



	<b>Experiment title: Structural origin of the thermally induced densification in SiO<sub>2</sub> and GeO<sub>2</sub> glasses: an O K-edge inelastic X-ray scattering study.</b>	<b>Experiment number:</b> HD-292
<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 22/10/2008 to: 28/10/2008	<b>Date of report:</b> 24/02/2009
<b>Shifts:</b>	<b>Local contact(s):</b> Dr Valentina GIORDANO Dr Giulio MONACO	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *Pr Georges CALAS, IMPMC, Paris *Dr Laurent CORMIER, IMPMC, Paris *Dr Guillaume FERLAT, IMPMC, Paris *Dr Laurence GALOISY, IMPMC, Paris *Dr G�rard LELONG, IMPMC, Paris *Pr Abhay SHUKLA, IMPMC, Paris		

### Report:

In the past decade, the notion of *polyamorphism* in glassy systems has been proposed to explain the existence of several disordered states when they are placed under extreme conditions. Vitreous GeO<sub>2</sub> shows distinct amorphous states in its P-T diagram when relatively high-pressure is applied. The glass structure changes from a distorted quartz-type structure at ambient pressure to a distorted rutile-type structure at about 10 GPa,<sup>1</sup> the germanium coordination changing from 4 (GeO<sub>4</sub>) to 6 (GeO<sub>6</sub>). However, it is not clear yet if this transition is a linear combination of the two structures or if it occurs through an intermediate state such as the five-coordinated GeO<sub>5</sub> polyhedra as suggested by molecular dynamics simulations.<sup>2</sup>

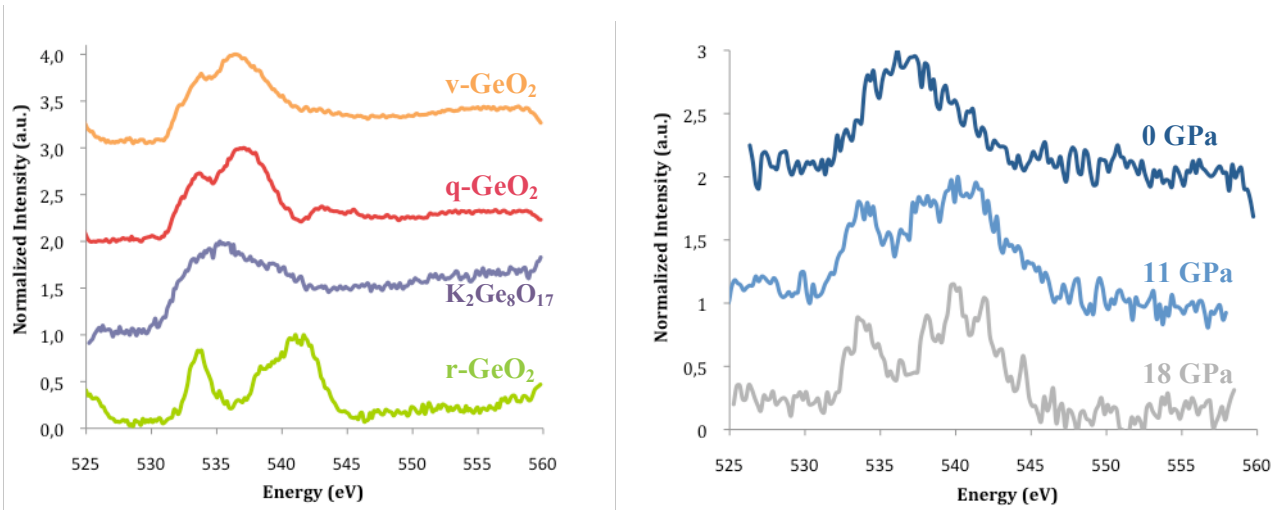
First-principles calculations on crystals<sup>3</sup> have shown that the profile of the O K-edge spectra in the pre-edge region strongly depends on the germanium coordination state, providing thus an efficient tool to investigate the GeO<sub>4</sub>-GeO<sub>6</sub> transition. We have performed an X-ray Raman scattering experiment on ID 16 in order to access the oxygen K-edge in a high-pressure environment. We have used a diamond anvil cell provided by our institute (IMPMC) offering a large aperture. Measurements were made through Be gasket from ESRF. An energy resolution as high as 0.5 eV was required in order to be more sensitive to slight changes in the pre-edge profile. For a better understanding of the high-pressure data, we have first measured three reference samples in the crystalline state, for which the Ge coordination is well known, and vitreous GeO<sub>2</sub> as well at room conditions:

- (i) q-GeO<sub>2</sub> (Quartz structure) – O coordination [II], Ge in GeO<sub>4</sub>
- (ii) r-GeO<sub>2</sub> (Rutile structure) – O coordination [III], Ge in GeO<sub>6</sub>

(iii)  $\text{K}_2\text{Ge}_8\text{O}_{17}$ , Ge in  $\text{GeO}_4$  and  $\text{GeO}_5$

(iv) v- $\text{GeO}_2$  (Glass), Ge in  $\text{GeO}_4$ .

The resulting spectra are shown on the Fig. 1 (Left). The crystalline samples give us the feature of each O coordination. Though the resolution is lower than X-ray absorption spectroscopy at O K-edge,<sup>4</sup> we observe the same features by comparing the two techniques. The coordinations 2 and 3 are clearly distinctive and  $\text{K}_2\text{Ge}_8\text{O}_{17}$  indicates that the five-coordinated polyhedra  $\text{GeO}_5$  can be detected in the energy range 533-536 eV, where the quartz-like and rutile-like structures present a decrease of their intensity. It appears also that v- $\text{GeO}_2$  at ambient pressure has a quartz-like structure which is in good agreement with literature. The high pressure spectra were collected at 0, 11 and 18 GPa and required at least 15h of counting time each in order to achieve a good statistics (Fig. 1 (Right)). The higher noise of the spectra can be understood in terms of the small size of the sample and the subtraction of the contribution from the beryllium gasket. O present in Be gasket was a severe problem, though the features appear at different position than for  $\text{GeO}_2$ . Thanks to the position-sensitive detectors developed on ID16, the O K-edge signal from the gasket has been assessed and successfully subtracted. Despite we experienced some technical problems concerning the alignment of the beam on the tiny sample and its position stability during the measurements, we have overcome the main difficulties and proven the feasibility of the experiment. Indeed, Fig. 1 (Right) shows that there is a clear evidence of the modification of the local structure around the oxygen as pressure is increased.



**Figure 1:** (Left) Reference samples measured at ambient pressure : vitreous  $\text{GeO}_2$  (orange), quartz- $\text{GeO}_2$  [II] (rouge),  $\text{K}_2\text{Ge}_8\text{O}_{17}$  (purple) and rutile- $\text{GeO}_2$  [III] (green). (Right) Vitreous  $\text{GeO}_2$  spectra measured in a diamond anvil cell at 0, 11 and 18 GPa, after subtraction of the beryllium background.

The applied pressure induces a coordination change of the oxygen, passing from a quartz-like structure composed of  $\text{GeO}_4$  tetrahedra to a rutile-like structure containing  $\text{GeO}_6$  octahedra. A slightly higher intensity in the energy range 535-537 eV at 11 GPa than at 18 GPa could suggest an intermediate coordination state. However, the present data are still too noisy to be conclusive in this sense and a better sampling of the critical pressure region (5-10 GPa) would be necessary.

In conclusion, the reference samples clearly indicate the possibility to detect the presence of GeO<sub>5</sub> in O K-edge spectra. Successful measurements have been obtained at high-pressure using our diamond anvil cell, though the signal of O present in the Be gasket was important, which will be improved in further experiments. An important time of these experiments has been devoted to solve alignment problems, beamtime stability and size, and our scientific program has not been fully achieved. More beamtime is thus mandatory to scan the region of coordination change and to determine which mechanisms drive pressure-induced polyamorphisms.

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<sup>1</sup> J.P. Itié, A. Polian, G. Calas, J. Petiau, A. Fontaine, H. Tolentino, *Phys. Rev. Lett.* **63**, 398 (1989).

<sup>2</sup> M. Guthrie, C.A. Tulk, C.J. Benmore, J. Xu, J.L. Yarger, D.D. Klug, J.S. Tse, H-K. Mao, R.J. Hemley, *Phys. Rev. Lett.* **93**, 115502 (2004).

<sup>3</sup> D. Cabaret, F. Mauri, G.S. Henderson, *Phys. Rev. B* **75**, 184205 (2007).

<sup>4</sup> H.M. Wang, G.S. Henderson, *J. Non-Cryst. Solids* **354**, 863 (2008).