



Experiment title:
Local structural changes in amorphous and crystalline
GeO₂ under pressure

**Experiment
number:**
IH-HC-1294

Beamline:
BM29

Date of experiment:
from: 03/07/2008 to: 08/07/2008

Date of report:
June 30, 2009

Shifts:
15

Local contact(s):
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Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):
(*) M. Vaccari

Report:

The experiment HD-325 was not allocated official beamtime. The same experiment was then performed during the in-house beamtime IH-HC-1294. The results have been published in Ref. [1].

The nature of amorphous-amorphous transformations (AATs) under pressure and the concept of polyamorphism in the classic tetrahedral network-forming glasses represent a strongly debated issue in modern condensed matter physics. Amorphous GeO₂ (a-GeO₂) is one of the most studied examples of materials for which an AAT occurs at high pressure. However, conflicting results were obtained in previous works and, despite two decades of investigations, the details of short range order changes were still not well established. Therefore, a new EXAFS experiment was performed in order to obtain new *in situ* high quality experimental data, characterized by a remarkable long energy range and unprecedented accuracy at high pressure. For comparison purposes, also crystalline quartz-like GeO₂ (q-GeO₂) has been studied in the same pressure range as a-GeO₂.

The EXAFS experiment was made in transmission mode at Ge K-edge at the BM29 X-ray absorption spectroscopy beamline of the ESRF. The high-stability fixed-exit monochromator was equipped with a pair of Si 311 crystals and primary slits vertical aperture was set to 0.7 mm. The harmonic rejection was obtained using a double reflection on a pair of Si mirrors with grazing incidence of 2 mrad. The lower mirror was bent in order to vertically focus the beam at the sample position. The beam size incident on the sample was about 70 μm and 500 μm vertically and horizontally, respectively. Energy was calibrated by setting the first inflection point of the absorption edge of amorphous germanium (a-Ge) to 11103 eV. A Paris-Edinburgh large volume V5 press, equipped with sintered diamond anvils and 5 mm boron-epoxy gaskets, was used as pressure device. A maximum pressure of 13 GPa was reached. High purity GeO₂ powders (99.999%, purchased from Aldrich Chemical Co.) have been finely ground, homogeneously mixed with a suitable quantity of h-BN and NaCl and prepared in the form of cylindrical pellets. The pressure was determined *in situ* on the sample through X-ray diffraction: a monochromatic beam ($E = 15$ keV) was used to collect diffraction rings of calibrants on a MAR345 image plate mounted in an offset position.

X-ray absorption spectra were treated through established procedures using the programs VIPER and ATHENA. In Fig. 1 the normalized spectra in the near edge (XANES) region, the extracted $k^3\chi(k)$

EXAFS signals and their Fourier transform moduli are shown at selected pressures for both crystalline and amorphous GeO₂. The overall quality is excellent and the k -range available for analysis extends up to about 13 Å⁻¹. In the Fourier transform of both compounds, the main peak at about 1.3 Å is due to the nearest neighbor oxygen atoms, which at ambient conditions are tetrahedrally coordinated to the central Ge atom. In crystalline GeO₂ the structure from about 1.8 and 3.4 Å is due - at ambient pressure - to second and third coordination shells (made up of four germanium and six oxygen atoms, respectively) and to multiple scattering contributions. In the case of amorphous GeO₂, a signal beyond the first coordination shell is evident and is explained by the considerable degree of intermediate range order of the glass.

A qualitative inspection of XANES spectra and EXAFS signals (Fig. 1) suggests that the structural modifications in a-GeO₂ are more sluggish with respect to quartz-like GeO₂. In the crystalline compound, the tetrahedral-to-octahedral transition is located at about 8.5 GPa; the analogous change in amorphous GeO₂ is much more gradual and extends over a larger pressure range. Interestingly, EXAFS signals of glassy GeO₂ beyond the first Ge-O shell qualitatively confirm the continuous breakdown of the intermediate range order up to 10 GPa.

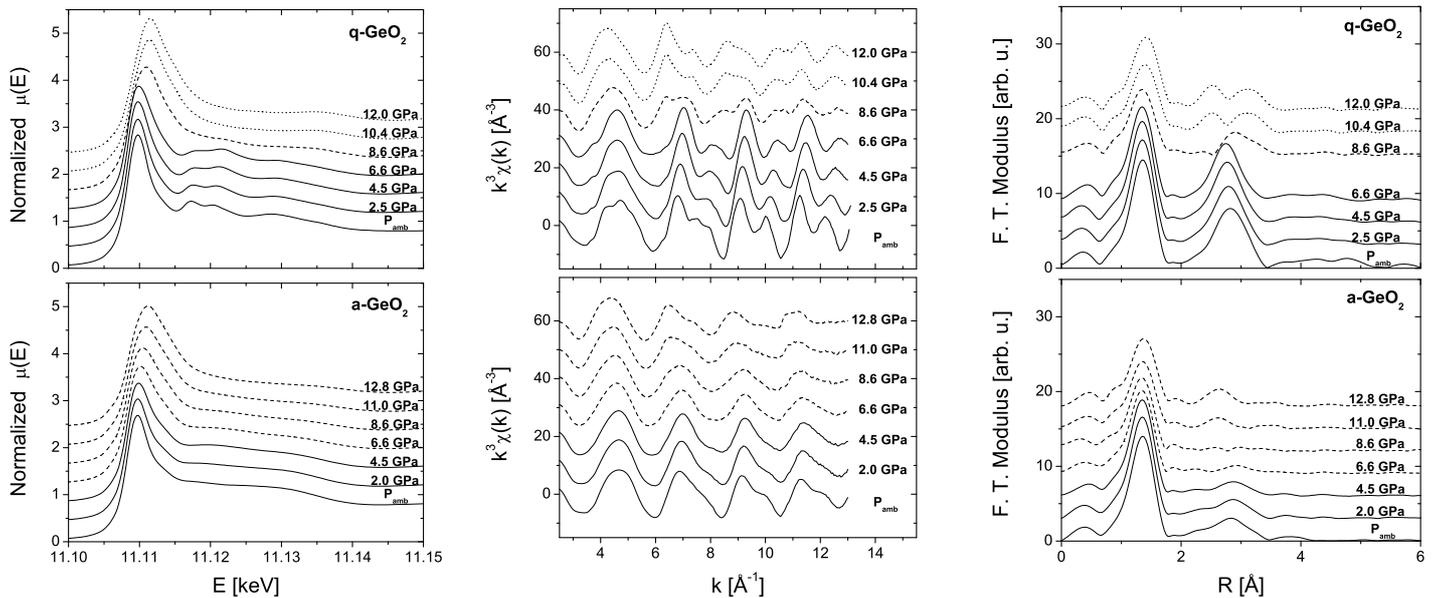


Figure 1: Normalized XANES spectra (left), extracted $k^3\chi(k)$ EXAFS signals (middle) and Fourier transform moduli (right) of crystalline and amorphous GeO₂ (top and bottom panels, respectively) at selected pressures. The spectra drawn in continuous line correspond to the low-pressure phase, in dashed line to the transition region and in dotted line (only for q-GeO₂) to the high-pressure phase.

A quantitative EXAFS analysis has been performed for the Ge-O first shell, whose contribution can be well separated and interpreted within the single scattering framework for both amorphous and crystalline GeO₂. The analysis has been carried out using the IFEFFIT package. The pressure evolution of the Ge-O average distance R , coordination number N and bond length disorder σ^2 (as well as the Ge K absorption edge position) are shown and discussed in detail in Ref. [1]: their behavior confirms the qualitative considerations described in this Report and gives further insight on the detailed mechanisms underlying the polymorphism in glassy GeO₂. In particular, no support is provided to the recently claimed intermediate state with a constant average coordination of five. Old evidences of a narrow transition fully completed at 13 GPa are also ruled out.

References

- [1] M. VACCARI, G. AQUILANTI, S. PASCARELLI, and O. MATHON, *J. Phys.: Condens. Matter* **21**, 145403 (2009).