Pressure-induced phase transitions in coesite

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Silica, SiO₂, exhibits a very rich polymorphism with more than 30 stable or metastable phases, most of which occur at ambient to moderate pressures (< 9 GPa). Some of these phases, such as quartz, tridymite and cristobalite consist of frameworks of SiO₄ tetrahedra and are abundant in nature. Coesite, thermodynamically stable above ca. 2.5 GPa and at temperatures in excess of 500 °C, is the densest known polymorph with silicon atom tetrahedrally coordinated to oxygen. Nowadays coesite is widely accepted as a high-pressure indicator in rocks related to meteorite impact sites, where quartz transforms to coesite due to the high-pressure and high-temperature regime of the impact and to the very rapid quenching conditions which prevent a reversion from coesite to quartz (e.g. [1]). Terrestrial occurrence of coesite was reported from deeply (>100 km) subducted crustal rocks (ultra-high pressure metamorphic rocks) or mantle derived rocks (kimebrlites), which have been exhumed under conditions that prevent retrograde transition to quartz (e.g. [2-6]). In these rocks coesite commonly occurs as an inclusion within clinopyroxene, olivine, garnet or diamond. Coesite-in-diamond assemblage was recently introduced as an important high-pressure barometer [7].

Because of the relatively strong Si-O bonding in silica, there are high kinetic barriers associated with the transitions to stable high-pressure phases consisting of SiO₆ ocathedra [8]. This results in complicated metastable phenomena at high pressures and ambient temperature such as the persistence of low-pressure phases far out of their stability fields and transitions to metastable crystalline and amorphous phases. Slow kinetics, enhanced metastability, formation of poorly crystallized or structurally disordered materials usually give rise to weak X-ray diffraction patterns difficult to interpret resulting in contradictory interpretations. In experimental study on the high-pressure behavior of coesite at ambient temperature, Hemley [9] observed changes in the Raman spectra of coesite collected at ambient temperature and at the pressures of 22-25 GPa, and reported that coesite becomes amorphous above 30 GPa. The authors attributed such changes to a high-pressure phase transformation occurring in coesite; however, no further investigation has been reported to better describe such behavior.

In this study we aim at giving an insight into the high-pressure behavior of coesite. We measure in situ Raman spectra and X-ray diffraction at pressures up to 55 GPa and complement them with theoretical computations of Raman spectra under similar pressure conditions.

Single crystal X-ray diffraction experiments in diamond anvil cells (DACs) up to about 55 GPa were performed at the P02.2 Extreme Conditions Beamline (ECB) beamline at Petra III in Hamburg. The experiment was carried out using a 0.29004 Å radiation and a MAR345 image plate detector, located at the distance of ~400 mm from the sample. Data were collected in a series of o-scans in a range of ± 26 ° or ± 40 ° with exposure time 1 sec/degree.

We find that coesite undergoes two phase transitions and does not become amorphous at least up to ~ 52 GPa. The first phase transition (coesite I to coesite II) occurs at ~ 23 GPa and the second transition (coesite II to coesite III) occurs at ~ 35 GPa. The quality of X-ray diffraction data
allowed us to refine the crystal structure of coesite I for several pressure points. In addition, we were able to solve crystal structure of coesite II. The compound crystallizes in monoclinic $P2_1/n$ unit cell with $a = 6.5581(16)$, $b = 23.2290(12)$, $c = 6.5741(9)\text{Å}$ and $\beta = 117.70(2)^\circ$ which corresponds doubling of $b$ unit cell parameter of the parent coesite I structure (Fig. 1).

The ab initio calculations gave an insight into the initiation mechanism of the first phase transition, implying, from analysis of unstable phonon modes, that it is probably a displacive phase transition due to shearing of the four-membered rings of SiO4 tetrahedra upon compression. The transition to the lowest-symmetry phase, coesite III, is possibly a first order phase transition, which leads to a very distinct structure. We are currently analysing crystallographic data of the high-pressure metastable polymorph coesite III.

![Figure 1: Unit cells of coesite I (doubled $b$-parameter) and coesite II. Dark and light colours designate neighbouring layers along $c$-direction.](image)

References