

RESPOND OF α -CRISTOBALITE TO HIGH PRESSURES UNDER DIFFERENT HYDROSTATIC CONDITIONS. Ana Černok¹, Katharina Marquardt¹, Elena Bykova¹, Hanns-Peter Liermann², and Leonid Dubrovinsky¹, ¹Bayerisches Geoinstitut, Universitätsstrasse 30, 95447 Bayreuth, Germany, ²Photon Sciences, Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany. (Ana.Cernok@uni-bayreuth.de)

Introduction: In contrast to its subordinate and rather exotic terrestrial occurrence among silica phases, α -cristobalite is observed as the predominant SiO₂ polymorph in various planetary materials: from dust particles in proto-planetary disks surrounding T-Tauri stars [1], over lunar basalts [2] to chondrules and matrix of chondritic meteorites [3]. Cristobalite was documented alongside all the natural occurrences of the high-pressure, post-stishovite silica polymorph seifertite, related to the heavily shocked meteorites [e.g. 4]. Notably, cristobalite has also been documented in the meteorites that lack any high-pressure silica polymorphs, albeit the rest of the mineral record indicated peak shock pressures exceeding 10 GPa [e.g. 5], at which at least coesite or stishovite should form. The response of α -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 ~10 GPa (hereafter cristobalite X-I), which is believed to be a direct link between the low-pressure (silicon in SiO₄ tetrahedra) and the high-pressure (SiO₆ octahedra) forms of silica remained elusive [e.g. 6, 7]. This study examined the response of α -cristobalite when compressed at different levels of hydrostaticity, with the special focus on formation and stability of cristobalite X-I. We reveal the structure of this polymorphs by means of single crystal XRD.

Experimental & Analytical: The structural behavior of cristobalite under pressure was investigated up to ~80 GPa and at ambient temperature. We used diamond anvil cells (DACs) with 250 μ m culet size and apertures of 80°. We investigated behavior of single crystals and powders, in either (quasy)-hydrostatic or non-hydrostatic environment. In (quasy)-hydrostatic experiments neon was used as pressure transmitting medium. Pressure was determined by ruby fluorescence or by the neon EOS. *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).

Results: *In situ* high-pressure Raman spectroscopy and XRD investigations demonstrate that the mecha-

nism which cristobalite adopts to respond to compression is very sensitive to stress conditions.

Effect of hydrostaticity. The experiment presented in Figure 1 displays three different in size α -cristobalite single crystals inside the same pressure chamber (see inset in Fig. 1), surrounded by neon pressure medium. Upon compression, the two larger crystals (C1 & C3) undergo a displacive phase transition to cristobalite-II near 1 GPa, as evident by the appearance of an additional Raman mode and an increase in intensity of the strongest A_g mode located near 410 cm⁻¹, in good agreement with earlier studies [8]. Following this transitional path, cristobalite-II transforms to cristobalite X-I just above ~11 GPa.

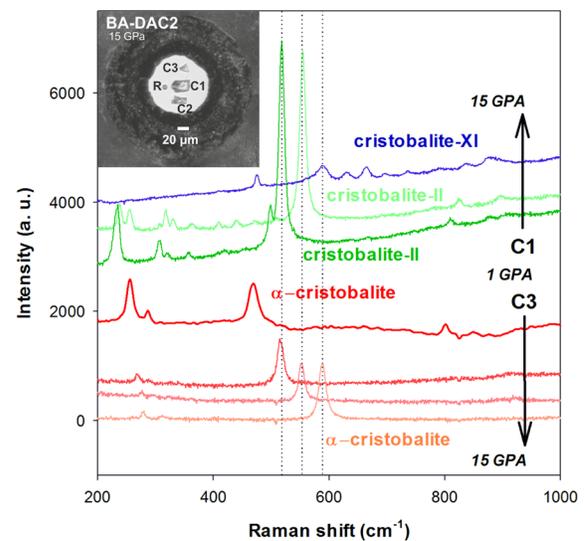


Figure 1. *In situ* Raman spectra collected on three different single crystals of α -cristobalite at 1.1, 4.6, 8.6 and 15.0 GPa (room temperature). Inset shows the DAC pressure chamber seen at 15.0 GPa. In moderate hydrostatic conditions the starting cristobalite (red) transforms via intermediate cristobalite-II (green) to cristobalite X-I (blue), but it retains its initial structure (orange) in the case of high hydrostaticity (smallest crystal size).

On the other hand, the smallest and the thinnest crystal C3 (~10 μ m), that does not bridge between the anvils, thus remaining in hydrostatic conditions, retains the structure of α -cristobalite up to at least ~15 GPa (Fig. 1). To our knowledge, this is the first Raman spectra collected on α -cristobalite overpressurized far outside its stability field. This observation is in good agreement with an earlier single-crystal XRD study on overpressurized α -cristobalite, performed to 9 GPa [7].

Structure & stability of cristobalite X-I. The polymorph found upon transformation of cristobalite-II above ~ 11 GPa in quasi-hydrostatic conditions exists at least up to 83 GPa, as evidenced by *in situ* Raman spectroscopy and single crystal XRD. It belongs to the family of the high-pressure silica phases suggested before [9, 10, 11] that are comprised of distorted close-packed array of oxygen ions in which silicon atoms fully or partially occupy octahedral sites. The reflections collected at ~ 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, $\beta=98.31(4)^\circ$, $V=186.6(3)$ Å³. The structure was solved and refined in $P2_1/n$ space group with the final R_1 indices of 9% for 209 unique reflections ($Z=8$ and $\rho=4.28$ g/cm³).

Structures of the recovered samples. In case of moderate hydrostaticity α -cristobalite crystals transform to cristobalite X-I above ~ 11 GPa. When quenched from various maximal pressures – 83, 60, 48 and 12 GPa – all recovered crystals show Raman signal similar to that of the starting α -cristobalite. TEM analysis revealed that the crystals which had cristobalite X-I structure at high pressures convert back to the starting cristobalite upon pressure release (Fig. 2), indicating that the high-pressure polymorph is not quenchable. In experiments under non-hydrostatic compression, cristobalite was found to transform to a seifertite-like phase which, as reported earlier [11, 12] can be recovered to ambient conditions (Fig. 3).

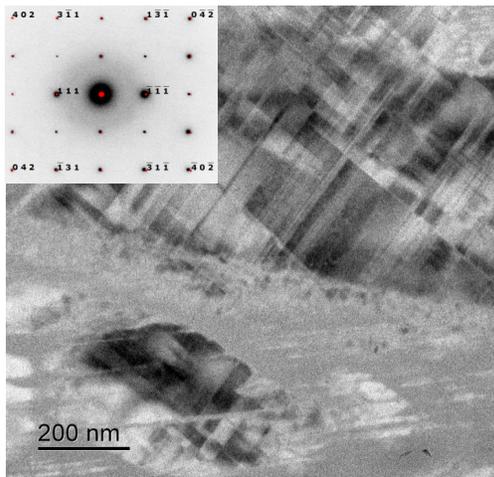


Figure 2. Twinned crystalline grain (dark grey to black) surrounded by amorphous matrix (light grey). The inset shows the diffraction pattern indexed as α -cristobalite along $[11-2]$ zone axis. Reflections in black are this study, red is from [7].

Conclusions: α -cristobalite responds differently to high pressure depending on the degree of the hydrostaticity. The highest attainable hydrostaticity preserves the initial structure of cristobalite. When the crystal experiences even slight stresses during an exper-

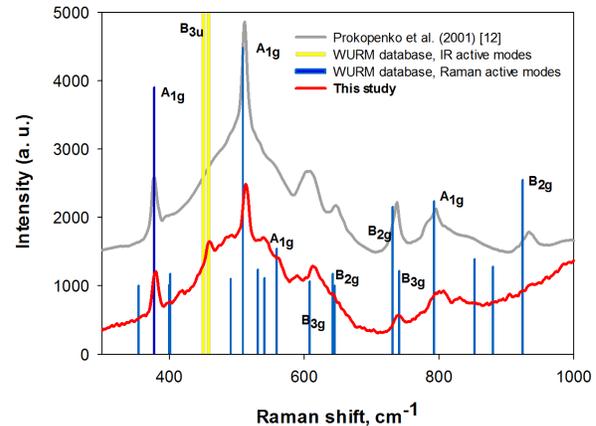


Figure 3. Raman spectra collected on powder samples recovered at room conditions after non-hydrostatic compression to ~ 50 GPa. Starting material was α -cristobalite. This study (red) and a previous experimental study (grey) show good agreement with computational Raman spectra of seifertite stored on the WURM website (blue).

iment, transformation sequence leads to cristobalite X-I – a monoclinic $P2_1/n$ polymorph with silicon in octahedral coordination. 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 (~ 11 GPa) and this structure could be accommodated in a (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 SiO₂, which is quenchable. Presence of seifertite may not always require the minimum shock pressures equal to that of thermodynamic equilibrium (~ 80 GPa) as it can be clearly formed at much lower pressures in an environment of uniaxial compression (e.g. dynamic event).

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