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THE HIGH PRESSURE BEHAVIOR OF CRISTOBALITE

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At low pressures, cristobalite shows significant compressibility, achieved by the progressive crumpling of its low-density silicate framework. There is a first-order, *displacive*, structural phase transition from tetragonal $P4_12_12$ to triclinic $P1$ at $P_c \sim 10\text{--}16$ kb, which produces transformation twins. Complete reversal, with disappearance of the twins, is possible on reducing pressure.

INTRODUCTION

The most abundant rock-forming minerals in the earth's crust are framework silicates with complex crystal structures. These materials display a remarkable chemical and structural diversity. In addition, structural phase transitions involving displacive distortions are particularly common, leading to yet more structural variation.

There have been suggestions that the distortive behavior of the framework 'skeleton' can be interpreted in terms of a *rigid unit model*. The flexible Si-O-Si linkage permits crumpling or shearing of frameworks, with little or no distortion of the polyhedra themselves. In essence, the bridging oxygens act as 'universal joints'. Yet at a practical level, understanding the precise rôle of the framework topology in many minerals is complicated by the effects of ionic substitutions, the presence of cavity-filling cations, non-stoichiometry, and order-disorder amongst the tetrahedral sites. Attention has therefore focused on the SiO₂ polymorphs, as most clearly demonstrating the intrinsic behavior of such linkages.

In many ways, cristobalite is the archetypal framework mineral. The cristobalite structure comprises a three-dimensional framework of corner-linked SiO₄ tetrahedra, arranged in six-fold and four-fold rings. At high temperatures cristobalite is cubic, and the structural topology is analogous to cubic-close-packing (c.f. high tridymite). Below $T_c \sim 490$ K, there is a displacive transition to a tetragonal phase with spacegroup $P4_12_12$. This transition involves a large volume change and is strongly first order in character.

The high pressure behavior of cristobalite has attracted much interest recently, with the reporting of a possible phase transition at moderate pressures (Yeganeh-Haeri *et al.*, 1991). It was the purpose of this work to follow the structural behavior of cristobalite on increasing pressure, working with high-quality specimens of natural cristobalite, under *hydrostatic* conditions.

SINGLE-CRYSTAL DIFFRACTION

The cristobalite sample used for this study is from the Ellora Caves, near Hyderabad, India (Harvard Collection, no. 97849) and consists of gem-quality octahedra, with interpenetrant twins. A single crystal was isolated for this work.

Table 1: Structural parameters for tetragonal cristobalite

P [kbar]	x (Si)	B(Si)	x(O)	y(O)	z(O)	B(O)
0.0	0.3003(1)	0.765(7)	0.2392(2)	0.1044(2)	0.1787(1)	1.48(3)
1.2(3)	0.3024(4)	0.84(4)	0.2383(8)	0.1084(6)	0.1815(4)	1.26(8)
6.9(3)	0.3085(4)	0.65(5)	0.2364(10)	0.1197(11)	0.1871(6)	1.07(9)
10.1(9)	0.3119(5)	0.65(6)	0.2351(11)	0.1265(11)	0.1905(8)	1.20(13)

A 1 atm X-ray structure refinement was carried out to verify that the crystal was completely *untwinned*. The crystal was then mounted in a *Merrill-Bassett* diamond-anvil cell using a 4:1 methanol/ethanol mixture as pressure medium. Cell parameters were determined using 10 to 20 reflexions with $30^\circ \leq 2\theta \leq 40^\circ$, centered at eight equivalent positions, following the procedure of King and Finger (1979). Initial unit-cell refinements were made without constraints, to test for non-tetragonal distortions, although none were found. The cell parameters were then determined by the vector least-squares method with tetragonal constraints (Ralph and Finger 1982). Full intensity data collections were made at 0.0, 1.2, 6.9 and 10.1 kbar. A second crystal (also untwinned) was used for additional cell parameter measurements. This showed no significant differences in structural behavior from the first crystal.

Pressure calibration was by the ruby fluorescence method, measuring a number of different rubies inside the cell, to test for possible pressure gradients. We took great care to ensure a consistent and relatively-accurate pressure calibration. Ruby R1 and R2 fluorescence peaks were fitted using least-squares profile refinement, and pressures calculated using 1 atm standards, and a temperature-correction.

Cristobalite is a relatively soft mineral, with a very low value for the isothermal bulk modulus, $K_{0T} \sim 128$ kbar ($K' \sim 7.0$). The mineral shows anisotropic behavior as a function of pressure, with the c axis more compressible than the a and b axes. The axial compressibilities, calculated from linear regressions of the cell parameters versus pressure are: $\beta_a \sim 1.64(5) \times 10^{-3}$ kbar $^{-1}$, $\beta_c \sim 2.40(7) \times 10^{-3}$ kbar $^{-1}$. Structure refinements show that the compressibility is at-

tained by a slight crumpling of the tetrahedral framework, changing Si-O-Si, with little, if any, distortion of the tetrahedra, measured by the two Si-O distances, R1 and R2.

Above 10–15 kbar, the crystal transformed to a new, non-tetragonal, phase, characterized by transformation twinning. Reflexion profiles were collected using $\theta/2\theta$ and ω scans across the positions of the former tetragonal 011 and 101 reflexions.

The phase transition is completely reversible and appears to be displacive in character. On decreasing pressure, the twins vanish and the former orientation of the tetragonal cell reappears. Clearly there is a crystallographic relationship between the two phases, i.e., a *super-group-subgroup relation*. By analyzing the possible subgroups of 422, and the number of twin components expected, we predict that the high pressure phase is triclinic, with spacegroup $P1$.

X-RAY POWDER DIFFRACTION

A small volume of powdered cristobalite was mounted within the sample chamber of a diamond-anvil cell, together with a number of tiny rubies, for pressure calibration. A 4:1 methanol/ethanol mix was used as pressure medium and the sample was compressed to 30 kb. Ruby fluorescence spectra displayed well-resolved R1 & R2 peaks, with no significant broadening, indicating that the mount was subject to hydrostatic pressure.

Diffraction experiments were carried out at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, using beamline X7A. An incident beam of wavelength 0.6984 Å was selected, using an asymmetric-cut, focusing Si (111) monochromator. Diffracted

intensity was collected, 2° 2θ at a time, using a linear position-sensitive detector. Between successive frames, the detector was scanned through the appropriate 2θ .

We were able to resolve a number of diffraction peaks in the 8 – 30° 2θ region, the most intense of which occurred at low angles. The tetragonal 101, 111 and 102 peaks are all split into four components, indicating that the high pressure phase has a triclinic unit cell. Despite this large drop in symmetry, preliminary attempts at indexing the diffraction pattern indicate the close similarity between the two unit cells, with relatively small changes in the lattice constants, on the order of a few percent.

RAMAN SPECTROSCOPY

Raman spectra were collected for a number of single crystals of cristobalite, over a range of pressures up to $P \sim 70$ kbar. The crystals were mounted in a *Mao-Bell* type diamond-anvil cell, using a 4:1 methanol/ethanol mixture as pressure medium. Unpolarised Raman spectra were collected on a number of different cycles of increasing and decreasing pressure, using the 5145 \AA line of an Ar-ion laser, operating at 400–500 mW.

On increasing pressure, a large shift in certain Raman modes (notably the A_1 mode near 230 cm^{-1}) was observed above 12 kbar, but there is a substantial hysteresis, with a pressure reduction to 2 kbar necessary to reverse this effect. This corresponds to the phase transition observed in our X-ray diffraction experiments.

The actual transition pressure changed once the crystal had been cycled through the phase transition three times, and some coexistence of phases was noted on decreasing pressure. This may indicate the existence of residual strain within the crystal, perhaps related to the transformation microstructure.

The 1 atm Raman spectrum for quartz shows many similarities to the high pressure cristobalite Raman spectrum. One must con-

clude that the local-scale structure of triclinic cristobalite is rather similar to that of quartz, e.g., in bond-angles and distances.

CONCLUSIONS

At low pressures, cristobalite undergoes a progressive distortion, described by the tilting of essentially-rigid SiO_4 tetrahedra. This mechanism makes tetragonal cristobalite highly compressible. Above $P_c \sim 12$ kbar there is a first-order *displacive* phase transition from tetragonal 422 to triclinic 1. This is characterized by transformation twinning, large offsets in the frequencies of certain Raman modes, and the appearance of new Raman modes. The triclinic distortion is also evident from the splitting of tetragonal powder diffraction lines. We rationalize the phase transition as the continued crumpling of the silicate framework, leading to a non-orthogonal unit cell. The transition is fully reversible, with a pronounced hysteresis of 10 kbar ($P_c' = 2$ kbar). The metastable coexistence of both high- and low-pressure phases may be observed within this interval. The precise transformation pressures may be modified by repeatedly cycling through the phase transition, or by applying non-hydrostatic stress.

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