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# XAFS study of GeO$_2$ glass under pressure

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**Abstract**
Using a large-volume high-pressure apparatus, Li$_2$O–4GeO$_2$ glass and pure
GeO$_2$ gel have been compressed to 14 GPa at room temperature and their local
structural changes have been investigated by an *in situ* XAFS (x-ray absorp-
tion fine-structure) method. On compression of Li$_2$O–4GeO$_2$ glass, the Ge–O
distance gradually becomes short below 7 GPa, showing the conventional com-
pression of the GeO$_4$ tetrahedron. Abrupt increase in the Ge–O distance occurs
between 8 and 10 GPa, which corresponds to the coordination number (CN)
changing from 4 to 6. The CN change is completed at 10 GPa. On decompres-
sion, the reverse transition occurs gradually below 10 GPa. In contrast to the
case for Li$_2$O–4GeO$_2$ glass, the Ge–O distance in GeO$_2$ gel gradually increases
over a pressure range from 2 to 12 GPa, indicating that continuous change in CN
occurs. The Ge–O distance at 12 GPa is shorter than that of Li–4GeO$_2$ indicat-
ing that the change in CN is not completed even at this pressure. On complete
release of pressure, the Ge–O distance reverts to that of the starting gel.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Like those of crystalline phases, it has been proposed that structures of liquid phases change
with pressure. However, the number of high-pressure *in situ* studies on this phenomenon is
still very small because of the experimental difficulties. Structural and physical properties of
silicate melts are very important for the fundamental understanding of magmatic processes. At
high pressure and temperature, coordination number (CN) changes of Si in silicate melts will
occur and probably result in drastic change in physical properties such as viscosity. However,
the structural mechanisms are still unclear. Germanates are structural analogues of silicates.
Since they show phase transitions at lower pressure than silicates, they can be used as model
compounds which are more accessible to high-pressure experiments. Ge can be conveniently
studied with an XAFS method, while the Si K edge occurs in the soft x-ray region which makes
it impossible to perform XAFS observations with a high-pressure apparatus.

Since the vitreous state is expected to be related to the high-temperature liquid state, several structural studies of vitreous GeO$_2$ under pressure have been performed [1–3]. By using a diamond anvil cell and the XAFS technique, Itie *et al* [1] were the first to report that pressure-induced CN change in vitreous GeO$_2$ occurs at 6–10 GPa and that the CN change is reversible. Since GeO$_2$ gel is thought to have less medium-range order than GeO$_2$ glass, it seems to be more closely related to the liquid phase than GeO$_2$ glass. Accordingly, it is of great importance to investigate the compression behaviour of GeO$_2$ gel for the understanding of the liquid state under pressure. 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 [4]. These phenomena are known as the germanate anomaly. It is interesting to examine the compression behaviour of alkali germanate glasses which originally involve a proportion of sixfold coordination. In this study, we have compressed GeO$_2$ gel (gel-GeO$_2$) and Li$_2$O–4GeO$_2$ glass (Li-GeO$_2$) to 14 GPa at room temperature and investigated the local structure change by an *in situ* XAFS method.
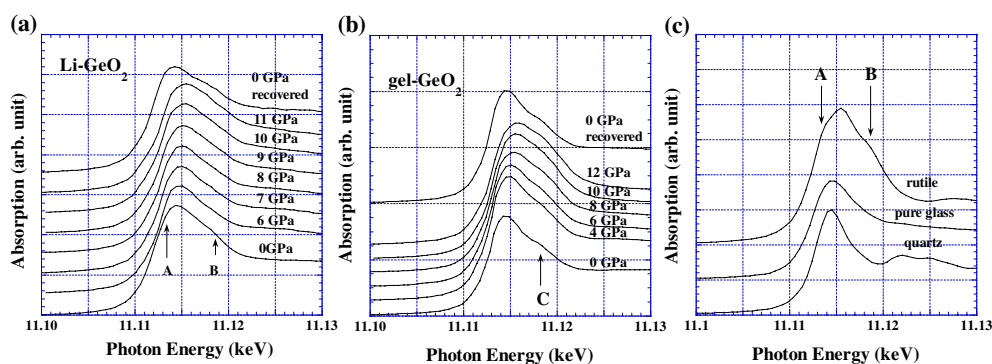
## 2. Experiments

Gel-GeO$_2$ was prepared by the hydrolysis of GeCl$_4$. Li-GeO$_2$ was synthesized by melting reagent grade Li$_2$CO$_3$ and quartz-GeO$_2$ at 1473 K in a platinum crucible. Gel-GeO$_2$ and Li-GeO$_2$ were mixed with amorphous boron, and then put in a high-pressure cell made of boron and epoxy resin. Au foil which works as a pressure marker was also charged in the cell separately. A cubic-type multi-anvil press, SMAP 180 [5], installed on a bending magnet beamline, BL14B1, at SPring-8 was used. We used sintered diamond anvils with 3 mm truncation for single-stage compression. The x-ray beam was monochromatized using the Si(111) reflection. The beam was focused vertically by two mirrors. The incident x-ray beam size was 0.2 mm in the vertical direction and 0.3 mm in the horizontal direction. X-ray absorption spectra near the Ge K edge and Au L edge were measured. A gas mixture in the ion chamber detector was employed to achieve optimum signal-to-noise ratio. The pressure generated was estimated using Au–Au distances determined from Au L-edge EXAFS on the basis of the equation of state of Au [6]. All the measurements were performed at room temperature. Details of the EXAFS data analysis have been given elsewhere [7].

## 3. Results and discussion

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 Li-GeO$_2$ and gel-GeO$_2$ recorded at various pressures are shown in figures 1(a) and (b), respectively, while those of rutile-type GeO$_2$, quartz-type GeO$_2$, and pure GeO$_2$ glass are shown in figure 1(c) for comparison. As clearly shown in the spectra of the rutile structure in figure 1(c), the characteristic of sixfold coordination of Ge is that the near-edge spectra show discernibly two shoulders, which are indicated by arrows A and B in the figures, on both the lower- and higher-energy sides of the most intense peak.

Li-GeO$_2$ at 0 GPa already has a slight trace of these two shoulders, indicating the germanate anomaly. On compression, the main peak gradually shifts to higher energies up to 6 GPa and a large peak shift is observed between 6 and 10 GPa. The shoulders for Li-GeO$_2$ become remarkable above 10 GPa, corresponding to the pressure-induced CN change. The spectra of Li-GeO$_2$ retrieved from high pressure are similar to those of the starting material, indicating that the pressure-induced CN change is reversible. Gel-GeO$_2$ and pure GeO$_2$ glass have similar local structures, i.e., corner-sharing tetrahedra and a broad distribution of Ge–O–Ge angles

**Figure 1.** Experimental Ge K-edge XANES spectra of Li-GeO$_2$ (a) and gel-GeO$_2$ (b) at various pressures; (c) shows XANES spectra of rutile, pure glass, and quartz GeO$_2$. The arrows indicate the peaks A, B, and C as discussed in the text.
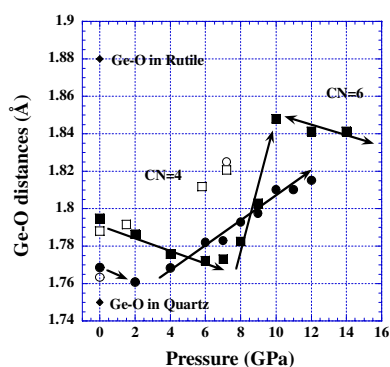


**Figure 2.** Variation of the Ge–O distance in Li-GeO$_2$ (squares) and gel-GeO$_2$ (circles) on compression (closed symbols) and decompression (open symbols). Solid lines are only a guide for the eye.

corresponding to the absence of long-range ordering. Accordingly, the XANES of gel-GeO$_2$ at 0 GPa resembles that of pure GeO$_2$ glass. However, gel-GeO$_2$ shows a small peak marked as C that pure GeO$_2$ glass does not have. Peak C is presumably due to the presence of OH$^-$ or short-range disordering, such as a fraction of fivefold coordination in gel-GeO$_2$. On compression of gel-GeO$_2$, the most intense peak shifts to higher energies and the two shoulders, A and B, become clear, indicating that the fraction of sixfold coordination is increased.

Figure 2 shows the variation of the Ge–O distances of gel-GeO$_2$ and Li-GeO$_2$ on compression and decompression. At ambient pressure, the Ge–O distance in Li-GeO$_2$ is 1.795 Å and clearly larger than that in quartz-type crystalline GeO$_2$ (1.75 Å). This result is explained by the combination of the loose structure of glass and a coexisting proportion of sixfold coordination introduced as the germanate anomaly. On compression of Li-GeO$_2$, the Ge–O bond is gradually shortened below 7 GPa indicating the compression of the GeO$_4$ tetrahedron. The Ge–O bond is then elongated between 7 and 10 GPa, which corresponds to the CN change. When the Ge–O distances obtained above 10 GPa are extrapolated to ambient pressure, they show fairly good agreement with that in rutile structure. Accordingly, it is concluded that the CN change is completed at 10 GPa. It should be noted that CN change in Li-GeO$_2$ occurs within a relatively narrow pressure range. Since the pressure-transmitting medium was amorphous solid boron and no annealing was carried out to reduce deviatoric stress, the pressure in the sample chamber is estimated to be 1–2 GPa which is comparable with the range of transition pressures. Itie *et al* [1] showed that the CN change occurs between 6.6 and 8.0 GPa for pure GeO$_2$ glass. Though the present Li-GeO$_2$ glass originally involved a proportion

of sixfold coordination as the germanate anomaly, a continuous CN change does not proceed by compression but abrupt CN change occurs within a narrow pressure range similar to that for pure $GeO_2$ glass. The present results indicate that the compression of the $GeO_4$ tetrahedron in the glass structure is energetically less costly up to about 7 GPa at room temperature than CN change even when the nucleus of the $GeO_6$ octahedron already coexists. On decompression, reversal of the CN change occurs below 10 GPa and there is hysteresis. On complete release of pressure, the Ge–O distance is 1.79 Å which is almost the same as that of the starting glass.

At room pressure, the Ge–O distance in gel-$GeO_2$ is 1.77 Å and slightly larger than that in quartz-type crystalline $GeO_2$. On compression of gel-$GeO_2$, the Ge–O distance increases almost linearly in the pressure range from 2 to 12 GPa. However, the value at 12 GPa is smaller than that of Li-$GeO_2$, which indicates that the CN change is not completed. The linear extrapolation of the Ge–O distances to higher pressures intersects the compression curve of sixfold coordination at around 15 GPa. On complete release of pressure, the Ge–O distance becomes 1.77 Å which is almost the same as that of the starting gel.

The present result for gel-$GeO_2$ differs remarkably from those for the present Li-$GeO_2$, $GeO_2$ glass [1], and quartz-type crystalline $GeO_2$ [1, 3] in which CN changes occur in a narrow pressure range and are completed below 10 GPa. Though the exact structure of gel-$GeO_2$ has not been well understood, it is thought that gel-$GeO_2$ consists of small clusters in which $GeO_4$ tetrahedra make up a corner-sharing network like in $GeO_2$ glass. The difference between gel and glass is in the dimension of the network—that is, gel has a much smaller network than glass. When such a small cluster is compressed, it has flexibility for deformation. Consequently, CN change occurs gradually. Since gel-$GeO_2$ seems to be closely related to the liquid phase, the present results imply that gradual CN change occurs in liquid $GeO_2$ under pressure.

## 4. Conclusions

Li-$GeO_2$ and gel-$GeO_2$ have been compressed to 14 GPa at room temperature and their local structural changes have been investigated by an *in situ* XAFS method. The nearest Ge–O distance in Li-$GeO_2$ shows three stages of compression behaviour: the conventional compression of the $GeO_4$ tetrahedron below 7 GPa, the compression of the $GeO_6$ octahedron above 10 GPa, and the transition zone between 7 and 10 GPa. On decompression, the reverse transition occurs gradually below 10 GPa. In contrast to the case for Li-$GeO_2$, the Ge–O distance in gel-$GeO_2$ begins to increase linearly above 2 GPa, indicating that CN change occurs continuously. The CN change is not completed even at 12 GPa. On complete release of pressure, the Ge–O distance reverts to that of the starting gel.

## Acknowledgments

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