ESRF	**Experiment title:** Structural Investigations of the Post-Rutile Phases of SiO_2 (stishovite) and GeO_2	**Experiment number:** HS-134
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Report:

There is a great deal of interest in the high-pressure transitions of silica due to the possible geophysical repercussions of such transitions. Both theory and Raman spectroscopy (1,2) concur in that there is a transition in stishovite (the high-pressure, tetragonal, rutile-structured phase of silica) to an orthorhombic $CaCl_2$-type phase at 50 GPa; however no structural data are available. The most appropriate model compound for silica is GeO_2 and the present results indicate that this compound also adopts a $CaCl_2$-type structure at high pressure.

High-pressure experiments were performed on powdered stishovite and rutile-type GeO_2 prepared under HT-HP conditions. Samples were loaded along with ruby crystals, platinum black to absorb the laser radiation, and a mixture of 16:3:1 methanol:ethanol:water as a pressure transmitting medium in stainless steel gaskets. Pressures were measured based on the shift of the ruby Rl fluorescence line and the equation of state (EOS) of platinum. Laser heating was performed between exposures using a 100 W Nd:YAG laser.

Angle-dispersive, x-ray diffraction experiments were performed on beamline ID30 at the ESRF using a diamond anvil cell with a full conical aperture (4θ = 56”). X-ray wavelengths of 0.4228 Å and 0.4273 Å were selected using a Si(111) Laue-Bragg monochromator. The incident beam diameter was 20 pm at half maximum. Image plates were placed at a distance of 398.41 mm from the sample and exposure times were of 10 to 15 minutes. The observed intensities on the imaging plates were integrated as a function of 2θ using FIT2D (3) in order to give conventional one-dimensional diffraction profiles.

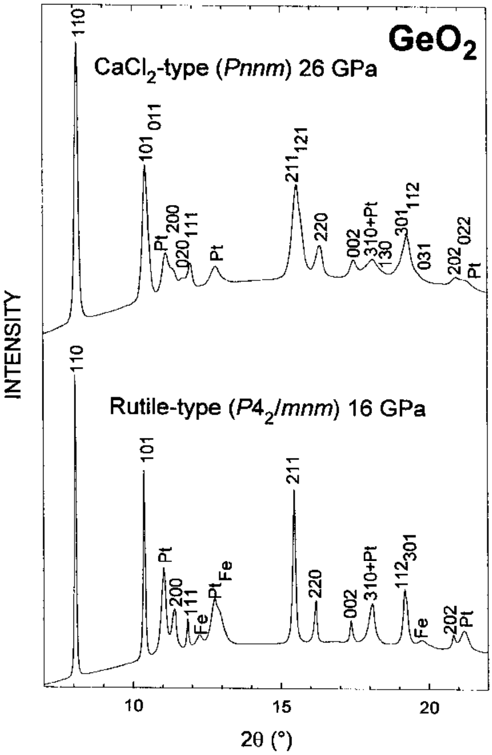

Fig. 1 High-pressure diffraction patterns for GeO_2

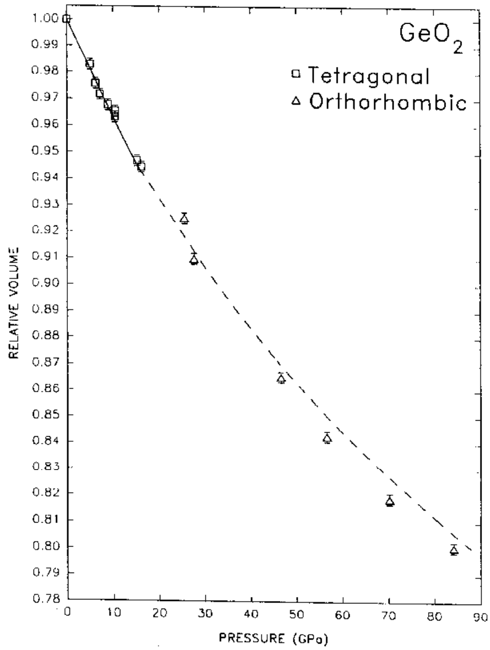

Fig. 2 P-V data for Ge02

GeO_2 was investigated up to 85 GPa and was found to undergo a tetragonal rutile to orthorhombic $CaCl_2$ phase transition above 20 GPa, Fig 1. The crystal structures of both phases were refined by the Rietveld method. The P-V data for the tetragonal phase were fitted to a Birch-Murnaghan EOS yielding B_0 = 254(4) GPa with B'_0 = 4, Fig 2. The data obtained for orthorhombic GeO_2 indicate that this phase is slightly more compressible than the tetragonal GeO_2 as is expected after a second-order, ferroelastic transition.

Due to the limited amount of beam time available, the experiment on stishovite could not be continued beyond 3.7 GPa and will have to be completed at a later date.

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