	Experiment title: **Influence of water on the glass structure of pure silica, SiO₂**	**Experiment number**: ES-1005
Beamline: ID20	**Date of experiment**: from: 22. June 2021 to: 29. June 2021	**Date of report**:
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Report:

Experiment ES-1005 was dedicated to understand how the high-pressure behavior of dry silica glass is affected by the incorporation of water. For this, we have performed high-pressure X-ray Raman scattering (XRS) experiments on a hydrous silica glass (granules with a water content of ~10.5 wt.%) at the beamline ID20. All measurements were performed in BX90 type diamond anvil cells (DAC), which were equipped with different types of diamonds, seats, and gaskets. Four of our DACs were equipped with mini-diamonds mounted in PCD seats (see ref. [1] for more details) and a rhenium gasket (in the following denoted as MDAC). A further DAC was equipped with conventional diamonds (200 μm culet size), WC seats, and a beryllium gasket (in the following denoted as Be-DAC). The sample was ground and the powder loaded together with a ruby chip in each DAC. The DACs were mounted on the sample stage of the spectrometer and the sample chamber was subsequently evacuated. High-pressure measurements were performed between $0-42$ GPa. The pressure was determined by using the ruby fluoresence system at the beamline ID15B. At each pressure point, we have measured the O K and Si $L_{2,3}$ spectra of the sample. All spectra were collected over several hours with an experimental resolution of about 0.7 eV and a beam focussing of 20×10 μm^2 (H × V). All O K spectra were collected between about $520-565$ eV using the following settings: $520-525$ eV: 24 points, 10 sec/point; $525-550$ eV: 124, 15; $550-565$ eV: 75, 12. Measurements of the Si $L_{2,3}$ spectra were performed as follows: $95-125$ eV: 125 points, 12 sec/point. For each measurement, four detectors collected data at low Q, whereas the remaining two detectors were used for high Q measurements. The subsequent data treatment of the XRS data was done by using the program XRStools [2].

At first, we investigated the stability of our sample under experimental conditions. For this, we measured the O K and Si $L_{2,3}$ spectra of our sample at 3.5, 7.5, and 32.0 GPa using the MDACs. At each pressure point, we shifted the beam by 30 μm in the *x-y* direction before the data collection was started in order to ensure that the data were collected on an non-preirradiated sample. We compared the resulting spectra to corresponding data of dry silica glass determined in an earlier study [3]. Due to the inferior quality of our spectra, it was impossible

to unambiguously analyse the differences between the O K and Si $L_{2,3}$ spectra of both samples. We assume that the inferior spectral quality can be attributed to the too small opening angle of the PCD seats which significantly reduces the detected signal. In addition, we measured the O K and Si $L_{2,3}$ spectra of the raw sample at ambient conditions. For this, a granule (diameter of about 0.5 cm) was glued on a sanple holder and subsequently mounted on the sample stage of the spectrometer. The measurement was performed without an evacuation of the sample chamber as we supposed that the sample may dehydrate during the measurements. Figure 1 shows a comparison between the Si $L_{2,3}$ and O K spectra of hydrous and dry silica glass [3] measured at ambient conditions.
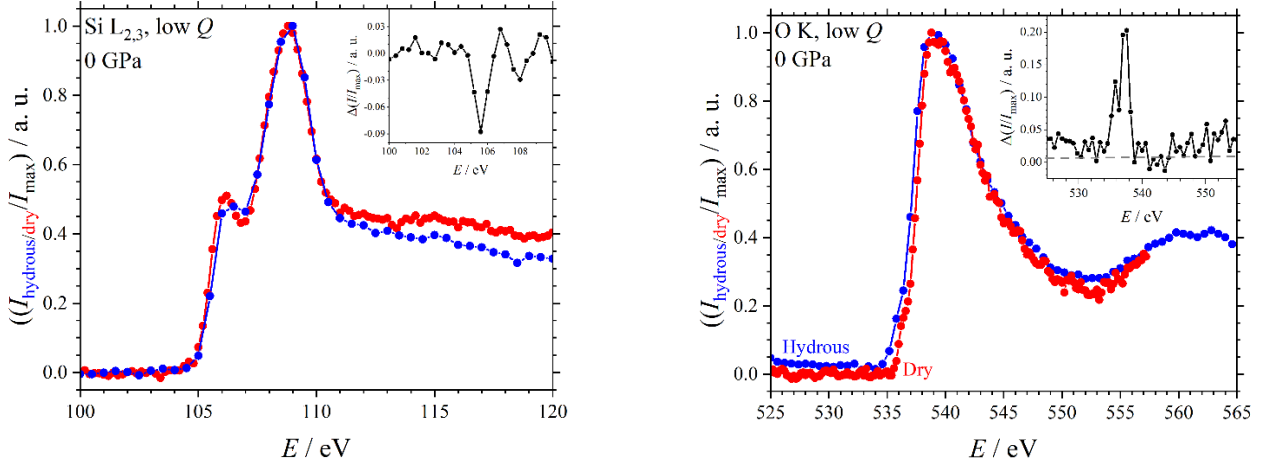

Figure 1: Comparison between the Si $L_{2,3}$ and O K spectra of hydrous and dry silica glass. All spectra were normalized to their maximum intensity. Insets show the difference between the Si $L_{2,3}$ and O K spectra of both samples. XRS data of dry silica glass were taken from reference [3].

Differences between the Si $L_{2,3}$ and O K spectra of both samples mainly occur at around 106 eV and 538 eV, respectively. It seems to be straightforward that these differences are caused by the water in the glass structure of hydrous SiO_2, however, further analysis is required.

Due to the abovementioned problems with the MDACs, we investigated the high-pressure behavior of hydrous silica glass by using the Be-DAC taking into account that the Be of the gasket significantly contributes to the Si $L_{2,3}$ spectra. The beam was focussed on the sample surface and all measurements were performed in the same position. O K and Si $L_{2,3}$ spectra were taken at 4, 9, 12, 16, 21, 30, 36, and 42 GPa. In general, the O K data measured at low and high Q and the high Q Si $L_{2,3}$ spectra allow a more detailed analysis of possible structural variations. In contrast to this, the Be contribution to the low Q Si $L_{2,3}$ is significantly too high and therefore, these data are only suited for qualitative analysis.

Figure 2 shows the resulting high-pressure Si $L_{2,3}$ (high Q) and O K (low Q) spectra of our sample. For this, we have binned the XRS data: Si $L_{2,3}$ (high Q): 0.5 eV; O K (low Q): 0.6 eV. In general, the development of the Si $L_{2,3}$ and O K features with increasing pressure is very similar to that of its anhydrous variant [3]. Our XRS data indicate that hydrous silica glass undergoes pronounced structural changes between about 10-20 GPa. In order to understand the structural changes in more detail, we have determined the position of the Si $L_{2,3}$ (high Q) and O K (low and high Q) edge from the first derivatives of the XRS spectra. In figures 3 and 4, the Si $L_{2,3}$ and O K edge positions are shown in dependence of the pressure. The Si $L_{2,3}$ edge shows a rather peculiar pressure-dependence which significanlty differs from the one report for dry silica glass [3]. A pronounced change is clearly visible at about 15 GPa. We found three regimes in the O K egde data which are nicely supported by our high-pressure Raman data. The first regime occurs between 0-10 Ga. Based on our Raman data we assume that this is the elastic regime in which only the volume of the glass structure is affected by the pressure whereas all bond length and angles are hardly affected by the pressure. Between 10-20 GPa, a rearrangement of the inter- and intratetrahedral angles and bond length takes place, whereas the the silicon coordination number remains unchanged. At even higher pressures an increase of the silicon coordination number is expected.
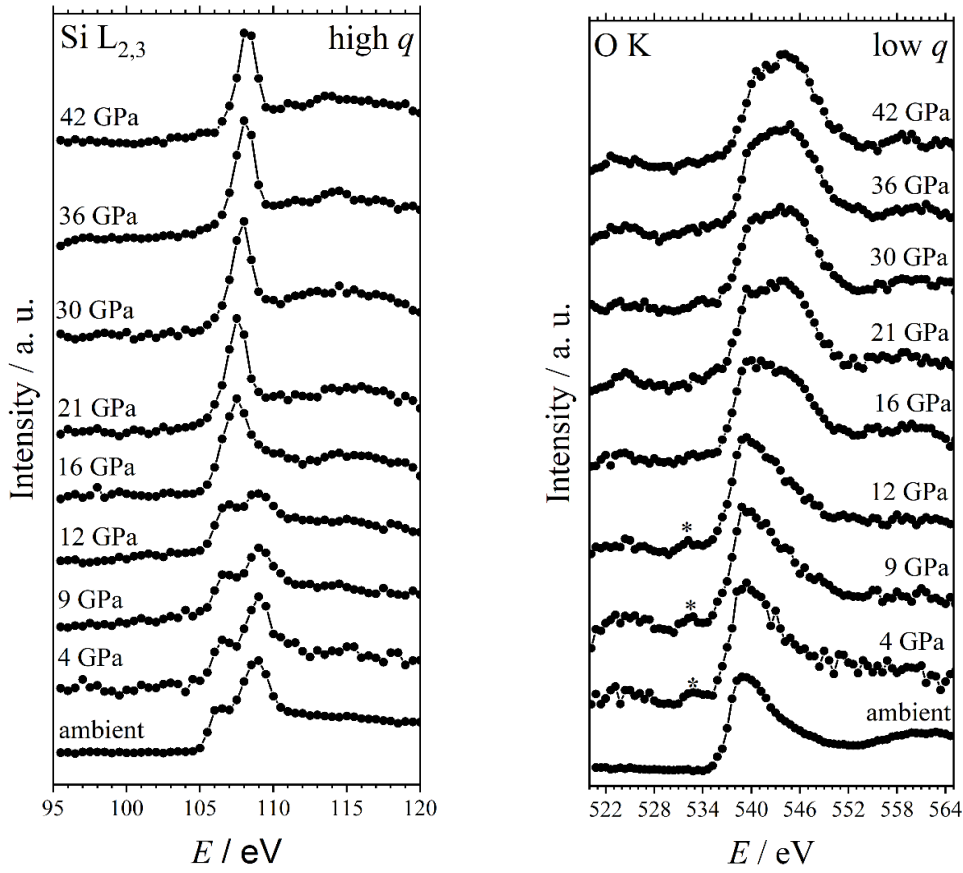
Figure 2: Pressure-dependence of the Si L$_{2,3}$ and O K XRS spectra of hydrous silica glass.
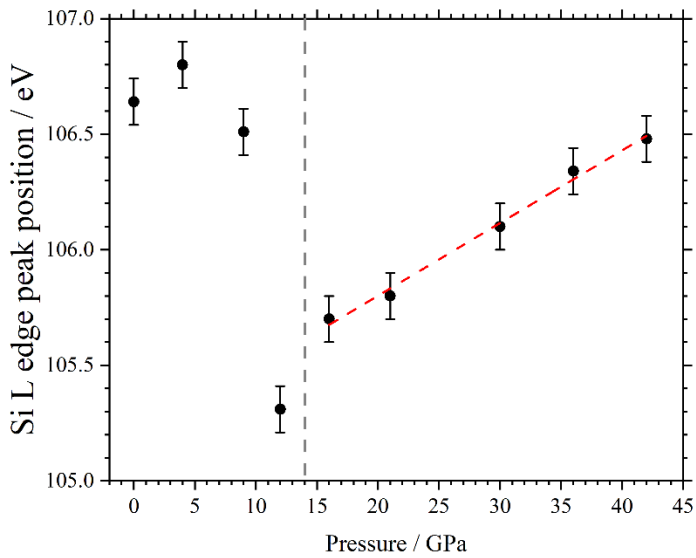

Figure 3: Pressure-induced changes of the peak position of the Si L$_{2,3}$ edge. At ab 15 GPa, a procounced change is clearly visible.
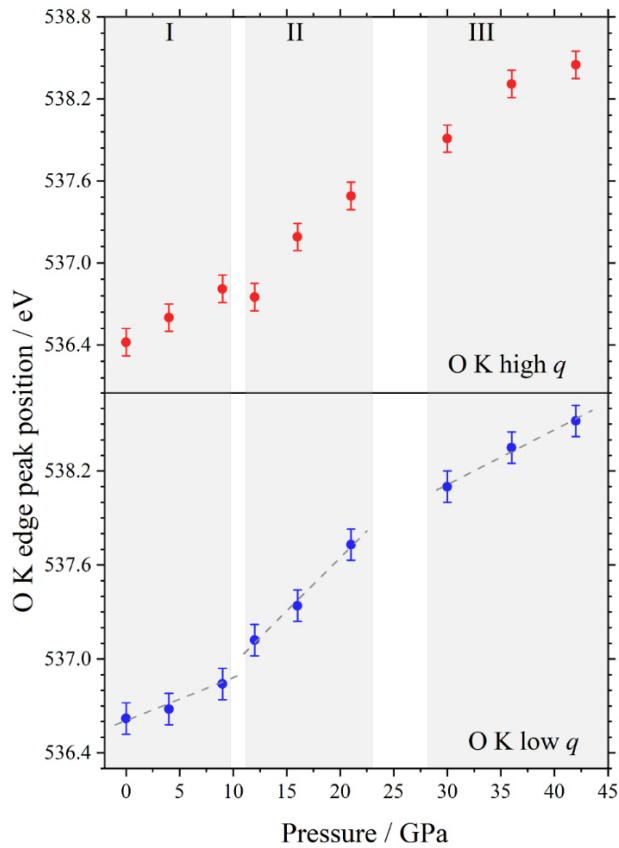
Figure 4: Pressure-induced changes of the peak position of the O K edge. I-III denote three regimes.

At 42 GPa, we performed a further measurement on an untreatet position in a distance of 10 μm to the original spot. We found that both data are very similar This clearly demonstrates that our sample is stable in the beam and no dehydration has taken place during the measurements.

References:
[1] S. Petitgirard, G. Spiekermann, C. Weis, C. Sahle, C. Sternemann, M. Wilke (2017). J. Sychrotron Rad., 24:276-282.
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