Experiment Report Form

	Experiment title: Local structure of glassy GeO2 at Mbar pressure conditions	**Experiment number**: HC-4435
Beamline: BM23	**Date of experiment**: from: 13/04/2021 to: 19/04/2021	**Date of report**: 24/05/2023
Shifts: 18	**Local contact(s)**: Joao Elias FIGUEIREDO SOARES RODRIGUES	*Received at ESRF:*

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Report:

The goal of this proposal was to characterize the pressure induced structural transitions of glassy GeO_2 using EXAFS technique. For this purpose, we have employed diamond anvil cells equipped with nanopolycristalline diamonds (NPDs) to obtain unprecedented high-quality glitch-free EXAFS data up to 161 GPa and a *k*-range of 16 $Å^{-1}$ at the beamline BM23 of the European Synchrotron Radiation Facility (ESRF).

Germanium oxide (GeO_2) GeO_2 represents a structural analog of SiO_2, which in turn is a major compound of industrial materials and the main constituent of silicate melts in Earth's interior. Studying structural properties of SiO_2 glass at high-pressure conditions remains however challenging due to the high signal absorption of high-pressure devices such as the diamond anvil cell. Local structural changes of GeO_2 glass can be in turn easily probed using X-ray absorption spectroscopy (XAS) coupled to the diamond anvil cell equipped with NPDs, which presents an ideal probe to investigate subtle changes of the local atomic arrangements (Krstulović et al 2020, 2021). Using Extended X-ray Absorption spectroscopy (EXAFS) at Ge *K*-edge, we could follow the coordination changes in glassy GeO_2 up to 161 GPa under hydrostatic and non-hydrostatic conditions. These include the transition from 4- to 6-fold that appears at ~20 GPa. The 4- to 6-fold coordination change has been studied previously mostly under non-hydrostatic conditions. In this work, we loaded a polished glass piece of

GeO_2 together with Ne in the sample chamber to probe structural changes for the first time under *quasi*-hydrostatic conditions. A potential second structural change associated with a coordination number increase from 6 to 7 beyond Mbar pressures remains presently an open but important question (Kono et al., 2016). Indeed, this would imply a superior density of glassy GeO_2 to its crystalline counterpart. This observation could in turn suggest a similar mechanism for silicate melts at the base of the Earth's mantle. Consequently, the seismic signals (ULVZ) at the core mantle boundary that remain also highly controversial could be explained by the presence of dense melts.

Two high-pressure X-ray absorption experiments were performed at Ge *K*-edge. For run1, the sample was loaded in a hole of 50 μm^2 drilled in a Re gasket and placed in a diamond anvil cell, equipped with two NPDs of 150 μm culet size. The first run was conducted up to 161 GPa and the sample was loaded without pressure transmitting medium. In the second run a polished glass piece of GeO_2 was loaded together with neon as pressure transmitting medium in a DAC equipped with NPDs of 250 μm cullet size. The run2 was conducted up to 40 GPa. The high-quality EXAFS data obtained at BM23 allow extracting information on the first and second shells (neighbors) including distances, coordination number, Debye-Waller factor for the pairs Ge–O and Ge–Ge.

Selected EXAFS functions [$k^3\chi(k)$] for glassy GeO_2 under quasi-hydrostatic compression at different pressures are shown in Fig. 1. A non-monotonic change of the EXAFS oscillations with increasing pressure is clearly visible, with most significant changes near 20 GPa. Preliminary EXAFS fittings by considering the two shells of Ge–O and Ge–Ge were performed up to 10.5 Å^{-1} in *k* space. In Fig. 2, part of the data extracted from the fitting procedure are displayed, in this case the pair bond distance Ge–O. Indeed, the behavior of this parameter provides a qualitative idea of changes in the degree of compaction/densification. Here, radial distances Ge–O are compared for three different experimental configurations: quasi-hydrostatic, Mbar solid loading (no pressure transmitting medium), and previous results for Ge in $NaAlGe_3O_8$ glasses (Krstulović et al., 2020). A detailed data analysis is currently in progress.

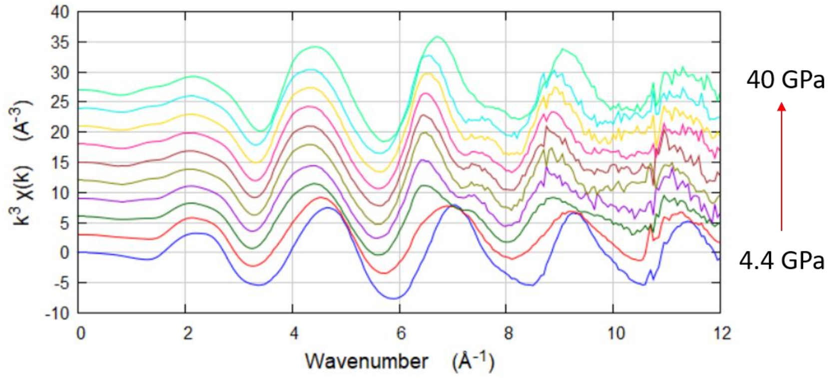

Figure 1. Representative k^3-weighted Ge *K*-edge EXAFS signals acquired on glassy GeO_2 in *quasi*-hydrostatic condition with neon as pressure transmitting medium between 4 up to 40 GPa.

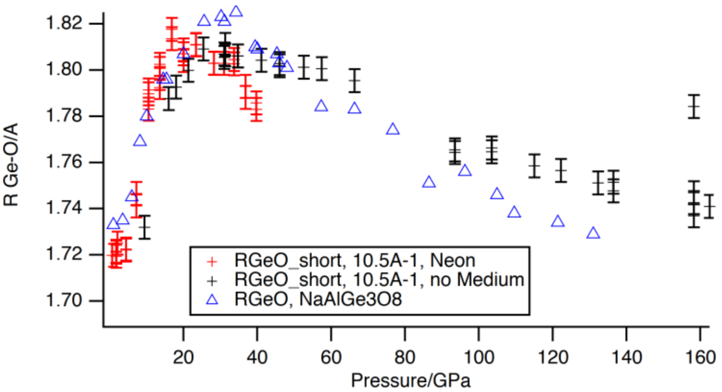

Figure 2. First neighbor distances extracted from the EXAFS fitting of the first-shell and compared to previous data on $NaAlGe_3O_8$.

References

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