

Pressure-Induced Sharp Coordination Change in Liquid Germanate

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Local structures around germanium in liquid germanate have been investigated by means of *in situ* x-ray absorption measurements up to 9 GPa at 1273 K. Liquid germanate consisting of tetrahedrally coordinated germanium contracts with increasing pressure without significant changes in the local structure up to 2.5 GPa and then shows an abrupt fourfold-to-sixfold coordination change around 3 GPa. The coordination change is completed below 4 GPa where upon a high-density liquid consisting of octahedrally coordinated germanium becomes stable. The GeO_6 octahedron in the high-density liquid is more compressible than that in solids.

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Crystalline solid can exist in different polymorphs with different structures and bonding patterns, whereas the idea of polymorphism in liquids was not considered seriously for a long time because of the view that liquids have rapidly changing structures that vary smoothly with temperature and pressure. The existence of liquid polymorphs is just beginning to be recognized. Growing evidence for liquid polymorphs has come from experimental and theoretical studies [1,2]. Recently a first-order liquid-liquid phase transition has been observed for phosphorus, that is, the structure of liquid phosphorus jumps suddenly from a relatively open molecular structure to a new polymeric form with higher density by increasing pressure [3]. Liquids with a locally tetrahedral molecular structure, such as Si, Ge, C, SiO_2 , and GeO_2 , have possibilities for observing pressure-induced polymorphism [1]. However, the direct structural studies have not been successful to date. Crystalline GeO_2 has two polymorphs, quartz-type structure with fourfold Ge and rutile-type with sixfold. The rutile-type phase is stable at ambient conditions. With increasing temperature at room pressure, it transforms to the quartz-type phase and then melts to form a network-structured liquid in which Ge ions are tetrahedrally coordinated. Since the rutile-type phase directly melts at pressures above 1 GPa [4], it is most plausible that liquid GeO_2 at pressures shows local structures different from that of the ambient pressure liquid. Liquid polymorphism of GeO_2 and germanate is also suggested from *in situ* glass studies under pressure; reversible fourfold-to-sixfold coordination changes have been observed around 9 GPa for pure GeO_2 and $\text{Li}_2\text{O}-4\text{GeO}_2$ glasses [5–7]. Kinetic effects are inextricably involved in the results of *in situ* glass studies because the structural changes in glass occur far from thermodynamical equilibrium conditions, whereas the kinetic effects are likely to be much less important in the high-temperature liquid state. Direct structural observations are hence essential for further understanding of pressure-induced structural changes in liquid. Structural

study of liquid GeO_2 under pressures is important not only because it is a prototype of network-forming liquids, but also because of geophysical reasons. In addition to an interest for the fundamental understanding of liquid polymorphism, our essential motivation for this work is to extract some implications for the evolution and dynamics of Earth's interior by the analogy of liquid GeO_2 to SiO_2 that is the main constituent of all geologically relevant liquids (magmas). Recent developments in synchrotron radiation technology and large-volume presses have made possible high-pressure and high-temperature x-ray absorption fine structure (XAFS) measurements [8]; XAFS is a powerful tool for the investigation of the local structure around the x-ray absorbing atom. Ge can be conveniently studied with XAFS, 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. The main experimental obstacles to studying liquid GeO_2 are the high melting temperature (e.g., 2000 K at 3 GPa) and the easy decomposition of GeO_2 into Ge and O [4]. Accordingly, we used an alkali germanate ($\text{Li}_2\text{O}-4\text{GeO}_2$ composition) instead of pure GeO_2 and an additive of B_2O_3 in order to lower the melting temperature and suppress the decomposition of GeO_2 . In this Letter, we report on the pressure-induced structural change of the liquid germanate.

High-pressure and high-temperature conditions for the *in situ* x-ray experiments were realized using a cubic-type multianvil press, SMAP180 [9], installed on a bending magnet beam line, BL14B1, at SPring-8. $\text{Li}_2\text{O}-4\text{GeO}_2$ glass synthesized by melting reagent grade Li_2CO_3 and quartz- GeO_2 was finely ground and mixed with B_2O_3 and BN powders (3 : 2 : 100 in weight ratio). BN was used to dilute the sample for XAFS measurements. The mixture was charged in a BN sample chamber. The sample chamber was put between a pair of LaCrO_3 disc heaters and encased in a cubic-shaped pressure-transmitting medium made of boron-epoxy resin. At low pressure conditions below 3 GPa, LaCrO_3 heaters were unstable and could not

be used. Accordingly, we used MoSi_2 heaters instead. The temperature was monitored by a W3%Re-W25%Re thermocouple attached to the BN sample chamber without correction for the pressure effect on the electromotive force. First, preliminary *in situ* x-ray diffraction measurements were carried out in energy dispersive mode. We thereby confirmed that the mixture of $\text{Li}_2\text{O}-4\text{GeO}_2$ and B_2O_3 melts completely without reacting with BN at 1273 K in the pressure range of interest. LaCrO_3 heaters generated oxidizing atmosphere and no decomposition of GeO_2 into Ge and O was observed. On the other hand, partial decomposition of GeO_2 was detected when MoSi_2 heaters were used. We also determined the relation between the press load and generated pressure at 1273 K using the lattice constant of Au put in the same high-pressure cell assemblage and the equation of state [10], because simultaneous pressure determination in XAFS measurements could not be carried out in this study. Second, *in situ* XAFS experiments were performed in transmission mode using a Si(111) double monochromator. 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. XAFS spectra near Ge *K* edge with an energy range of 1000 eV above the edge were successfully measured up to 9 GPa at 1273 K. In order to avoid the uncertainty in pressure determination caused by multiple heating and compression during an experiment, the data collection in each run was conducted only for one pressure condition by first compressing the sample to a given pressure, followed by increasing the temperature to 1273 K. After each measurement the sample was quenched and recovered to ambient conditions. The fluctuation of temperature during the XAFS measurements, which took about 30 min, was within 1.0%. The generated pressure was determined using the pressure-load calibration curve mentioned above, and the absolute error was estimated to be within 0.5 GPa.

The extended x-ray absorption fine structure (EXAFS) interference function was extracted from the measured x-ray absorption spectra using the standard procedure [11] and normalized using MacMaster coefficients [12]. Figure 1 shows the Fourier transform of Ge *K*-edge EXAFS spectra of liquid germanate recorded at 6 GPa and 1273 K in the *k* range from 4 to 10 \AA^{-1} . No phase-shift corrections are made at this stage of data analysis. When the same $\text{Li}_2\text{O}-4\text{GeO}_2$ glass was compressed at room temperature in our previous study [6], the second-neighbor Ge-Ge distance was clearly assigned. The present result of only one intense peak in Fig. 1 suggests that the sample was melting. For further quantitative analyses, the distance range of interest was filtered with a smooth filtering window, and transformed back to *k* space. We carried out a nonlinear least-square fitting method by comparing Fourier-filtered observed and calculated EXAFS interference functions [13]. Parameter

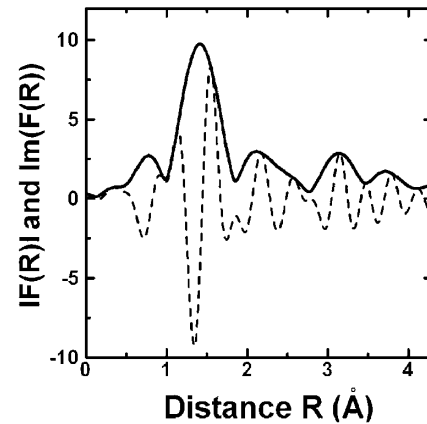


FIG. 1. Fourier transform of Ge *K*-edge EXAFS spectra of liquid germanate recorded at 6 GPa and 1273 K. No phase-shift corrections are made.

fitting was performed with an anharmonic potential model. The resulting well-fitted profile is shown in Fig. 2. Since the spectra measured below 3 GPa were composed of those of germanate and metallic Ge, the data were analyzed assuming the two phase mixture. Details on the EXAFS data analysis have been given elsewhere [14].

X-ray absorption near-edge structure (XANES) spectra are useful for distinguishing between fourfold and sixfold coordination because they are sensitive to the electronic states and three-dimensional atomic configuration around the x-ray absorbing atom. The XANES spectra of liquid germanate recorded at 4, 6, and 9 GPa and 1273 K are shown in Fig. 3 together with those of the rutile-type and quartz-type crystalline GeO_2 at ambient conditions [14]. As shown in the spectrum of the rutile-type structure, the characteristics of sixfold coordination of Ge is that the near-edge spectra show discernibly two shoulders, which are indicated by the two arrows

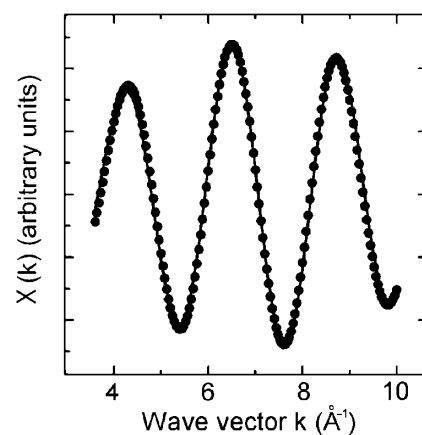


FIG. 2. Fourier-filtered EXAFS spectra (dotted curve) and least-square fits (solid curve) for the first-nearest neighbor of Ge in liquid germanate at 6 GPa and 1273 K.

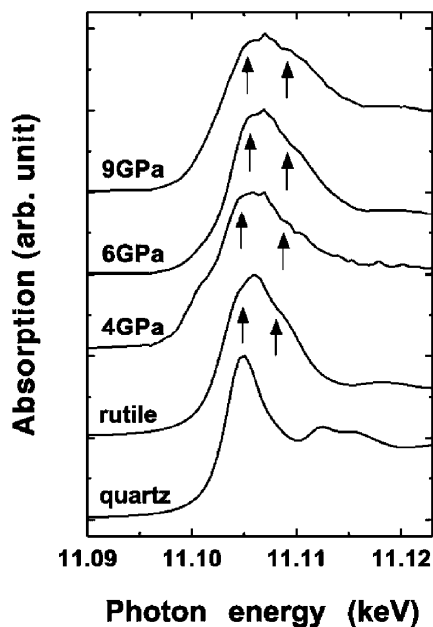


FIG. 3. Experimental Ge K edge XANES spectra of liquid germanate recorded at 4, 6, and 9 GPa and 1273 K together with those of the rutile- and the quartz-type crystalline GeO_2 at ambient conditions. The arrows indicate the shoulders as discussed in the text.

in the figure, on both the lower- and higher-energy sides of the most intense peak. The observed spectra of liquid germanate have the pronounced shoulders, indicating that the sixfold coordination is dominant.

Figure 4 shows the variation of the first-neighbor Ge-O distances in the present liquid germanate at various pressures and 1273 K as well as those in $\text{Li}_2\text{O}-4\text{GeO}_2$ glass on room temperature compression [6,7]. At ambient pressure, the Ge-O distance of the present liquid is about 1.82 Å, whose value is slightly larger than that of the $\text{Li}_2\text{O}-4\text{GeO}_2$ glass. The same tendency is reported for liquid $\text{Na}_2\text{O}-4\text{GeO}_2$ (1.81 Å at 1373 K) and its glass (1.80 Å at room temperature) [17]. The distance remains almost unchanged up to 2.5 GPa, indicating that the fourfold coordination is dominant. At 3 GPa, the distance increases abruptly, which indicates that components with higher coordination than fourfold are introduced. The distance shows a maximum at 4 GPa and then decreases monotonically with pressure. Because the observed distances between 4 and 9 GPa are comparable to those calculated for the rutile-type crystalline GeO_2 at 1273 K (solid line) and the XANES spectra of this pressure region as shown in Fig. 3 indicate the characteristics of sixfold coordination, we conclude that the transition to sixfold coordination is completed below 4 GPa and then a high-density polymorph of liquid germanate in which Ge is octahedrally coordinated is stabilized. The fourfold-sixfold coordination change occurs around 9 GPa for both pure GeO_2 glass [5] and $\text{Li}_2\text{O}-4\text{GeO}_2$ glass [6,7].

The higher transition pressure for these glasses is due to the kinetic limitations on glass structure.

It should be noted that the coordination change occurs in a narrow pressure range of less than 1 GPa, although the densification accompanied by the coordination change has long been assumed to proceed monotonically over a wide pressure range [18]. We cannot clarify whether this transition state is composed of the time-averaged mixture of fourfold and sixfold coordination or includes intermediate states such as the fivefold component suggested for some silicate glasses [19,20]. If the observed transition state is caused by a slight pressure and temperature gradient in the high-pressure cell, the transition can be a first-order type. By analogy with this liquid germanate, we expect that a sharp transition occurs in liquid silicates. Details of the geophysical implications derived from this study will be given elsewhere [21].

As shown in Fig. 4, anomalous compressibility of the GeO_6 octahedron in the present liquid (solid circles) is observed. The compressibility of the GeO_6 octahedron in $\text{Li}_2\text{O}-4\text{GeO}_2$ glass (open circles) is consistent with that in the rutile GeO_2 at room temperature (dashed line) [22], whereas the GeO_6 octahedron in the present liquid is more compressible than that in the crystal and glass. The Ge-O distances for the rutile GeO_2 at 1273 K (solid line) are calculated using a thermal expansion coefficient at ambient pressure, and consequently, the slope is considered as the shallowest limit since thermal expansion is

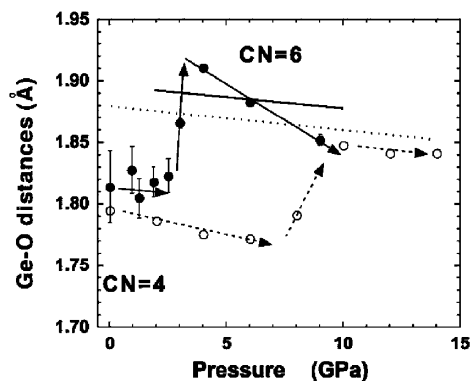


FIG. 4. Variation of the first-neighbor Ge-O distances in the present liquid germanate at 1273 K (solid circles) and $\text{Li}_2\text{O}-4\text{GeO}_2$ glass at room temperature (open circles). Errors for the distances are estimated from the statistical fitting errors. The relatively large errors in the low pressure region, where MoSi_2 heaters were used, are given rise to by the data analysis of the two-phase mixture due to the partial decomposition of GeO_2 . The arrows are only guides for the eye. CN indicates the coordination number. Averaged Ge-O distances (four short bonds and two long bonds in distorted GeO_6 octahedron) in the rutile-type crystalline GeO_2 at room temperature and 1273 K are shown by dashed and solid lines, respectively. The compression curves are calculated using room-temperature compression data [15] and a room-pressure thermal expansion coefficient [16].

suppressed with pressure. However, the thermal expansion itself is small (e.g., the linear expansion by 1% between room temperature and 1237 K at room pressure). The present result therefore indicates that the GeO_6 octahedron in the present liquid contracts and expands with pressure more easily than that in the crystalline rutile GeO_2 at the same temperature. This anomalous compression behavior of the GeO_6 octahedron is presumably due to the lack of long- and medium-range order in liquids. Although the bulk density of the present liquid is not known, the present result suggests the possibility that, given sufficient pressure, the liquid germanate becomes denser than the equivalent crystalline phase. Since the present liquid is composed of GeO_2 , Li_2O , and B_2O_3 , multicomponent effects, which are not yet clear, should be considered for further discussion on the transition mechanism and the compression behavior of the whole system.

The present study is consistent with the general argument that liquids having a locally tetrahedral molecular structure such as GeO_2 and SiO_2 are among the best candidates to exhibit a pressure-induced liquid-liquid transition. To our knowledge, this work is the first direct observation of high-density liquid consisting of octahedrally coordinated Ge. It is worthy of attention that the coordination change occurs in a narrow pressure range. The present result reveals that the transition can be a first-order type.

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[20] A possible method that meets this requirement is to examine whether the XANES spectra at the transition state can be reproduced by a weighted sum of the spectra of fourfold and sixfold Ge. However, we could not attempt this method, because the samples below 3 GPa were composed of germanate and Ge and the respective peak shapes and peak shifts on compression were unknown.
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[22] The absolute values of Ge-O distance for $\text{Li}_2\text{O-4GeO}_2$ glass are slightly smaller than those calculated for the rutile-type crystalline GeO_2 . This is probably because a harmonic potential model, which underestimates interatomic distances when applied to amorphous materials, was used for the EXAFS data analysis [6,7].