ESRF	**Experiment title:** Local structure of Si and O in glassy SiO_2 at high pressure by means of X-ray Raman scattering	**Experiment number**: ES-431
Beamline: ID20	**Date of experiment**: from: 15/06/2016 to: 21/06/2016	**Date of report**:
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Report:

Scientific Background

SiO_2 glass is one of the most studied compounds in both material and Earth sciences, but still holds controversy about its structure and evolution at high pressure. Recently, we measured the density of SiO_2 glass up to 90 GPa at ID13 (report from ES-354) and found that it becomes as dense as the crystal counterpart at high pressure (>60 GPa). The mechanisms associated with this high densification at high pressure are still debated as a result of a lack of clear information for the coordination of elements in glasses and melts. For instance, there is no consensus on the transformation pressure from 4-fold to 6-fold coordination for Si (1, 2). This transformation has even put into doubt, based on an earlier X-ray Raman scattering report (3). Furthermore, it is not sure whether the coordination number of silicon at pressures above 60 GPa remains at 6 or goes higher (4, 5). To investigate the electronic and coordination changes and elucidate the transformation occurring in SiO_2 glass, we measured the Si L-edge and O K-edge and probed their local environments at high pressure up to 66 GPa by means of X-ray Raman scattering at ID20 beamline.

Experimental procedure

A suprasil-type SiO_2 glass was grinded and used as the sample for this experiment. Because we used an incident beam of ~10 keV, the absorption of the X-rays by the diamond considerably attenuates the incoming beam as well as the out coming signal from the sample. Also, the sample thickness at high pressure produces a weak signal. To circumvent these problems, we used two collection geometries for this experiment: 1) through very thin perforated diamonds (i.e. parallel to the compression axis) and 2) through a transparent gasket (i.e. perpendicular to the compression axis).

In both cases, the signal to background has been considerably improved:

1. With the on-axis geometry, we have introduced thin diamonds of less than 500 micron thickness, still maintaining a 70 degree opening geometry, allowing for high angle

scattering geometry (Figure-1). Doing so, the attenuation of the ~10 keV X-ray beam and background produced by the X-ray scattering were minimized. Recesses of 20 microns depth were also milled in each diamond culets, increasing the sample volume by a factor 2 to 3.

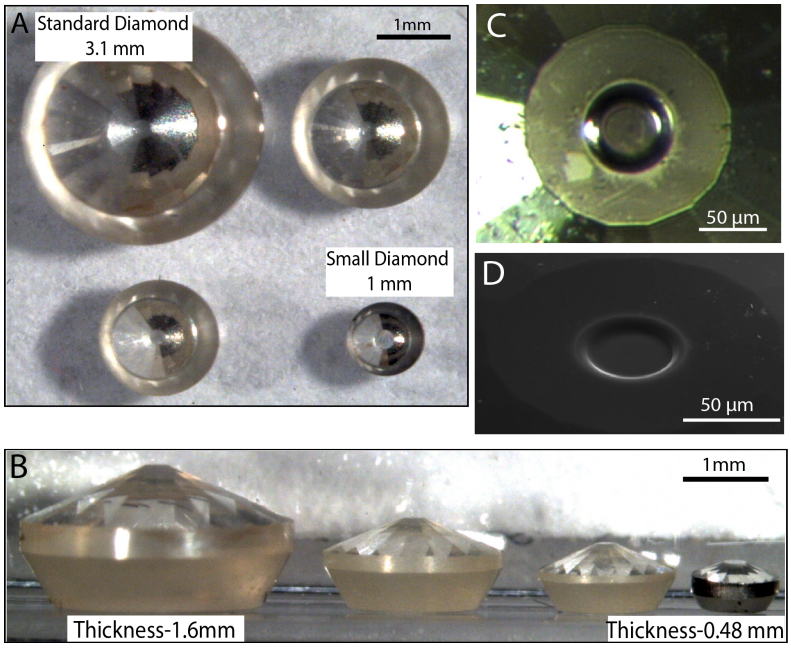

Figure-1. Picture of custom-made conical diamonds for XRS experiments at ID20. A-B- different types of anvils tested and compared to the standard type. The 1mm diameter and 0.48mm thick diamonds gave the best results. C-D- perforation of the culet machined with the FIB to increase the sample volume.

2. With the radial geometry, through the gasket, we used a combination of transparent materials, with a cubic-Boron-Nitride (cBN) insert contained in a supporting beryllium outer ring. This type of gasket was recently tested and developed on the beamline by C. Sahle with extremely good results. This geometry increases the sample thickness by a factor of three to four while reducing the background intensity. This geometry considerably reduces the acquisition time down to 5-6 hours per pressure step.

Both geometries have advantages and disadvantages. Overall it seems that the radial geometry is more suitable for the O K-edge and the axial geometry gives better results for the Si L-edge.

Preliminary results

In this section we present preliminary results for both the O K-edge as well as the Si L-edge measured through the diamonds up to 56 GPa (Figure-2). For silicon L-edge at low pressures between 0 and 18 GPa, we can identify a double peak feature characteristic of the 4-fold coordinated silicon. We can identify subtle changes in the spectra for this pressure range thanks to the outstanding data quality. These changes might be attributed to the compaction of the tetrahedral network and the onset of the shrinking of the O-Si distances. At about 20 GPa, a clear change appears in both edges, where the double Si L-edge peak transforms to a single peak. The transformation is completed at about 40 GPa. This can be attributed to the changes of coordination from 4-fold to 6-fold. These findings are confirmed by the spectral changes observed for the oxygen K-edge at the same sample conditions. Our XRS data collected so far will be confronted with calculations utilizing the OCEAN code on basis of MD simulations and will shade a new light on the structural changes that occur in amorphous silicate networks at high pressure.

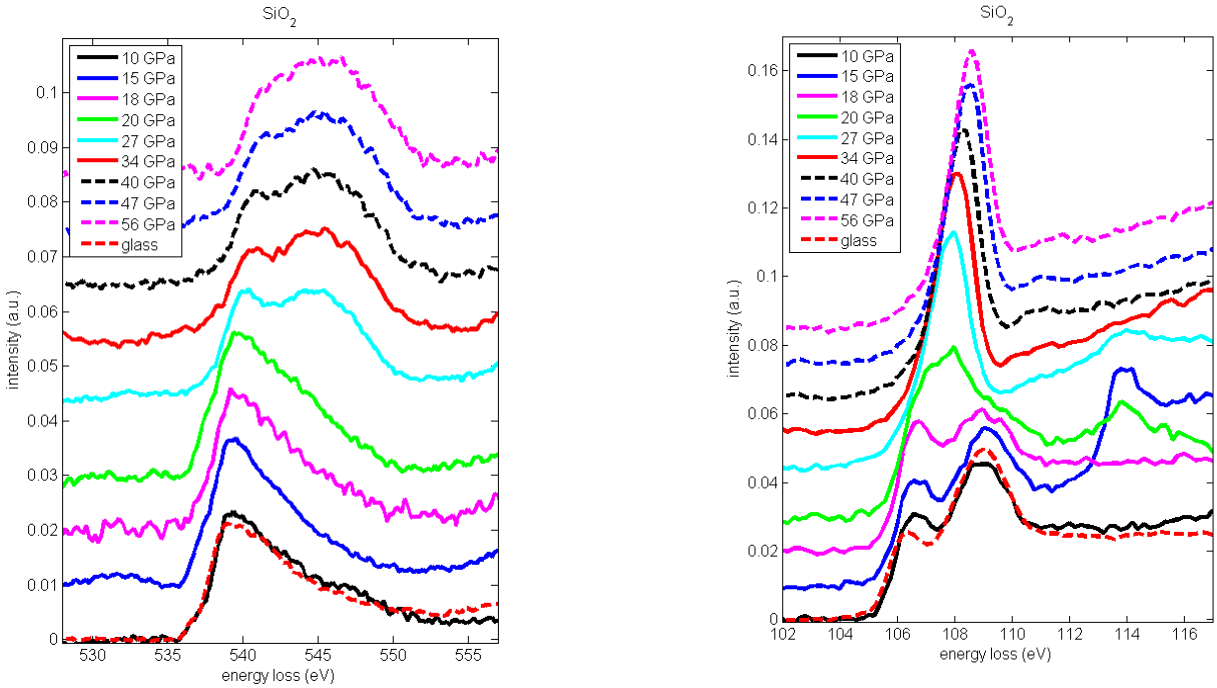

Figure-2. Left panel, results obtain for the O K-edge from 0 to 56 GPa. Right panel, spectra obtained for the Si L-edge as a function of pressure from 0 to 56 GPa.

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