

XAFS STUDY OF LIQUID GERMANATE UNDER PRESSURE

A 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. Liquids with a locally tetrahedral molecular structure, such as Si, Ge, C, SiO₂, and GeO₂, have possibilities for observing pressure-induced polymorphism [1]. Because the glasses retrieved from high pressures and high temperatures do not fully preserve their high-density liquid structure, direct structural observations are essential for further understanding of pressure-induced structural changes in these liquids. However, direct structural studies have not been successful to date. Crystalline GeO₂ has two polymorphs, a quartz-type structure with fourfold Ge and a rutile-type structure with sixfold Ge. The rutile-type phase is stable at ambient conditions. With increasing temperature at atmospheric 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, it is most plausible that liquid GeO₂ at pressures of several GPa shows local structures different from those of the ambient-pressure liquid. We have investigated the local structures around Ge in liquid germanate by means of *in situ* X-ray absorption measurements up to 9 GPa for the first time [2].

High-pressure and high-temperature conditions were realized using a cubic-type multi-anvil press (SMAP180) installed at beamline **BL14B1**. The main experimental obstacles to studying liquid GeO₂ are the high melting temperature (e.g., 2000 K at 3 GPa) and the easy decomposition of GeO₂ into Ge and O. Accordingly, we used an alkali germanate (Li₂O-4GeO₂ composition) instead of pure GeO₂ and an additive of B₂O₃ in order to lower the melting temperature and suppress the decomposition of GeO₂. XAFS spectra near the Ge *K*-edge with an energy range of 1000 eV above the edge were successfully measured up to 9 GPa at 1273 K. EXAFS data analysis is described in detail elsewhere [3].

The XANES spectra of liquid germanate recorded at 4, 6 and 9 GPa and 1273 K are shown in Fig. 1 together with those of the rutile-type and quartz-type crystalline GeO₂ at ambient conditions. As shown in the spectrum of the rutile-type structure, the

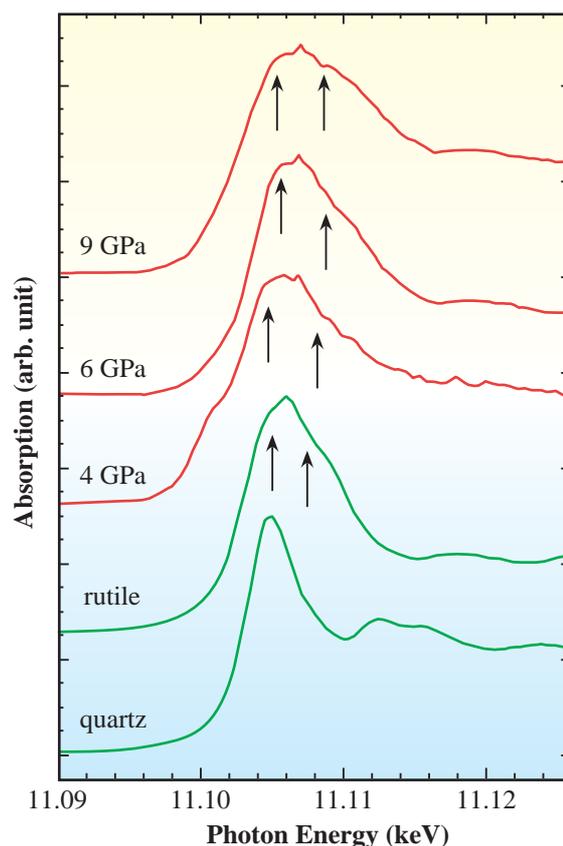


Fig. 1. Experimental Ge *K*-edge XANES spectra of liquid germanate recorded at 4, 6 and 9 GPa and 1273 K (red), together with those of the rutile- and the quartz-type crystalline GeO₂ at ambient conditions (green). The arrows indicate the shoulders as discussed in the text.

characteristic of the sixfold coordination of Ge is that the near-edge spectra show two shoulders discernible on both the lower- and higher-energy sides of the most intense peak, which are indicated by the two arrows in the figure. The observed spectra of liquid germanate have the pronounced shoulders, indicating that the sixfold coordination is dominant at these pressures.

Figure 2 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 Li₂O-4GeO₂ glass at room-temperature compression [4,5]. The distance in the liquid 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 a higher coordination than fourfold are introduced.

The distance shows a maximum at 4 GPa and then decreases monotonically with pressure. 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). Also, the XANES spectra of this pressure region, as shown in Fig. 1, indicate the characteristics of sixfold coordination. Therefore, 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. 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. The present result reveals that the transition can be a first-order type.

As shown in Fig. 2, 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 at room temperature (solid diamond) is consistent with that in the rutile GeO_2 at room temperature (dashed line), whereas the GeO_6 octahedron in the present liquid is more compressible than those in the crystal and glass; the GeO_6 octahedron in the liquid contracts and expands with pressure more easily than that in the crystalline rutile GeO_2 . This anomalous compression behavior of the GeO_6 octahedron is presumably due to the lack of long- and medium-range order in liquid.

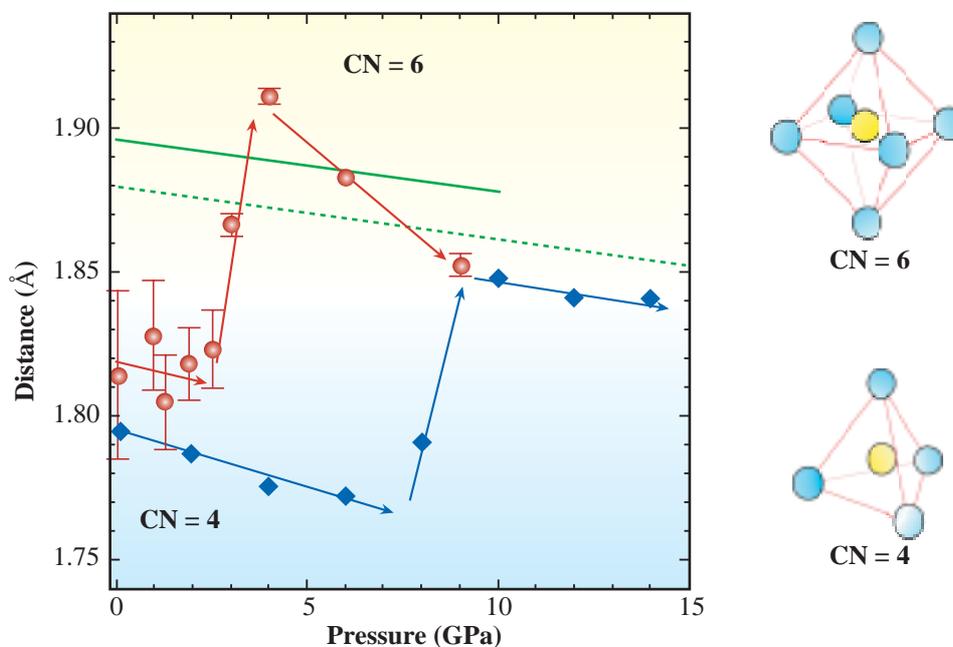


Fig. 2. Variation of the first-neighbor Ge-O distances in the present liquid germanate at 1273 K (red solid circles) and in $\text{Li}_2\text{O}-4\text{GeO}_2$ glass at room temperature (blue solid diamond). Errors for the distances are estimated from the statistical fitting errors. The arrows are guides for the eye. CN indicates the coordination number. Averaged Ge-O distances (4 short bonds and 2 long bonds in distorted GeO_6 octahedron) in rutile-type crystalline GeO_2 at room temperature and 1273 K are shown by green dashed and green solid lines, respectively.

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