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# High-pressure X-ray absorption fine structure in the diamond anvil cell and its applications in geological materials

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**Abstract.** Although coupling the X-ray absorption fine structure (XAFS) technique to the diamond anvil cell (DAC) has long been recognized as potentially important for understanding the behavior and evolution of the local and electronic structure of matter under extreme conditions, the DAC has been regarded as poorly suited for XAFS due to the DAC imposed glitches. Recently, an iterative method was proposed to distinguish and eliminate the serious interference of the diamond Bragg peaks, and succeeded in acquiring high quality ‘reflection-free’ XAFS spectra at high pressure under the DAC environment. In this paper, we use this method and present demonstration XAFS spectra for GeO<sub>2</sub> glass, which is the archetype of network forming glasses with important geophysical implications, at pressures to 64 GPa. This is far above the change in coordination from tetrahedra to octahedra occurring at 6-13 GPa. The results provide important insight into the structural polymorphism of GeO<sub>2</sub> glass at high pressure.

## 1. Introduction

Diamond anvil cells (DAC) are commonly used to investigate the high-pressure phase behavior of condensed matter. It is well known that XAFS including the near edge (XANES) and extended (EXAFS) spectra can offer critical information on the local electronic structure and atomic arrangement of absorber atoms in materials at high pressure or ambient conditions [1-4]. The coupling of the diamond anvil cell technique to the XAFS technique is of general importance in physics, chemistry, materials science and earth sciences, and has long been regarded as potentially important for understanding the behavior and evolution of the local and electronic structure of matter under extreme conditions [5-7]. However, the use of diamond anvil cells results in distortion of XAFS spectra due to the Bragg reflections from the diamond anvils, restricted sample thickness, and reduced signal quality due to absorption by diamond at low energy. The Bragg reflection of the diamond anvils can suddenly reduce the transmitted intensity and makes a strong contribution to the measured attenuation of x-ray photons, i.e. glitches, at certain x-ray energies and orientations of the diamonds.

Because of the DAC Bragg glitches, which are often more intense than EXAFS and XANES oscillations and spoil the high-quality XAFS data necessary for precise structural information, diamond anvils has long been recognized as not suited for the conventional energy scan XAFS measurements in high-pressure experiments [5]. In recent work, it was found that by using nano-polycrystalline diamond instead of single crystal anvils, the influence of diamond diffraction could be significantly mitigated [8, 9]. However, nano-polycrystalline diamond is not widely available and small DAC-induced ripples are still visible in the resulting EXAFS data [8].

Another method to acquire high quality X-ray absorption spectra (XAFS) over a long energy range at high pressure using the diamond anvil cell has been recently developed [10]. It was found that the DAC imposed glitches, whose energy positions are very sensitive to the relative orientation between the DAC and incident X-ray beam, can be effectively eliminated using an iterative algorithm based on redundant measurements over a small angle range of DAC orientations, e.g. within  $\pm 3^\circ$  around the X-ray beam [10]. It has been demonstrated that XAFS spectra obtained for crystalline  $\text{GeO}_2$  recorded by traditional Scotch Magic tape and the DAC method, respectively, show nearly identical good quality to 440 eV above the absorption edge. High pressure ‘reflection-free’ XAFS data were obtained for  $\text{GeO}_2$  glass up to 55 GPa.

The polyamorphism of classic network-forming glasses such as  $\text{GeO}_2$  or  $\text{SiO}_2$  is of great interest due to their Earth science implications [11] and importance in glass theory [12]. These network-forming glasses have been intensively studied for several decades [11]. Due to the recent findings of pressure-induced intermediate states in  $\text{GeO}_2$  glass [10, 13-15], considerable renewed investigations have been performed both experimentally and theoretically during the last few years [16-22].

It is desirable to make an exhaustive check on the reliability of the emerging method of Ref. 8. It is also important to apply the proposed method to probe the possible new polyamorphism in  $\text{GeO}_2$  glass at pressures much higher than the completion pressure of the change from tetrahedral to octahedral coordination at 13-15 GPa. To this end, we have carried out high-pressure Ge K-edge XAFS experiments. High quality XAFS spectra of  $\text{GeO}_2$  glass have been obtained at pressures up to 64 GPa. It should be mentioned that the developed method is not limited by the applied pressure of the DAC, and should be applicable for in situ XAFS measurements using DAC to ultra-high pressures in the Mbar region.

## 2. Experimental

XAFS experiments were carried out on the Ge K-edge (11.103 eV) of  $\text{GeO}_2$  glass in transmission mode at the GeoSoilEnviroCARS bending magnet beamline 13-BM-D, Advanced Photon Source (APS), Argonne National Laboratory. The X-rays were monochromatized using a Si(111) double-crystal monochromator. Higher harmonics were rejected by detuning the second crystal of the monochromator to reduce the total intensity to  $\sim 50\%$  of the intensity at full tune. A 1000-mm Pt-coated mirror was used to focus the beam in the vertical to  $\sim 50 \mu\text{m}$ . The horizontal X-ray beam was then focused down to a diameter of approximately  $15 \mu\text{m}$  at the sample position using a 200-mm long Kirkpatrick-Baez (KB) mirror. Details of the equipment and X-ray optics of this beamline are described elsewhere [23, 24].

$\text{GeO}_2$  glass samples with good quality as determined by X-ray examination at ambient condition were made by quenching  $\text{GeO}_2$  melt annealed at  $1600^\circ\text{C}$  for six hours, and generously donated by Liping Huang from Rensselaer Polytechnic Institute, New York. Details of the  $\text{GeO}_2$  glass preparation can be found elsewhere [13]. Princeton-manufactured standard and large-opening symmetrical DACs with 300- $\mu\text{m}$  culets and 2.1 mm thickness for each anvil, were employed for XAFS measurements. Rhenium gaskets (250- $\mu\text{m}$  thick) were pre-indented to about 40- $\mu\text{m}$  thickness, and a hole of

approximately 100- $\mu\text{m}$  in diameter in the gasket center was made using a laser cutting system installed at GSECARS. This served as the sample chamber for loading of amorphous  $\text{GeO}_2$  powder. Pressures were determined using the pressure-dependent fluorescence of small ruby balls which were scattered oppositely at the corner of sample chamber. The DAC position was placed on the rotation center of the diffractometer prior to spectral collection so as guarantee that the X-rays pass through the same sample area at each diamond cell orientation with respect to the incident X-ray beam. This is necessary to avoid sample inhomogeneities and thickness effects due to lack of parallelism or deformation of diamond anvils at high pressure [14] [25].

XAFS spectra were collected by scanning the monochromator energy from 10,953 to 11,747 eV at 5 eV steps before the main edge, 0.5 eV steps from -10 eV to 25 eV across the main edge (11,103 eV), and 0.05  $\text{\AA}^{-1}$  steps in photoelectron wave number above the main edge to 13  $\text{\AA}^{-1}$  in  $k$ -space. Each XAFS spectrum consists of 310 data points, and the signals from the ion chambers were typically recorded for 1 s before and across the main edge while a  $k$ -weighted collecting time was applied above the main edge at each energy point. It took about 7 minutes to collect an XAFS scan at each specific DAC orientation relative to the incident X-ray beam covering an angular range of  $\pm 3^\circ$ . Seven scans, which were collected at an angle step of  $1^\circ$ , have 2,170 data points. In total, it took about one hour to complete all 7 spectra at each pressure step. Other details regarding sample preparation and XAFS experiments can be found in Ref. [10], and will not be duplicated here.

To identify and remove the DAC-imposed glitches in the raw absorption spectra, an iterative method, which is described in detail in Ref. [10], was employed. Further XAFS data processing and analysis were then performed with the ATHENA and ARTEMIS programs [26] of the IFEFFIT package [27]. Theoretical models for the XAFS were constructed with FEFF (Refs.[28] and [29]) by using crystallographic atomic positions of  $\text{GeO}_2$ . The models were fitted to the data by using ARTEMIS [26] which was also used for error analysis and calculated goodness-of-fit parameters.

### 3. Results and discussion

Figure 1 shows the multiple datasets of transmission Ge K-edge XAFS for  $\text{GeO}_2$  glass at 64 GPa with the diamond anvil cell at different angle settings of  $0^\circ$ ,  $\pm 1^\circ$ ,  $\pm 2^\circ$ ,  $\pm 3^\circ$  with respect to the incident beam. All these spectra were overlapped and aligned using the iterative algorithm [10] for the elimination of glitches. The overlap is excellent for all of the spectra with glitches removed, and after three iterations, the standard deviation of seven independent spectra to the average one is as low as 0.1% in the whole spectra.

It has been pointed out that high data redundancy of DAC orientations to the X-ray beam would significantly improve the data quality of the final composite XAFS spectra [10]. Usually a measurement of seven DAC orientations respective to the incident X-ray beam should be sufficient to get a smooth composite spectrum (bottom curve, Figure 1) suitable for further data analysis and modeling. It should be mentioned that each composite point is typically based on at least three independent XAFS scans, as shown in Figure 1.

It can be noted that the composite data shows a clear drop starting at 11,562 eV, which coincides with the L3-edge energy of platinum (11,564 eV). This is due to the platinum layer employed to coat the upstream vertical focusing mirror at sector13-BM-D of the APS. An alternative coating material on the mirror would eliminate such an artefact in Ge  $k$ -edge XAFS. The coating material of focusing mirrors should be considered for a dedicated high-pressure XAFS beamline for geosciences in the future. To allow reliable data extraction of  $\mu(E)$ , the extent of the energy range is then limited below 11,560 eV.

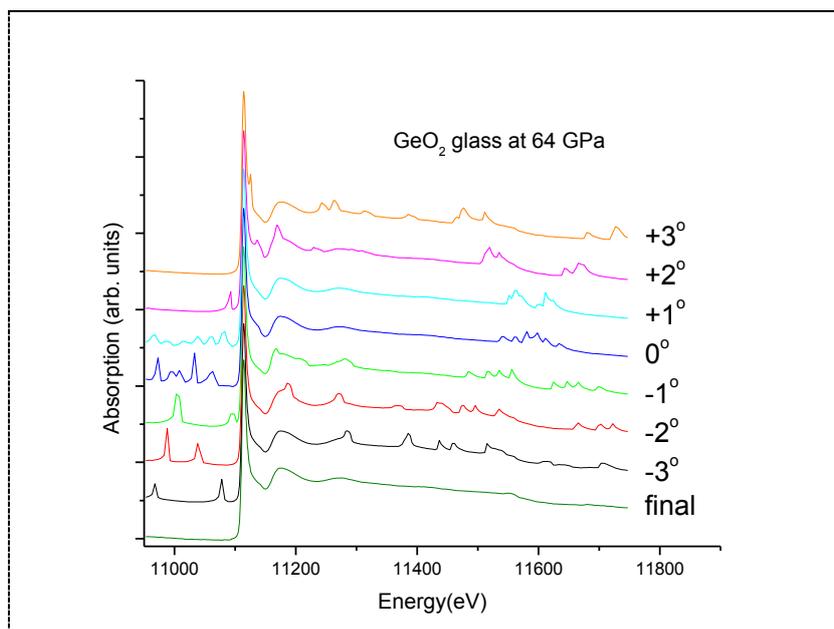


Figure 1. Ge K-edge XAFS of  $\text{GeO}_2$  glass at 64 GPa obtained by classic energy-scan transmission mode across the diamond anvils (300  $\mu\text{m}$  culet) at different angle settings. The X-ray absorption spectrum shows extra peaks due to Bragg diffraction by the single-crystal diamond anvils. The bottom curve shows the spectrum obtained after application of the glitch removal algorithm.

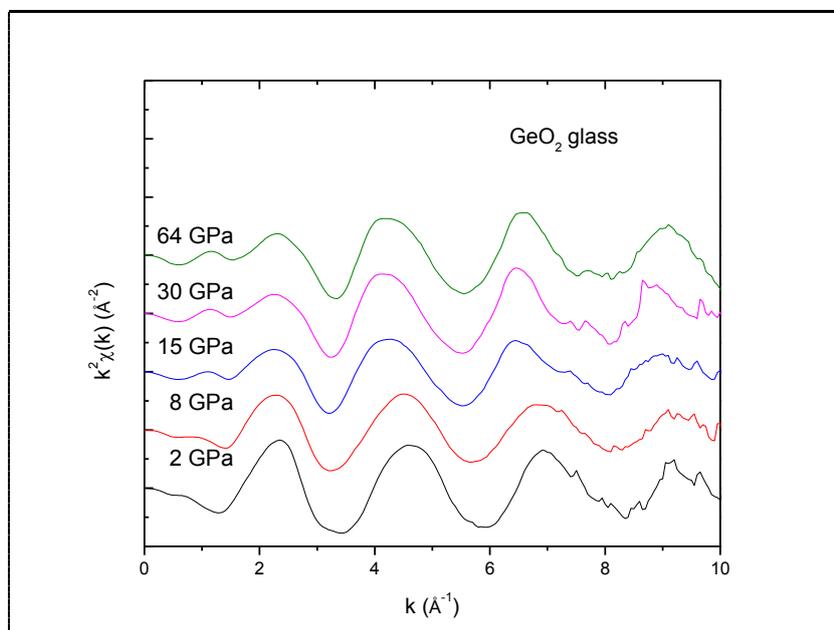


Figure 2. The  $k^2$ -weighted  $\chi(k)$  plots of  $\text{GeO}_2$  glass under pressure. Due to the  $L_3$  edge of Pt (11,564 eV) coating layer in the focusing mirror, all data are limited to 11,560 eV.

The  $k^2$ -weighted  $\chi(k)$  plots of  $\text{GeO}_2$  glass under high pressures are shown in Figure 2. As pressure increases, the EXAFS oscillations shift to lower  $k$  values, which mean some elongation of local bond

lengths as a result of coordination change in the glass. However, it appears that these oscillations shift to higher  $k$  values at pressures above 15 GPa. In other words, the material exhibits the normal reduction of bond length with compression above 15 GPa. It can be noticed that the most remarkable change in EXAFS oscillations occurs in the  $k$  range between 6-8.5  $\text{\AA}^{-1}$ . Considering the margin effect of the forward Fourier transformation window, the extent of EXAFS oscillations should be above 9.5  $\text{\AA}^{-1}$ , otherwise the limited data range will impair the reliability of further structure modeling. The independent points are 3, 4 and 6, for the  $k$  maximum values of 7, 8, and 10  $\text{\AA}^{-1}$ , respectively, suggesting the importance of wide  $k$  space coverage for a reliable structure modeling even for a simple first shell analysis. The good data quality shown in Figure 2 illustrates the validity of the iterative algorithm [10].

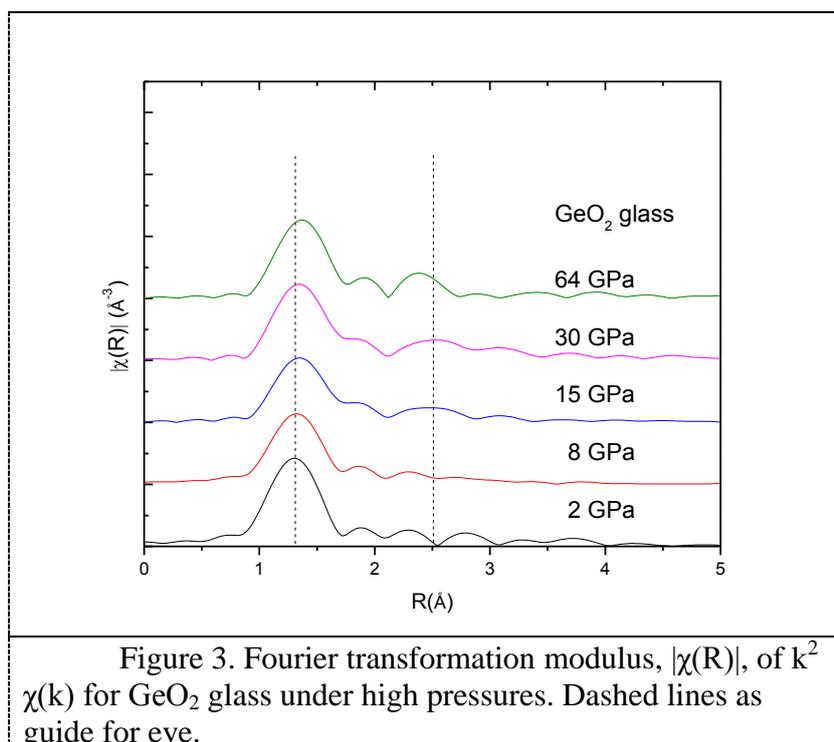
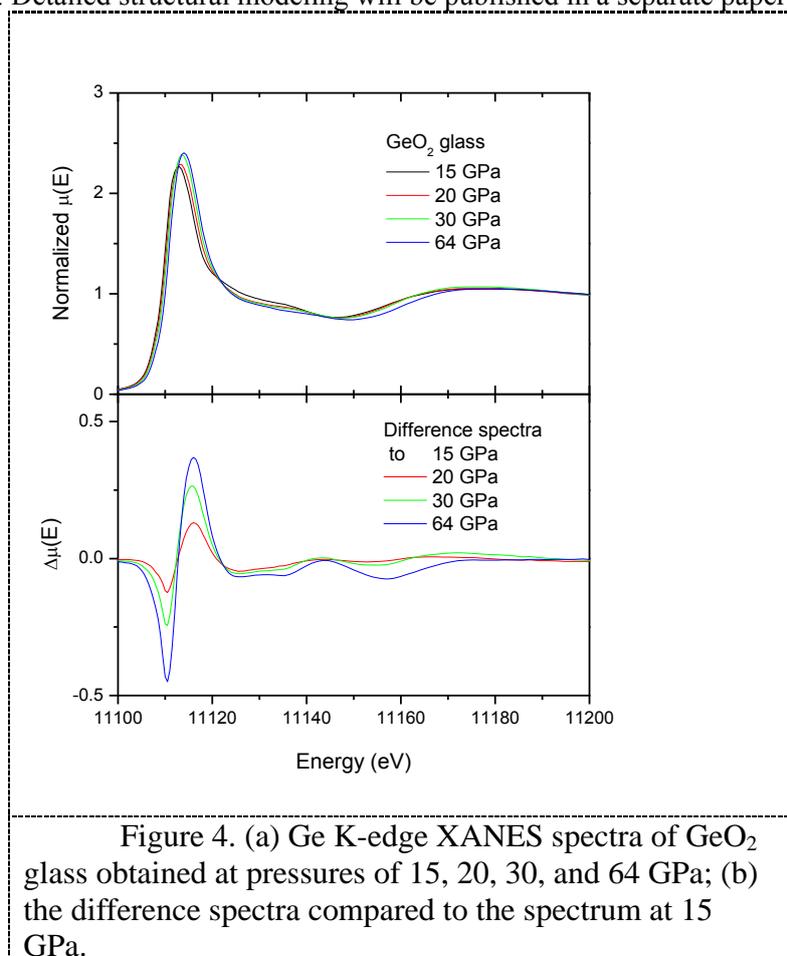


Figure 3 shows the Fourier transformation modulus,  $|\chi(R)|$ , of the  $k^2 \chi(k)$  plots that are exhibited in Figure 2. While a slightly progressive elongation in the Ge-O bond length at 1.3  $\text{\AA}$  is observed, a more evident change occurs in the range of 2.3-3.0  $\text{\AA}$ , where the intermediate range order (IRO) or interchain bonds are located, as observed by a recent EXAFS study of  $\text{GeO}_2$  glass to 44 GPa [20]. Of interest is that the overall spectrum at 30 GPa is quite similar to that at 15 GPa, suggesting that the transition from tetrahedral to octahedral coordination of Ge atoms should be essentially completed before 15 GPa, rather than the previous estimation of as high as 30 GPa [20]. The smaller  $k$  range ( $<8 \text{\AA}^{-1}$ ) in the previous work [20] might be the source of the difference [29]. Nevertheless, the IRO region of 64 GPa data shows a considerable enhancement in comparison with those of 30 and 15 GPa, suggesting a sign of possible new polyamorphsim.

To crosscheck the possible amorphous-amorphous transition at pressures above 15 GPa in  $\text{GeO}_2$  glass, it is necessary to inspect if there exists any significant evidence in the XANES spectra, as XANES is sensitive to the valence state and local symmetries around the Ge atom. Figure 4(a) shows the Ge K-edge XANES spectra of  $\text{GeO}_2$  glass at pressures of 15, 20, 30, and 64 GPa, and Figure 4b is the difference spectra compared to the spectrum at 15 GPa. The XANES spectra of  $\text{GeO}_2$  glass at 20 and 30 GPa looks quite similar except for the height of the white line. Little change above the edge is

observed. As shown in Figure 4b, a strong peak appears at  $E = 11,116$  eV, and there is a dramatic change in oscillation for the spectrum of 64 GPa, confirming the EXAFS observation as discussed above, i.e. the possible existence of a new polymorph, which was first reported in a previous paper from an independent high-pressure XAFS measurement [10]. This provides clear evidence that at pressure above 15 GPa the octahedral form in  $\text{GeO}_2$  glass would change to a more compact arrangement of atoms, i.e. the so-called “post-octahedral transition” as noted in X-ray diffraction experiments [13]. Detailed structural modeling will be published in a separate paper.



In summary, we have shown that the serious problem caused by the interference of diamond Bragg peaks can be effectively addressed based on repeated measurements over a small angular range of DAC orientation relative to the x-ray beam. Using the developed iterative method [10], we can eliminate these DAC imposed glitches effectively. We have demonstrated that ‘reflection-free’ high-quality XAFS spectra can be achieved at high pressure up to 64 GPa using the diamond anvil cell for  $\text{GeO}_2$  glass. The obtained results provide insight into the structural polymorphism of  $\text{GeO}_2$  glass at high pressure. With the advent of sub-micron focused x-ray beams at synchrotron facilities, there would be no upper limit in pressure for the proposed iterative method in XAFS data reduction.

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