

PRESSURE-INDUCED LANDAU-TYPE TRANSITION IN STISHOVITE

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Rietveld structural analysis of SiO₂-stishovite could be performed up to 120 GPa by angle-dispersive X-ray diffraction in a YAG-laser heated diamond anvil cell. At 54 GPa, a second-order pressure-induced lattice modification occurs. Above this pressure, the CaCl₂-type SiO₂ compresses without additional decrease of the shortest known O-O bond found in stishovite.

There is no close-packed compact ionic arrangement for metal dioxides. The most common dense form of XO₂ compounds (where X is Si, Ti, Ge,...) is rutile, in which the oxygen sublattice can be seen as largely distorted face centered cubic, and where only one of the two octahedral sites is filled by silicon (Figure 1). There are several other dense forms for the XO₂ compounds, because comparable energies are found for slightly different octahedral inter-links. For example, six polymorphs have been reported for PbO₂, between ambient pressure and 47 GPa [1]. The sequence of the SiO₂ phase transformations down to the core-mantle boundary (CMB) of the Earth needed further analysis because it can affect the lower mantle composition through a possible breakdown of the major lower mantle mineral, the (Mg,Fe)(Al,Si)O₃ perovskite, into a mixture of stishovite and magnesiowustite.

Synthetic crystals of quartz were finely ground, mixed with platinum black, and loaded in a membrane-type diamond anvil cell. After each pressure increase, the sample chamber was slowly scanned by the infrared radiation of a multimode regulated YAG-laser. This laser-annealing technique is a very efficient method of relaxing the sample stress and leads to a quasi-hydrostatic pressure in the pressure chamber, improving the quality of the X-ray diffraction spectra [2,3]. Angle-dispersive X-ray diffraction spectra were recorded at the ID9 beamline. A water-cooled Si (111) bent Laue

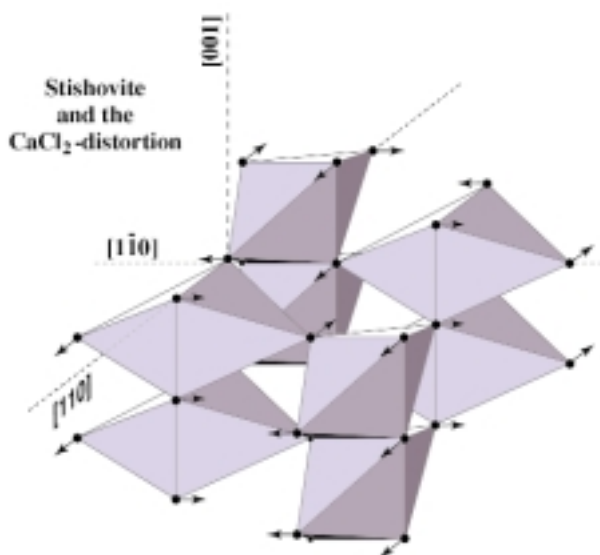


Fig. 1: Dense atomic arrangement for silica. One half of the octahedral sites of the oxygen sublattice are filled by Si atoms. SiO₆ octahedra show 4 equatorial and 2 polar Si-O bonds. The CaCl₂-distortion occurs when oxygen escapes from the diagonal of the (a,b) plane, thus changing symmetry from tetragonal to orthorhombic.

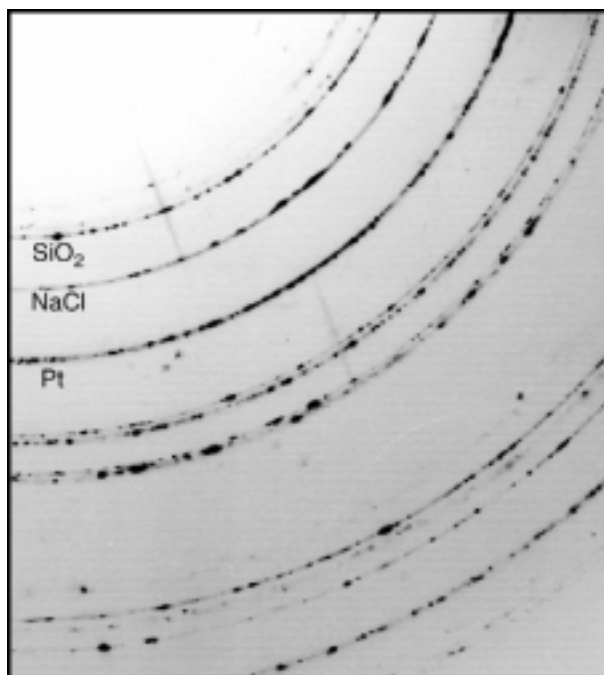


Fig. 2: Typical two dimensional diffraction pattern recorded on a mixture of SiO₂-stishovite, NaCl pressure transmitting medium, and Pt YAG-absorber. This pattern was recorded at 11.7 GPa, after laser heating to about 2200 K in the diamond anvil cell.

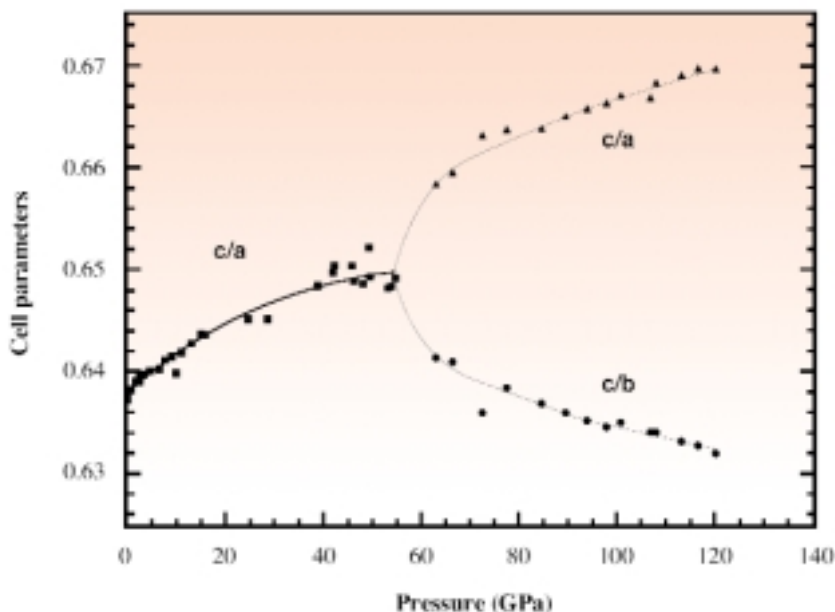


Fig. 3: Pressure evolution of the unit cell parameters showing a rapid increase in the difference between a and b axes above 54 GPa. The evolution with pressure of the (a-b)/a order parameter indicates a classical Landau-type evolution, with the CaCl_2 -form being the lower entropy polymorph.

monochromator was used to produce a bright monochromatic X-ray beam at a wavelength of 0.4561 Å. Vertical and horizontal focusing was achieved with a spherical mirror and a monochromator, respectively. The X-ray flux on a $15 \times 15 \mu\text{m}$ spot allowed acquisition on an imaging plate in about 10 minutes [4]. The two-dimensional images (Figure 2) were integrated using the program Fit2d. Le Bail and Rietveld profile refinements were applied to all diffraction patterns to extract cell parameters and volumes for SiO_2 and platinum, and to compare experimental intensities with those calculated for different structural models of SiO_2 .

Analysis of the X-ray diffraction spectra indicates that the sample consists of a mixture of platinum and stishovite up to 53.2 GPa. The spectrum recorded at 54.8 GPa shows slight modifications related to the onset of a transformation from stishovite to a CaCl_2 -distortion of stishovite. At 62.4 GPa, the diffraction peaks located at around 1.45 and 1.78 Å become doublets, which the stishovite model fails to explain. Instead, the modelled spectrum of the CaCl_2 -distortion of stishovite fits the experimental profile. The occurrence of the CaCl_2 -polymorph at about this

pressure agrees with previous experimental reports using either X-ray diffraction [5] or Raman spectroscopy [6]. It also agrees with *ab-initio* structure simulations that proposed a CaCl_2 -distortion, but is in disagreement with other experimental or theoretical studies that proposed the occurrence of a post- CaCl_2 polymorph at pressures below 120 GPa, at the pressure conditions of the Earth's lower mantle.

Evolution of c/a and c/b cell parameter ratios (Figure 3) clearly shows the stishovite to CaCl_2 -form transition: there is an increase in the CaCl_2 -distortion with increasing pressure up to 120 GPa. The rapid modification of the a and b cell parameters above 54 GPa is achieved by a rapid rotation of the SiO_6 octahedra in the (a,b) plane, as supported by the pressure evolution of the (x,y,0) oxygen coordinates. We note a change in the pressure evolution of the shortest O-O distance above the transition pressure. In the CaCl_2 -structure, the compression occurs without further decrease in this shortest O-O distance. Instead, the other O-O distances diminish toward a comparable value, and consequently the oxygen sublattice becomes more symmetrical.

The pressure evolution of the a and b cell parameters is similar to that usually found for a Landau-type temperature-induced transition. Using a standard type of representation for such a transition with the (a-b)/a ratio as an order parameter, results indicate that the CaCl_2 -form is the lower entropy polymorph. Therefore, the CaCl_2 -form may be the low-temperature polymorph of stishovite. This gives weight to the argument for a positive slope of the boundary between the two silica polymorphs in a P-T diagram. The critical temperature of the phase transition ($T_c(P)$) would reach $T = 300 \text{ K}$, when pressure reaches 54 GPa. This means that while further compressing silica at room temperature (T_{exp}) above 54 GPa we increase the gap between the experimental and critical temperatures (the gap is $T_c - T_{\text{exp}}$). For such a second order transition, an increase in ($T_c - T_{\text{exp}}$) explains the increase of the CaCl_2 -distortion that was observed.

We observed a continuous increase in the SiO_2 density up to pressures found at the Earth's CMB, because the phase transformation to the CaCl_2 polymorph do not involve noticeable modification of volume or bulk modulus. From these new data we calculate a positive ΔV for the $\text{MgSiO}_3 \Rightarrow \text{MgO} + \text{SiO}_2$ breakdown reaction at all pressures. Therefore, the silicate perovskite is denser than a mixture of its oxides down to the CMB. **Consequently, the proposal that free silica could occur in the Earth's lower mantle is not supported by the present data, as long as an excess of magnesiowustite (Mg,Fe)O is believed to be present in the lower mantle.** ■

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