

**Experiment title:**

Polyamorphism in oxyde glasses

**Experiment  
number:**  
HS-2562**Beamline:**

ID 24

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IPGP, Case 115, 75252 PARIS Cedex 05, France**Report**

Framework glasses have been extensively investigated on account of their fundamental importance and technological applications. Their structure is an archetypal three-dimensional network of corner-sharing tetrahedra. The structural properties of these glasses, including the degree of short-and intermediate-range order, are deeply modified at high-pressure, leading to the so-called polyamorphism. Modification of inter-tetrahedra angles and coordination changes lead to important reorganization of the glass structure, with a subsequent densification, which is partly retained permanently after the experiment (Sugai and Onodera, 1996; Sampath et al., 2003). Although silica is a more widely investigated glass, the softer germania (GeO<sub>2</sub>), a structural analogue to silica, is easier to investigate because of the lower transformation pressure range and the possibility to use Ge K-edge EXAFS and XANES spectroscopy. An additional difficulty of a detailed investigation of polyamorphism arises from the fact that this structure is not retained upon decompression and, therefore, must be studied *in situ*. Described for the first time in 1989 (Itié et al., 1989), the nature of the structural processes involved in the pressure-induced transformation has been recently discussed at the light of complementary neutron and x-ray scattering data (Guthrie et al., 2004).

The aim of our experiment was to investigate the structural modifications suffered by multicomponent three-dimensional network glasses at high-pressure. Ge- and Ga-oxide glasses are generally considered as structural analogues of silicate and aluminosilicate glasses, and are more suitable for investigation in a diamond anvil cell. The composition of the glasses investigated at ID 24 has been chosen in order to investigate the influence of Si-Ge and Al-Ga substitution in framework glasses on the pressure-induced coordination change of network forming elements. The reversibility of pressure-induced coordination changes requires *in situ* investigations, with an important hysteresis of the coordination changes between upward and downward transformations (Itié et al., 1989; Majérus et al., 2004).

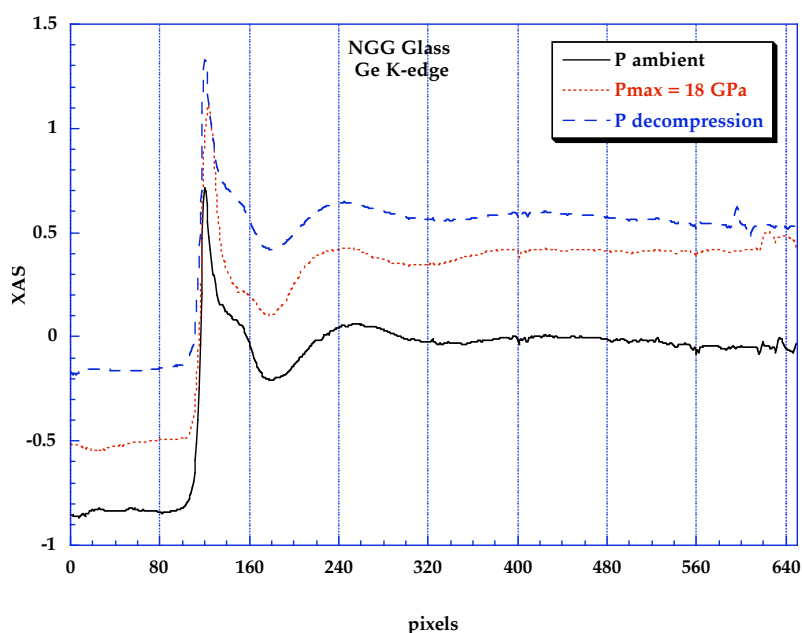
## Experimental method

Three Ge- and Ga-oxide glasses have been synthesized by melting oxide components at 1300°C in a platinum crucible and quenched in air. In order to avoid hole effects and ensure sample homogeneity, glass slabs with parallel faces have been prepared, the thickness of which was calculated according to the chemical composition of each glass. These slabs were loaded together with rubis chips for pressure calibration in a diamond anvil cell with a 400  $\mu\text{m}$  diameter table. The gasket was made of rhenium or inox alloy. The pressure-transmitting medium was silicone oil, and the pressure was controlled using a gas membrane device. The pressure range investigated covered from ambient pressure up to 14 to 24 GPa, depending on the experiments. We checked that pressure remained quasi-hydrostatic up to the highest pressures achieved as shown by the limited broadening of the rubis fluorescence lines. EXAFS and XANES measurements were investigated at Ge- and Ga-K absorption edges. Spectral measurements were undertaken at both increasing and decreasing pressure, in order to investigate the reversibility of the transformation process. The accessible energy-range was about 500 eV at the Ge and Ga-K edges.

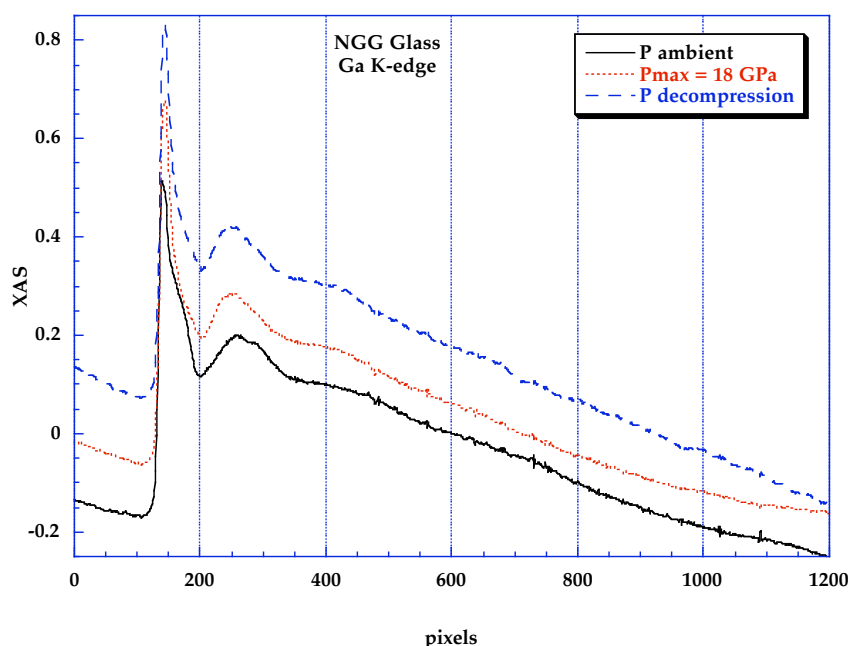
## First results

The high intensity and fast data acquisition conditions have given us the opportunity to record the evolution of EXAFS and XANES spectra as a function of pressure. As can be seen on the figures enclosed, most glitches arising from the Bragg peaks of the diamond anvil cell have been rejected from the energy range investigated by taking advantage of the characteristics of the dispersive setup of ID 24 beamline facilities. A dramatic change is observed with increasing pressure at both Ga (Figure 1) and Ge (Figures 2) edges. At ambient pressure, the Ge-K edge XANES region of these multicomponent glasses is similar to that observed in  $\alpha\text{-GeO}_2$ . However, it is less resolved, an indication of a larger disorder arising from the substitution of Ge by other network formers (Si, Al, Ga). The presence of a lighter backscatterer as a second neighbor (Si or Al) is responsible for a further modification of the XANES spectrum, which only exhibits one peak in the high energy range. With increasing pressure, the major modifications of the XANES spectra are an increase of the resonance line and the disappearance of the characteristic high energy resonance. They indicate a coordination change of Ge and Ga. The shift of the EXAFS features towards the edge together with an increase of their frequency indicate an increase of the (Ga, Ge)-O distances in the high-pressure glass, another confirmation of the pressure-induced coordination change in these glasses. Upon decompression, most initial characteristics of the EXAFS contribution are recovered, although the reverse transformation is observed at much lower pressures than when increasing the pressure, an indication of an important hysteresis.

However, even at full decompression -i.e. after opening of the diamond anvil cell- the XANES region of the recovered glass is not similar to that observed in the starting glass. This may be due to the specific structure of the permanently densified framework glasses, with a permanent modification of the inter-tetrahedral angle. All these observations indicate that the Ge coordination changes occurs on a wide energy range, with a different behavior of Ge and Ga, which exhibit a coordination changes at different pressure. These preliminary observations indicate a complex mechanism of the polyamorphic transformations in these multicomponent glasses. A detailed analysis of these data is currently underway.



**Figure 1.** Ge-K edge XANES of a Ge-Ga oxide glass at room pressure and 18 GPa.



**Figure 2.** Ga-K edge XANES of the same glass at room pressure and 18 GPa.

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