



## Compression of $\alpha$ -cristobalite under different hydrostatic conditions

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The response of  $\alpha$ -cristobalite to high-pressure has been a subject of numerous experimental and theoretical studies for more than two decades. The results indicated prolific polymorphism under high pressures, yet no consensus has emerged on what is the sequence of these pressure-induced transformations. In particular, the structure of the high-pressure polymorph that appears above  $\sim 10$  GPa (hereafter cristobalite X-I), which is believed to be a direct link between the low-pressure (silicon in  $\text{SiO}_4$  tetrahedra) and the high-pressure ( $\text{SiO}_6$  octahedra) forms of silica remained elusive. This study examined the response of  $\alpha$ -cristobalite when compressed at different levels of hydrostaticity, with the special focus on formation and stability of cristobalite X-I.

The structural behavior of cristobalite under pressure was investigated up to  $\sim 80$  GPa and at ambient temperature. We investigated behavior of single crystals and powders, in either (quasi)-hydrostatic or non-hydrostatic environment. In situ high pressure transformation path and structural behavior was studied by means of Raman spectroscopy and synchrotron X-ray diffraction (XRD). The samples recovered after pressure release were additionally investigated by transmission electron microscopy (TEM).

Low- or  $\alpha$ -cristobalite responds differently to high pressure depending on the degree of the hydrostaticity. The highest attainable hydrostaticity preserves the initial structure of cristobalite at least up to  $\sim 15$  GPa. When the crystal experiences even slight stresses during an experiment, transformation sequence leads to cristobalite X-I – a monoclinic polymorph with silicon in octahedral coordination. This polymorph belongs to the family of the high-pressure silica phases that are comprised of distorted close-packed array of oxygen ions in which silicon atoms fully or partially occupy octahedral sites. The reflections collected on a single crystal at  $\sim 11$  GPa can be indexed by a monoclinic unit cell  $a=6.658(9)$  Å,  $b=4.1077(6)$  Å,  $c=6.8947(11)$  Å,  $\beta=98.31(4)^\circ$ ,  $V=186.6(3)$  Å<sup>3</sup> ( $Z=8$  and  $\rho=4.28$  g/cm<sup>3</sup>). The structure was solved in  $P2_1/n$  space group and refined at this pressure with the final  $R_1$  indices of 9% for 209 unique reflections. The increase in coordination number of silicon from cristobalite to its six-fold coordinated polymorph does not require any thermal activation; however the high-pressure polymorph cannot be preserved at ambient conditions. No other silica polymorph was found to transform to an octahedra-based structure on cold compression at such low pressures ( $\sim 11$  GPa). This structure could be accommodated in (quasi)-hydrostatic environment where temperature is not sufficient to form stishovite. In non-hydrostatic conditions in the presence of uniaxial stress, cristobalite eventually transforms to seifertite-like  $\text{SiO}_2$ , which is quenchable. Presence of seifertite might not always require the minimum shock pressures equal to that of thermodynamic equilibrium ( $\sim 80$  GPa) as it can be clearly formed at much lower pressures in an environment of uniaxial compression (e.g. dynamic event).