

The ideal crystal structure of cristobalite X-I: A bridge in SiO₂ densification

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SiO₂ is one of the most common, yet important, compounds found on Earth. Despite its compositional simplicity, SiO₂ exhibits a complex phase diagram featuring a variety of thermodynamically stable crystalline phases, as well as numerous metastable crystalline polymorphs and glasses. This includes phase transition sequences and resulting polymorphs that are strongly path-dependent. In the solid state silicon strongly prefers four-coordinated tetrahedral crystallographic sites. This low coordination number results in pronounced structural flexibility, with a tendency to form extended silicate chains, sheets, and framework polyhedral motifs, and accounts for a majority of the mineral diversity observed in shallow-depth terrestrial rocks and commonly utilized SiO₂-derived materials. Densification of silicates involving a change of the coordination number of the Si⁴⁺ cation is one of the sources of stratification of the Earth's mantle, and is responsible for the major seismic discontinuities that are observed as a function of depth [1,2].

A number of intermediate metastable silica phases have been reported, but their crystal structures have not been reliably determined, despite decades of research. Computational efforts employing density functional theory (DFT) and molecular dynamics identified a number of candidate structure models; however, extensive metastability results in a Gibbs free energy hyper-surface pitted with abundant local minima, and selecting the structures that are actually realized in nature has proven challenging [3-5]. One of these little-understood phases is cristobalite X-I, which forms on compression of α -cristobalite at ambient temperature above about 12.9 GPa [6-10]. Cristobalite, found typically in nature as the α -polymorph, is a high-temperature, four-coordinated form of SiO₂ with well-documented occurrences in a variety of different geologic environments, including terrestrial igneous rocks, protoplanetary disks around young stars [11], and meteorites that were shocked beyond 10 GPa [12]. α -cristobalite was also the starting material for the first successful high-pressure synthesis of quenchable octahedral seifertite-SiO₂ [4], found in heavily shocked meteorites such as Shergotty and Zagami [13,14], where it is considered a possible proxy of the peak pressure during shock metamorphism.

Here, we report the results of single-crystal synchrotron x-ray diffraction experiments with α -cristobalite, using a diamond anvil cell, in which a well-diffracting specimen of the X-I phase was formed via a single-crystal to single-crystal transformation at ambient temperature. Our X-I structure model features only two symmetry independent Si sites, which are sufficient to produce the ideal SiO₂ stoichiometry. All Si atoms reside in octahedral sites, which are arranged in an edge-sharing zigzag chain pattern. Our experimental results are compared with those of previously proposed structures [15], and are supplemented with density functional theory calculations that compare the enthalpy of various silica polymorphs on compression, and examine the dynamic stability of the X-I structure. These calculations show that cristobalite X-I's enthalpy and stability sits between other tetrahedrally and octahedrally coordinated SiO₂ phases above 5 GPa. Additional phonon density of states calculations do not predict any imaginary frequencies, confirming the dynamic stability of the structure determined from our X-ray diffraction experiment.

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