

Phase Transitions of SiO₂ under Dynamic Compression and up to 1200 K

E.-R. Carl¹, A.N. Danilewsky², H.-P. Liermann³, U. Mansfeld⁴, F. Langenhorst⁴, L. Ehm⁵ and T. Kenkmann¹

¹Institut für Geo- und Umweltnaturwissenschaften, Geologie, Albertstr. 23b, D-79104 Freiburg, eva-regine.carl@geologie.uni-freiburg.de, thomas.kenkmann@geologie.uni-freiburg.de

²Institut für Geo- und Umweltnaturwissenschaften, Kristallographie, Hermann-Herder-Str. 5, D-79104 Freiburg, a.danilewsky@krist.uni-freiburg.de

³DESY, Forschungsbereich PS, Notkestr. 85, 22603 Hamburg, hanns-peter.liermann@desy.de

⁴Institut für Geowissenschaften, Mineralogie, Fürstengraben 1, Friedrich-Schiller-Universität Jena, 07742 Jena, Germany, ulrich.mansfeld@uni-jena.de, falko.langenhorst@uni-jena.de

⁵Stony Brook University, Mineral Physics Institute, Stony Brook, NY 11794-2100, lars.ehm@stonybrook.edu

Introduction: SiO₂ is among the best studied geologic equilibrium systems due to its great importance in near-surface rocks of the continental lithosphere and its role as the most widely used shock barometer [1].

The thermodynamic stability fields of high pressure polymorphs of SiO₂ have been experimentally and theoretically investigated since 1953 [2] and this knowledge is now in an advanced state. However, a great mismatch exists when the static stability field of high-pressure SiO₂-polymorphs, such as coesite [2] and stishovite [3], are compared to the occurrence of these during shock metamorphism. Coesite forms at 2 GPa and transforms to stishovite at 8 GPa under static conditions. In stark contrast, coesite is found in impact craters only in diaplectic SiO₂ glasses that were exposed to shock pressures in excess of 35 GPa, e.g. [4]. Stishovite, on the other hand, is observed at lower shock conditions than coesite [1]. It is believed that stishovite may nucleate during shock compression, whereas coesite crystallizes upon shock pressure release [4]. Hence, the formation and preservation conditions for coesite and stishovite seem to depend on the pressure-temperature-time profile during shock compression and decompression.

Furthermore, high-pressure quasi-static or dynamic experiments reveal a complex behavior of SiO₂ under compression, e.g. [5]. Reconstructive phase transitions to the stable high-pressure polymorphs are often hindered by high kinetic barriers resulting in formation of complex metastable phases without sufficient heating, e.g. [6]. Because of this great complexity and the difficulties in studying SiO₂, the results of previous work on α -quartz at high pressure have left many unanswered questions concerning the behavior of the material.

Methods: The experiments were carried out at the Extreme Conditions Beamline (ECB) at PETRA III at DESY, Hamburg, Germany [7]. The combination of a membrane-driven diamond anvil cell and *in situ* powder x-ray diffraction was used to study the phase transi-

tions of α -quartz at pressures up to 66 GPa at room temperature and different compression rates up to 3.0 GPa/s. We used synthetic α -quartz powder and mixed in Au flakes for determining the pressure in the diamond anvil cell. Furthermore, additional experiments were conducted at elevated temperatures up to 1200 K and low compression rates around 0.3 GPa/s using a graphite resistance heater.

During compression and decompression of the material, diffractograms were collected every 1-10 seconds. After surveying all experimental data, single interesting diffractograms were selected for further analysis with the Rietveld method [8].

Results: All experiments reveal that α -quartz transforms directly to stishovite, skipping the stability field of coesite. This phase transition occurs between 20.7 GPa and 28.0 GPa during compression. With increasing compression rate, a slight increase of the transition pressure of the phase transition occurs for the experiments at room temperature. Stishovite remains stable upon reaching maximal pressure and during the time while the maximal pressure is kept for more than one hour. During decompression, stishovite reflections remain observable, while no reflections of α -quartz appear in the patterns. These experimental results seem to fit the observations made in the field given that stishovite is found in rocks exposed to shock pressures, e.g. [4]. Coesite could not be identified in the analyzed data at any stage of the experiments.

In the course of compression, new reflections can be observed in the pressure range between 0.5 and 19.8 GPa, which could be assigned to a number of reported metastable/transient SiO₂ phases. These new reflections remain detectable until maximum pressure is reached. The reflections are not influenced by the phase transition of α -quartz to stishovite. Upon decompression, these reflections do not vanish in most experiments. Some experiments, however, show those reflections disappearing during decompression. Although there is no evidence of a second phase transition, the reflec-

tions can be contributed to the monoclinic post-quartz phase [9]. This phase is closely related to stishovite with both being very close in activation energy [10]. However, a phase transition from α -quartz to this phase is displacive as revealed by theoretical calculations, e.g. [11], while the phase transition to stishovite is highly reconstructive.

Figure 1 shows a diffraction pattern of the recovered sample of an experiment at 600 K and a compression rate of 0.4 GPa/s. The pattern shows the reflections of gold as the strongest reflections. While the reflections of stishovite are clearly visible, the reflections of the monoclinic post-quartz phase can only be observed in the detail. Besides the reflections of gold and the two silica phases, there are also reflections of rhenium in the pattern which is the material of the gasket. The reflections of the high-pressure phases become stronger and slimmer by additional heating.

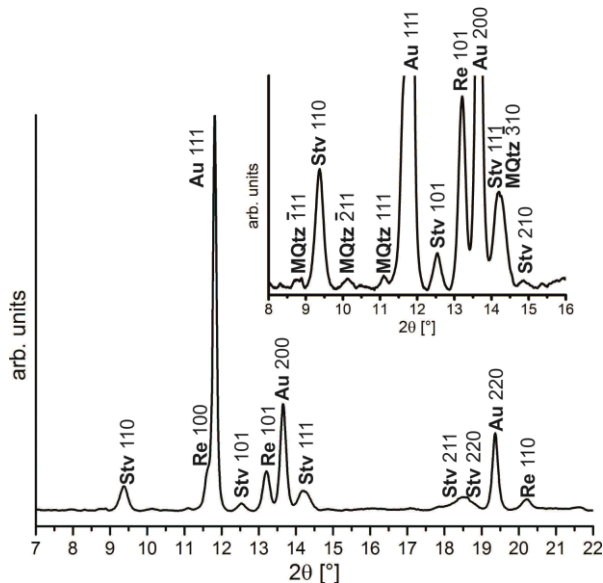


Figure 1: The diffraction pattern of the recovered sample of an experiment conducted at 600 K and a compression rate of 0.4 GPa/s. The reflections of stishovite (Stv) are clearly visible but the reflections of the monoclinic post-quartz phase (MQtz) can only be observed in the detail. Furthermore, there are reflections of gold (Au) for internal pressure calibration and rhenium (Re) that originates from the gasket.

The formation of stishovite was confirmed by an analysis of the recovered samples in the TEM. This analysis also reveals that most of α -quartz became amorphous during compression. This result correlates with earlier studies that discovered a pressure induced

amorphization of α -quartz between 18-35 GPa, e.g. [12].

Conclusions: Our dynamic compression experiments provide insight into the kinetics of high-pressure phase transitions of α -quartz. Although the compression rates in the context of impact cratering are much higher, these *in situ* investigations of phase transitions are a necessary first step to understand the behavior of SiO_2 under the much faster compression rates of impact events. The latter is envisaged to be studied with a laser shock compressed sample at x-ray free electron lasers (XFELs) in the future.

[1] French B.M. and Koeberl C. (2010) *Earth-Science Reviews*, 98, 123-170.

[2] Coes L. (1953) *Science*, 118, 131-132.

[3] Stishov S.M. and Popova S.V. (1961) *Geochemistry*, 10, 923-926.

[4] Stöffler D. and Langenhorst F. (1994) *Meteoritics*, 29, 155-181.

[5] Dubrovinsky L.S. et al. (2004) *Phys. Earth Planet. Inter.*, 143-144, 231-240.

[6] Choudhury N. and Chaplot S.L. (2006) *Phys. Rev. B*, 73, 094304.

[7] Liermann H.-P. et al. (2015) *J. Synchrotron Rad.*, 22, 908-924.

[8] Rietveld H.M. (1967) *Acta Crystallographica*, 22, 151.

[9] Haines J. et al. (2001) *Phys. Rev. Lett.*, 87, 155503.

[10] Teter D.M. and Hemley R.J. (1998) *Phys. Rev. Lett.*, 80, 2145-2148.

[11] Martoňák R. et al. (2007) *Phys. Rev. B*, 76, 014120.

[12] Kingma K.J. et al. (1993) *Phys. Rev. Lett.*, 70, 3827-3930.