# Structural changes of quartz-type crystalline and vitreous GeO₂ under pressure

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Using a large volume high pressure apparatus, quartz-type crystalline $GeO_2$ and $Li_2O$-$4GeO_2$ glass have been compressed up to 14 GPa at room temperature and their local structural changes have been investigated by an in-situ XAFS method. In quartz-type crystalline $GeO_2$, the change of the coordination number from 4 to 6 begins above 8 GPa and finishes below 12 GPa. On decompression, reversal transition begins below 8 GPa and there is a large hysteresis. Almost no sixfold coordination of Ge is preserved after releasing pressure. Change of coordination number in vitreous $Li_2O$-$4GeO_2$ begins above 6 GPa and is completed below 10 GPa. Reversal transition begins below 10 GPa and the hysteresis is smaller than that of quartz-type $GeO_2$. Change of coordination number in vitreous $Li_2O$-$4GeO_2$ is also reversal.

**Keywords: quartz-type GeO2, alkali germanate glass, high pressure, coordination change, XAFS**

## 1. Introduction

The high-pressure behaviour of quartz-type crystalline $GeO_2$ (q-$GeO_2$) has been investigated by a large variety of experimental techniques including x-ray diffraction, x-ray absorption, Brillouin scattering and infrared and Raman spectroscopy. By the compression of 6-10 GPa at temperatures low enough to inhibit the crystallization of high pressure thermodynamically stable phases, a transition which accompanies the coordination number (CN) change of Ge from 4 to 6 has been found to occur (Itie et al., 1989). The high-pressure phase is reported to be amorphous, pressure induced amorphous, in several studies (Madon et al., 1991; Durben & Wolf, 1991; Wolf et al., 1992; Yamanaka et al., 1992; Kawasaki et al., 1994), while others indicate that the phase is crystalline (Vannereau et al., 1991; Haines et al., 2000). The sixfold coordination of Ge is reported to be partly (Itie et al., 1989; Wolf et al., 1992; Yamanaka et al., 1992) or completely (Haines et al., 2000) preserved after releasing pressure. Quenchability of sixfold coordination of Ge has been explained by the fact that rutile-type $GeO_2$ consisting of $GeO_6$ octahedra is essentially the stable phase at ambient condition. Pressure-induced CN change has also been observed in vitreous $GeO_2$ at 6-10 GPa, however, this CN change is reported to be reversible (Itie et al., 1989; Smith et al., 1995). Alkali germanate glasses prepared at ambient conditions contain a maximum of about 20% of the sixfold coordination of Ge over the composition range of 10-30 mol% alkali oxide (Verweij & Buster, 1979; Sakka & Kamiya, 1982). These phenomena are known as germanate anomaly. In this study, we have compressed q-$GeO_2$ and $Li_2O$-$4GeO_2$ (20 mol% $Li_2O$) glass (g-$GeO_2$) up to 14GPa at room temperature and observed the local structural change by an in-situ

XAFS method in order to investigate the nature of pressure induced transition accompanying CN change.

## 2. Experimental and analysis

g-$GeO_2$ was prepared by melting reagent grade $Li_2CO_3$ and q-$GeO_2$ at 1473K in a platinum crucible. q-$GeO_2$ and g-$GeO_2$ were well-ground, mixed with amorphous B, and then put in a high pressure cell made of B and epoxy resin. Au foil that works as a pressure marker was also charged in the cell separately. A cubic-type multi anvil press, SMAP 180, (Utsumi et al., 1998) installed on a bending magnet beam line, BL14B1, at the SPring-8 was used for compression. X-ray beam was monochromatized using Si(111) reflection. The beam was focused vertically by two mirrors. The incident x-ray beam size was 0.2 mm in a vertical direction and 0.3 mm in a horizontal direction. X-ray absorption spectra near Ge *K*-edge and Au *L*-edge were measured. A gas mixture in the ion chamber detector was employed for optimum signal-to-noise ratio. Generated pressure was estimated using Au-Au distances determined by Au *L*-edge EXAFS based on the equation of state of Au (Jamieson et al., 1982). All the measurements were performed at room temperature.

The EXAFS interference function was extracted from the measured x-ray absorption spectra using the standard procedure (Maeda, 1987) and normalized using MacMaster coefficients (Lytle et al., 1989). For further quantitative analyses, the distance ranges of interest were filtered with a smooth filtering window, and transformed back to k-space. We carried out a non-linear least-square fitting method by comparing Fourier-filtered observed and calculated EXAFS interference functions (Ishii, 1992). Details on the EXAFS data analysis have been given elsewhere (Yoshiasa et al., 1999).

## 3. Results and discussion

Table 1 summarizes the Ge-O bond distances and Debye-Waller factors ($\sigma^2$) for q-$GeO_2$ and g-$GeO_2$ obtained at various pressures. Figures in the parentheses indicate the experimental errors, which are estimated from statistical fitting errors according to the EXAFS workshop report (Lytle et al., 1989).

Figure 1 shows the variation of Ge-O distances of both q-$GeO_2$ and g-$GeO_2$ by compression and decompression. By the compression of q-$GeO_2$, Ge-O distance gradually becomes short

**Table 1**

Pressure dependence of the Ge-O distances, $R_{Ge-O}$, and Debye-Waller factors, $\sigma^2$, at 300K.

| | q-GeO2 | | g-GeO2 | |
|---|---|---|---|---|
| P(GPa) | $R_{Ge-O}$ (A) | $\sigma^2$ (A²) | $R_{Ge-O}$ (A) | $\sigma^2$ (A²) |
| 0.0 compression | 1.749(1) | 0.0034(1) | 1.795(37) | 0.0069(3) |
| 2.0 | 1.742(2) | 0.0036(1) | 1.787(13) | 0.0069(2) |
| 4.0 | 1.738(2) | 0.0041(1) | 1.776(16) | 0.0068(2) |
| 6.0 | 1.731(2) | 0.0038(1) | 1.772(15) | 0.0061(2) |
| 8.0 | 1.727(2) | 0.0042(1) | 1.791(17) | 0.0070(2) |
| 10.0 | 1.778(3) | 0.0069(2) | 1.848(38) | 0.0082(2) |
| 12.0 | 1.856(3) | 0.0078(2) | 1.841(14) | 0.0097(2) |
| 14.0 | 1.846(2) | 0.0079(3) | 1.841(51) | 0.0095(4) |
| decompression | | | | |
| 8.5 | 1.860(2) | 0.0075(3) | | |
| 5.8 | 1.845(2) | 0.0075(2) | 1.812(43) | 0.0081(3) |
| 1.5 | 1.815(4) | 0.0077(3) | 1.792(22) | 0.0076(3) |
| 0.0 | 1.782(2) | 0.0075(2) | 1.788(18) | 0.0074(3) |

below 8 GPa indicating the conventional compression of quartz-type crystalline structure. Abrupt increase in Ge-O distance that corresponds to the CN change occurs between 8 and 12 GPa. When the Ge-O distances obtained at 12 and 14 GPa are extrapolated to ambient pressure, they show fairly good agreement with that in rutile structure. Accordingly, the CN change is regarded to be completed below 12 GPa. By decompression, reversal transition occurs gradually below 6 GPa and sixfold coordination seems to be partly maintained to low-pressure range. At the complete release of pressure, the Ge-O distance is 1.78 Å which is larger than that in the initial q-GeO$_2$ and almost the same as that reported for q-GeO$_2$ recovered from 30 GPa (Itie et al., 1989). Itie et at. (1989) insist that the sixfold coordination be partly quenched in the recovered sample. The quenchability of sixfold coordination is discussed later considering the present results of XANES spectra.

In the case of g-GeO$_2$, CN change begins above 6 GPa and finishes below 10 GPa, which is lower than that in q-GeO$_2$ by about 2 GPa. Reversal CN change occurs below 10 GPa and the hysteresis is much smaller than that of q-GeO$_2$. At the complete release of pressure, the Ge-O distance is 1.79 Å which is almost the same as that of starting g-GeO$_2$. Stolper & Ahrens (1987) proposed a displacive mechanism for the continuous transition of tetrahedral SiO$_4$ to octahedral SiO$_6$ in SiO$_2$ glass under pressure. As the present g-GeO$_2$ originally involves a portion of sixfold coordination, we expected a continuous CN change would proceed by compression. However, the Ge-O bond is, in fact, gradually shortened below 6 GPa and then elongated within a relatively narrow pressure range. Present results indicate that the compression of GeO$_4$ tetrahedron is energetically less costly than CN change even when the nuclei of GeO$_6$ octahedron already coexists.

et al., 1999) but smaller than that of g-GeO$_2$ in the same pressure range. This result indicates that the local structure around Ge atoms of the high-pressure phase is more random than rutile phase but less random thang-GeO$_2$ with sixfold Ge. From present results, accordingly, we cannot affirm whether the high-pressure phase is amorphous or crystalline. Because present CN change occurs at low temperatures where thermally activated diffusion process is restrained, it is likely that the transition takes place by a kind of martensitic mechanism. Consequently, we propose that the high-pressure phase consists of very fine crystalline domain with a lot of defects. The relatively large value of σ$^2$ for the phase indicates its poor crystallization caused by defects heavily introduced by a martensitic transition. The crystallite size is thought to vary depending on experimental conditions; samples and ways of compression. When the crystallite size is too small for x-ray diffraction, the transition is observed as pressure induced amorphization (Madon et al., 1991; Durben & Wolf, 1991; Wolf et al., 1992; Yamanaka et al., 1992; Kawasaki et al., 1994), while broad diffraction lines are recorded in other cases (Haines et al., 2000).
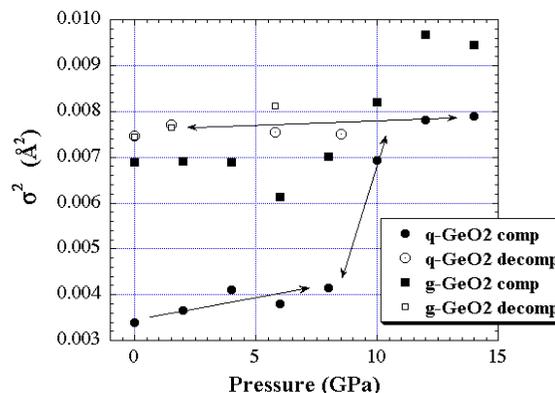


**Figure 2**
Variation of Debye-Waller factors, σ$^2$ of q-GeO$_2$ and g-GeO$_2$ by compression (filled symbols) and decompression (open symbols). Circles are q-GeO$_2$ and squares g-GeO$_2$. Solid lines are only a guide for the eye.

XANES spectra are quite sensitive to the electronic states and three-dimensional atomic configuration around x-ray absorbing atoms. Accordingly, they are useful for distinguishing between fourfold and sixfold coordination. The XANES spectra of q-GeO$_2$ and g-GeO$_2$ recorded at various conditions are shown in Fig. 3 together with those of rutile-type GeO$_2$ and pure GeO$_2$ glass for comparison. Characteristics in the XANES spectra of sixfold coordination of Ge is that the near-edge spectra show discernible two shoulders, which are indicated by arrows in Fig. 3, at both lower- and higher-energy sides of the most intense peak. q-GeO$_2$ under 14 GPa shows the shoulders, however, after releasing pressure, the shoulders disappear. The Ge-O distance of q-GeO$_2$ recovered from 14 GPa is 1.78 Å which is larger than 1.75 Å the initial q-GeO$_2$. There are two possible interpretations for the elongated Ge-O distance; one is that the observed distance is an average of coexisting fourfold and sixfold coordination (Itie et al., 1989), the other is that fourfold coordination is dominant and Ge-O distance is elongated by random glassy state. Because XANES spectra shows the characteristics of fourfold coordination, we conclude that almost complete reversal transition occurs in the present q-GeO$_2$ sample. The sixfold



**Figure 1**
Variation of Ge-O distance of quartz-type q-GeO$_2$ and g-GeO$_2$ by compression (filled symbols) and decompression (open symbols). Circles are q-GeO$_2$ and squares g-GeO$_2$. Solid lines are only a guide for the eye.

Figure 2 shows the variation of σ$^2$ of q-GeO$_2$ and g-GeO$_2$. The initial value of g-GeO$_2$ is larger than that of q-GeO$_2$ reflecting its glassy state. By compression, both the σ$^2$ of q- and g-GeO$_2$ remarkably increase corresponding to their CN change. Through decompression, once increased σ$^2$ of q-GeO$_2$ remains almost the same values, while reversal change in g-GeO$_2$ occurs below 10 GPa with a hysteresis. There are several arguments whether the high pressure phase transformed from q-GeO$_2$ is amorphous or crystalline. Present σ$^2$ of 0.008 Å$^2$ for q-GeO$_2$ above 10 GPa is considerably larger than 0.004 Å$^2$ in rutile-type GeO$_2$ (Yoshiasa

coordination of Ge has been reported to be partly (Itie et al., 1989) or fully (Haines et al., 2000) preserved after releasing pressure. These different results are due to the fact that all the phenomena studied occur under metastable conditions. The quenchability of sixfold coordination is highly sensitive to the origin and nature of samples as well as to the experimental conditions; hydrostaticity, duration of high pressure treatment, decompression rate and so on.

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**Figure 3**
Experimental Ge *K*-edge XANES spectra of various $GeO_2$ samples.

In the case of g-$GeO_2$, the spectra of starting glass already have a slight trace of the shoulders, which indicate the germanate anomaly. At 14 GPa, the spectra have characteristics of sixfold coordination of Ge. The spectra of g-$GeO_2$ retrieved from high pressure are similar to those of starting glass. Considering the results of XANES spectra and observed Ge-O distances, coordination change in g-$GeO_2$ is concluded to be reversible.

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