

High-pressure studies of cristobalite

The crystal structure of the high-pressure phase of cristobalite, a form of silica, has been solved through a combination of neutron diffraction and atomistic modelling.

Silica, SiO_2 , is one of the most important materials known to man. It has many important technological applications, such as the uses of quartz oscillators, silica glass ceramics, and as sand in construction. Silica is also important for geology as one of the most significant rock-forming minerals. Silica exists in many different crystalline phases, as well as in its glass phase. There is considerable interest in understanding the structures of the different phases, and in being able to understand the processes that lead to stabilising the different phases under different conditions of temperature and pressure.

One of the important phases of silica is cristobalite. At high temperature and ambient pressure the structure of this phase is cubic, and can be described as being similar to that of the crystal structure of silicon with oxygen atoms lying half-way between neighbouring pairs of silicon atoms. This structure gives the average structure, but it only tells part of the story because the linear Si–O–Si bonds would prefer to have an angle nearer 145° . How this is accomplished through dynamic reorientations of the SiO_4 tetrahedra was discussed in a feature article of ISIS'98 (pp 44–45). On cooling the bond-angle problem is resolved by a displacive phase transition to a tetragonal structure, which can be accomplished by the SiO_4 tetrahedra adopting specific orientations without distorting. Recently it was reported that the tetragonal phase undergoes an additional phase transition to a monoclinic phase on increasing pressure, but its structure could not be solved. The intuitive approach, based on our understanding of the usual processes of displacive phase transitions, would be to suppose that the phase transition involves a distortion that breaks the symmetry of the tetragonal structure. However, using a theoretical approach developed in our group, the “Rigid Unit Model” model, it appears that such a mechanism would not be likely. Instead, we proposed that the phase transition could arise from another distortion of the cubic phase. This proposition is represented schematically in Figure 1. Taking this idea as our

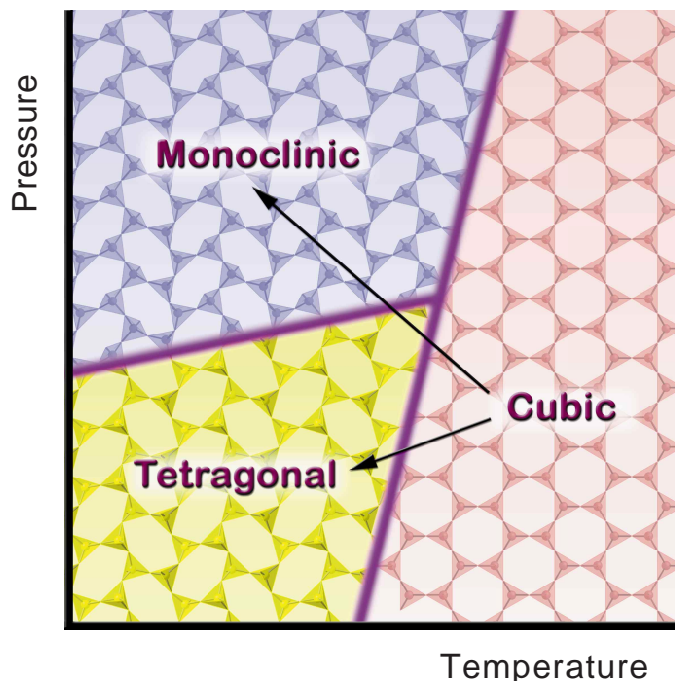


Figure 1. Proposed symmetry transformations of cristobalite mapped onto a schematic pressure–temperature phase diagram. In this scheme, both the tetragonal and monoclinic phases are obtained as separate distortions of the parent cubic phase. The phase fields contain tetrahedral representations of the respective structures viewed down a common direction that corresponds to $[111]$ in the cubic phase. The cubic structure has linear Si–O–Si bonds, which are bent in different ways in the tetragonal and monoclinic structures through rotations of the SiO_4 tetrahedra and buckling of the framework.

starting point, we had a fresh assault on the structure of the high-pressure monoclinic phase using neutron high-pressure diffraction.

The experiment was performed using the Paris–Edinburgh high-pressure cell on the HiPr/Pearl beam line at ISIS. The diffraction pattern at a pressure of 3.5 GPa is shown in Figure 2. The diffraction pattern could be indexed from the earlier results, but it is not at all straightforward to deduce the structure from a complex, albeit indexed, powder diffraction pattern. Our approach was to use a variety of modelling methods to propose a trial structure for the data analysis. We started from the atomic coordinates of the cubic phase with the lattice parameters of the monoclinic phase, and allowed the atoms to relax to a new equilibrium structure using both lattice energy minimisation and molecular dynamics methods using two different empirical potential energy functions. The different approaches both gave the same structure, and whether this

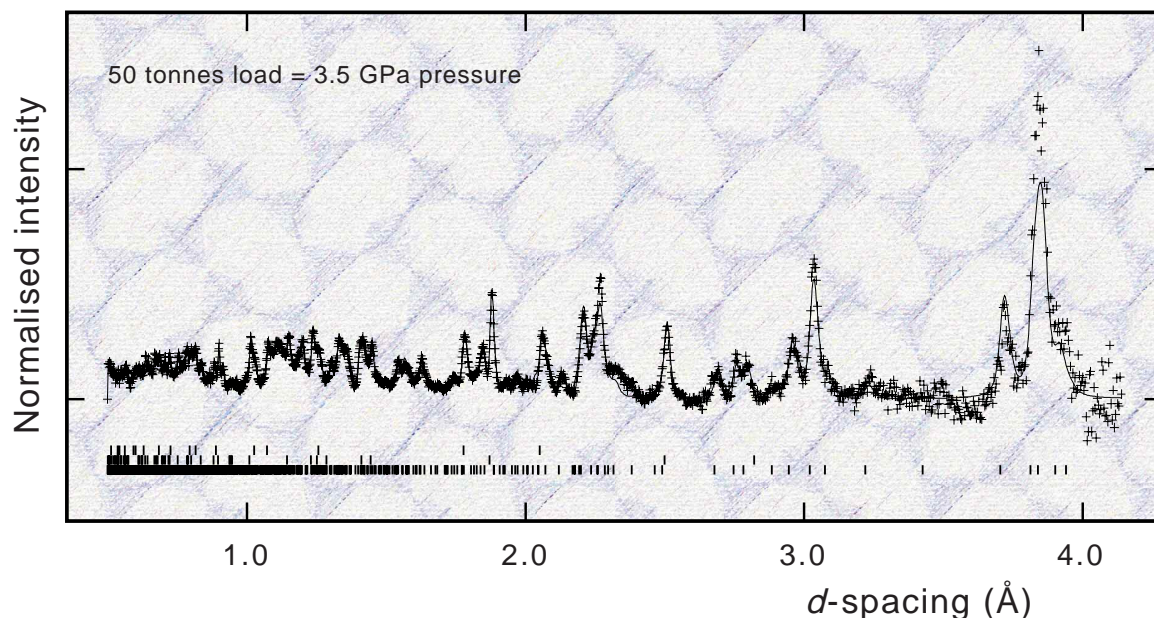


Figure 2. Diffraction pattern of the high-pressure monoclinic phase of cristobalite (3.5 GPa) obtained on the HiPr/PEARL beam line at ISIS.

was reasonable was then checked using quantum mechanics calculations. This trial structure was used as the starting model in the Rietveld refinement, and the refinement locked into it straight away and gave a good refined structure. We were immediately able to conclude that we had obtained the correct crystal structure of the high-pressure monoclinic phase using the combination of modelling and high-pressure neutron diffraction methods.

The crystal structure of the high-pressure monoclinic phase is shown in Figure 3. In Figure 1 we show this structure with the SiO_4 tetrahedra highlighted, and compared with the corresponding projections of the cubic and tetragonal phases. The rotations of the SiO_4 tetrahedra, leading to a buckling of the network of connected tetrahedra, is clearly seen. The new structure is clearly a distortion of the cubic structure, and is not directly related to the structure of the tetragonal phase although there are superficial similarities. In fact, the transition mechanism consistent with the new structure is fully consistent with the predictions of the Rigid Unit Mode analysis.

This study has shown two main points. First, it has highlighted the value of combining neutron diffraction with modelling methods to determine relatively complex crystal structures. Secondly, it

has shown that high-pressure phase transitions may have more complex group-subgroup symmetry transformations than we usually find in phase transitions caused by changes in temperature. It appears that pressure-induced changes in the free-energy surfaces can give rise to cases, such as in cristobalite, where phases at different pressures have common high-temperature parent phases instead of there being a progressive continuous change in symmetry through the sequence of phase transitions.

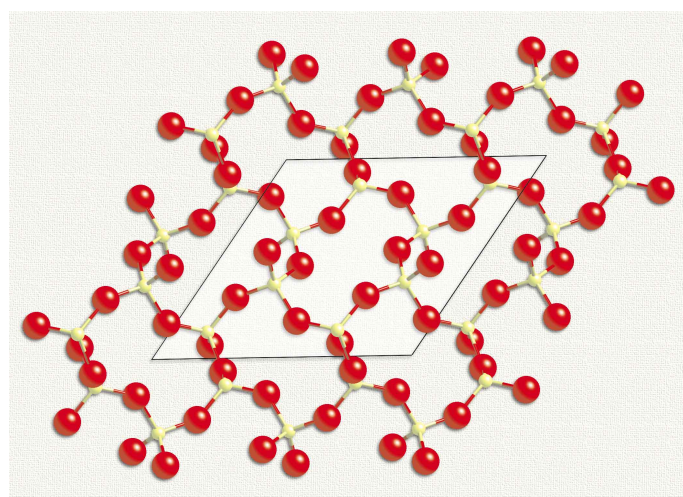


Figure 3. Projection of the crystal structure of the high-pressure monoclinic phase of cristobalite (3.5 GPa) viewed down $[010]$.

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