



	<b>Experiment title:</b> <b>Role of initial topology on the structural behavior of depolymerized lithium silicates under high-pressure.</b>	<b>Experiment number:</b> HC-4270
<b>Beamline:</b> ID20	<b>Date of experiment:</b> from: 07/10/2020 to: 14/10/2020	<b>Date of report:</b>
<b>Shifts:</b> 21	<b>Local contact(s):</b> Christoph SAHLE and Emmanuelle de CLERMONT GALLERANDE	<i>Received at ESRF:</i>
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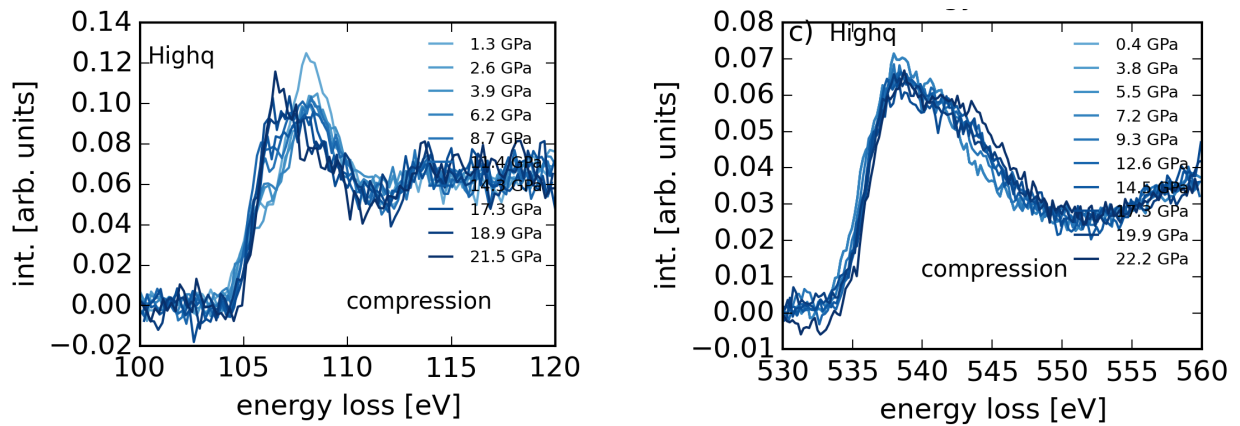
### Report:

At room pressure, the addition of alkali oxide to pure  $\text{SiO}_2$  leads to a dimensional reduction of the silicate network. In the particular case of crystalline lithium silicates, the 3D structure of  $\text{SiO}_2$  made of corner-sharing  $\text{SiO}_4$  tetrahedra is sequentially modified, while Li deconstructs the framework so as to obtain layers ( $\text{Li}_2\text{Si}_2\text{O}_5$ ), then chains ( $\text{Li}_2\text{SiO}_3$ ), and clusters made of two  $\text{SiO}_4$  ( $\text{Li}_6\text{Si}_2\text{O}_7$ ), to end up with a fully saturated framework made of isolated  $\text{SiO}_4$  tetrahedra surrounded by Li in the end-member  $\text{Li}_4\text{SiO}_4$ . [1] While the network structure is usually described in terms of connections between the basic structural units, i.e. the  $\text{SiO}_4$  tetrahedra, the non-bonding O sites also reflect the network topology and degree of network polymerization. A lower degree of polymerization in the starting glass should result in important changes of the compressibility properties in comparison with a pure  $\text{SiO}_2$  glass resulting in a quite different behaviour of the bonding transformation under pressure.

Due to COVID sanitary restrictions, the present experiments were carried out remotely thanks to the excellent work of C. Sahle and E. de Clermont Gallerande from the ID20 beamline. Amorphous  $\text{Li}_2\text{SiO}_3$  was measured in a diamond-anvil cell with 500  $\mu\text{m}$ -culet diamonds provided by ESRF. Measurements were done through beryllium gasket in the case of the O K-edge or through a mixture of cubic boron nitride epoxy and diamond powder in the case of Si  $L_{2,3}$  edge. X-ray Raman scattering measurements were carried out at the ID20 beamline. In order to create losses in the vicinity of the silicon  $L_{2,3}$ -edge and the oxygen K-edge, incident energy was scanned from 9.79 to 9.84 keV and 10.22 to 10.26 keV respectively at a constant analyzer energy of 9.7 keV with an overall energy resolution of 0.7 eV (FWHM). All data were processed using the XRStools software package [2]

Si  $L_{2,3}$ -edge and O K-edge XRS spectra of glassy  $\text{Li}_2\text{SiO}_3$  were measured *in situ* as a function of pressure. (Figure 1) Spectral changes are clearly pointed out on both edges, and mostly around 20-25GPa. Through comparison to vitreous  $\text{SiO}_2$ , we show that up to 25GPa the densification mainly involves recombination of NBO, increase of the network polymerization and topological reorganization without increasing the coordination of silicon atoms. After 25GPa, it is

unclear if amorphous  $\text{Li}_2\text{SiO}_3$  undergoes similar structural changes as  $\text{SiO}_2$  or if the presence of lithium atoms has an influence on the densification processes. Additional pressure points would be necessary in order to terminate probing the full pressure induced structural transformation.



**Figure 1: Si L<sub>2,3</sub>-edge (left) and O K-edge (right) XRS spectra of  $\text{Li}_2\text{SiO}_3$  glass as a function of pressure.**

In conclusion, thanks to the great capabilities of the ID20 beamline, successful measurements have been obtained at high-pressure using a panoramic diamond anvil cell with an excellent signal to noise ratio. The observed modifications are indicative of a spatial reorganisation of atoms induced by pressure without any coordination change of Si or O atoms.

## REFERENCES

- [1] G. Rousse et al. Inorg. Chem. 53(12), 6034 (2014)
- [2] Ch. Sahle, J. Sync. Rad. 22(2), 2015