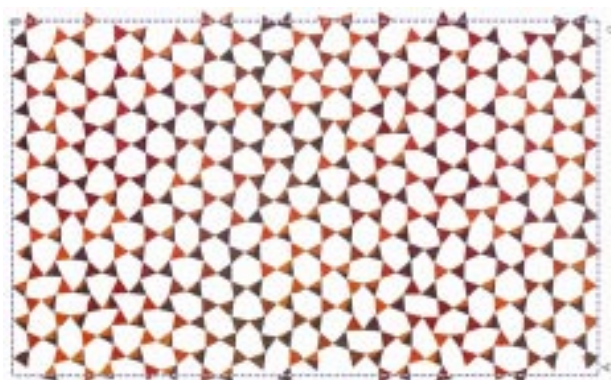


Figure F3.3. A section perpendicular to the *c*-axis of the RMC refined model of HP-tridymite where each tetrahedra corresponds to an individual SiO_4 unit.