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ESRF	Local structure in silicate melts and glasses at high pressure		Experiment number: ES 706
Beamline:	Date of experiment:		Date of report:
BM23	from: 18.04.18	to: 24.04.18	30.5.19
Shifts:	Local contact(s):		Received at ESRF:
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## **Report:**

This study aims at understanding the structural properties of silicate melts relevant to magmatic processes in the deep Earth. Silicate melts represent major component of the Earth's interior and as such, they are responsible for most geodynamical processes. Understanding the structural properties of silicate melts is fundamental to explaining their chemical and physical behavior as well as the processes operating in the deep Earth [1], [2], [3]. A good experimental technique to probe atomic structure is XAFS and is well compatible with high-pressure instrumentation, such as diamond anvil cell (DAC). In our study we probed synthetic silicate glasses combining XAFS with resistively heated diamond anvil cell (RH-DAC). The introduction of the temperature component brings us to the conditions that are more authentic for the deep-Earth interior. High absorption of the diamonds prevents us however to directly probe geologically relevant elements using XAFS, because they are all light elements. We therefore use synthetic silicate glasses and we substitute partially our elements of interest by their chemical and structural analogs. A well-known analog for Si, the most abundant network modifier in the Earth, is Ge and the similarities in the structural respond of these two elements upon compression have been confirmed in numerous studies [4], [5], [6], [7]. Here we put our focus on local structural environment of Ge in silicate melts in the albite-diopside joint system and in particular on the effect of the temperature on the compression induced structural changes in the glass. These experimetrs are now possible thanks to the advances in the high pressure and high temperature development, providing us a new reliable tool to simulate in-situ conditions of the deep planetary interior.

We collected Ge K-edge EXAFS on glass samples at the micro-XAS station of the ESRF beamline BM23. The beam was monochromatized using an Si(111) double-crystal fixed exit monochromator. The spectra were collected in transmission mode measuring beam intensity before and after the sample using ionization chambers. Using two Pt-coated KB-mirrors inclined to an angle of 4 mrad the beam was focused to the spot size of 5x5 μm. As the sample the pieces of glass were loaded in the DAC equipped with nano-polycrystalline diamonds of the Le Toullec type. The culet size of the diamonds was 200, 250 and 300 μm. In the center of the 200 microns thick Re-gaskets a small hole was drilled and served as a sample chamber. The size of the sample chamber corresponds approximately to the half of the culet diameter. As a pressure monitor for high pressure and high temperature experiments a small piece of gold was placed near the gasket rim and served to monitor the pressure in the sample by measuring the diffraction pattern on the gold. For this purpose, a MarCCD diffraction detector was installed in the beamline. In addition, one series of high-pressure experiments at Ge K-edge at room temperature was performed. For this experiment a small ruby crystal was placed near the gasket rim and served as a pressure indicator. The ruby was probed by a green laser and the shift of the ruby fluorescence line served as a pressure indicator.

The temperature in the RH-DAC was monitored using thermocouples, which were precisely attached to the back side of the diamonds leaving central part of the diamond surface free for the penetration of the X-rays through the sample.

We collected data at isothermal condition at 515  $^{\circ}$ C by varying pressure (from 3 to 23 GPa), as well as at isobar conditions at about 3 GPa by varying the temperature (from 25 to 550  $^{\circ}$ C). The data on compression at room temperature were acquired up to  $\sim$  95 GPa.

The representative XANES spectra on Ge K-edge collected at 515 °C and varying the pressure between 3 and 23 GPa are plotted in Figure 1. As the pressure increases the network formers Ge and Si undergo a transformation from tetrahedral to octahedral geometry. This structural change is manifested in the Ge XANES spectra. We observe a shift of the first XANES peak to higher energies and a relative intensity decrease of the shoulder after the first XANES peak. It seems that this trend is not finished at 23 GPa, which indicates that at 515 °C the conversion to octahedral coordination is not completed.

Figure 2 shows first EXAFS fit results on the first shell bond distance evolution as a function of pressure on the sample measured at room temperature.

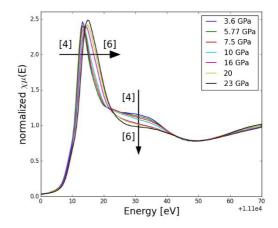


Figure 1. Normalized Ge K-edge XANES spectra collected at 515 °C at pressure between 3 and 23 GPa on amorphous Na<sub>0.45</sub>Ca<sub>0.1</sub>Mg<sub>0.05</sub>Sr<sub>0.5</sub>Si<sub>1.95</sub>Ge<sub>0.5</sub>O<sub>7.8</sub>

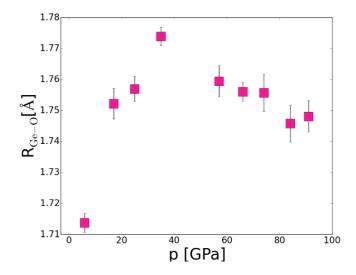


Figure 2. First fit results on Ge K-edge of the glass as a Function of increasing pressure at room temperature. First shell Ge-O bond distance  $R_{Ge-O}$  reaches maximum at 35 GPa.

These first fit results show that maximum Ge-O bond length is reached at ~ 35 GPa, which indicates full conversion to octahedral coordination. Beyond this pressure the bond distance shows a decreasing trend up to

92 GPa. Compared to GeO<sub>2</sub> glass in our complex alumino-silicate-germanate glass the completion of the conversion to octahedral coordination is at slightly higher pressure [4, 5, 6]. Whereas compared to SiO<sub>2</sub> glass, it is completed at lower pressure [7]. As seen above, at 515 °C and 23 GPa the octahedral coordination seems not to be reached. An interesting question is whether a temperature of 515 °C significantly influences the compression of silicate-geramanate glasses compared to the room temperature. For the glassy state i.e. at temperatures below the glass transition, there is the general question whether the conversion to octahedral coordination may be shifted to lower pressure due to thermal enhancement of the structural relaxation during compression. For these and similar questions further experimental investigations are needed.

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## **Acknowledgements:**

We thank BM23 beamline for the support, in particular Florian Perrin and Sebastien Pasternak. We also thank Jeroen Jacobs from the high pressure sample environment for his support. Special thank to Tetsuo Irifune from the Geodynamic Research Center of the Ehime University in Matsuyama, Japan for providing us nano-polycristalline diamonds.