

XAFS STUDY OF GeO₂ UNDER PRESSURE

When quartz-type crystalline GeO₂ (q-GeO₂) is compressed to pressures of 10 GPa at temperatures capable of inhibiting the crystallization of thermodynamically stable high-pressure phases, a pressure-induced phase transition occurs altering the coordination number (CN) of Ge from 4 to 6 [1]. Some groups have reported the high-pressure phase to be amorphous, while others insist the phase is crystalline in nature [2]. The sixfold coordination of Ge is either partly [1] or completely [2] preserved after the release of pressure. Pressure-induced CN changes have also been observed for vitreous GeO₂ at 6 - 10 GPa, although these changes are reversible [1]. Alkali germanate glasses, prepared under ambient conditions, contain a maximum of 20% of the sixfold coordinated Ge, throughout a composition range from 10 to 30 mol% alkali oxide. This phenomenon is known as germanate anomaly [3].

We have compressed quartz-type crystalline GeO₂ (q-GeO₂) and vitreous Li₂O-4GeO₂ (g-GeO₂), at room temperature to pressures up to 14 GPa to observe local structural changes by *in-situ* XAFS; this method allowed the investigation of the nature of the pressure-induced transition [4].

q-GeO₂ and g-GeO₂ were well-ground, mixed with amorphous boron, and placed in a high-pressure cell made of boron and epoxy resin. Au foil, serving as a pressure marker, was separately charged in the cell. A cubic-type multi-anvil press (SMAP 180), installed on the **BL14B1** bending magnet beamline, was used for compression. The X-ray beam, monochromatized by Si (111) reflection, was focused vertically by two mirrors. The incident X-ray beam was directed into the sample using vertical (0.2 mm) and horizontal (0.3 mm) slits. We then measured the X-ray absorption spectra near the Ge *K*-edge and the Au *L*-edge.

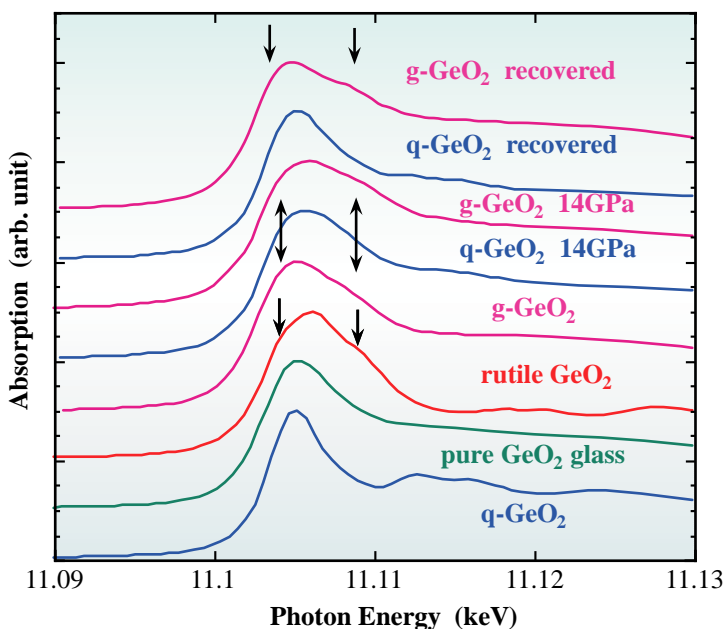


Fig. 1. Experimental Ge *K*-edge XANES spectra of various GeO₂ samples. Arrows indicate the two shoulders characteristic of six-fold coordination of Ge.

The pressure generated was calculated from the equation of state of Au using Au-Au distances determined by Au *L*-edge EXAFS measurements. Measurements were made at room temperature. EXAFS data analysis is described in detail elsewhere [5].

To distinguish between fourfold and sixfold coordination, we recorded the XANES spectra of q-GeO₂ and g-GeO₂ under various conditions (Fig. 1). The XANES spectra display two discernible shoulders, characteristic of a sixfold coordination of Ge. At 14 GPa, q-GeO₂ demonstrates the shoulders. These features, however, disappear when q-GeO₂ is restored to ambient pressure, indicating an almost complete reverse transition in the q-GeO₂ sample. The spectra of starting g-GeO₂ glass already



displays slight traces of the shoulders, demonstrating the germanate anomaly. At 14 GPa, the spectra possess the characteristics of sixfold Ge coordination. The spectra of g-GeO₂ allowed to recover from high pressure are similar to those of the starting glass.

Compression and decompression greatly varies the Ge-O distances of both q-GeO₂ and g-GeO₂ (Fig. 2). Throughout the compression of q-GeO₂ below 8 GPa, the Ge-O distance gradually shortens, indicating the conventional compression pattern of quartz-type crystalline structures. An abrupt increase in Ge-O distance, however, occurs between 8 and 12 GPa, corresponding to the CN change. The extrapolation of Ge-O distances at pressures ranging from 12 or 14 GPa to ambient pressure correlates well with a rutile structure; therefore, the CN change

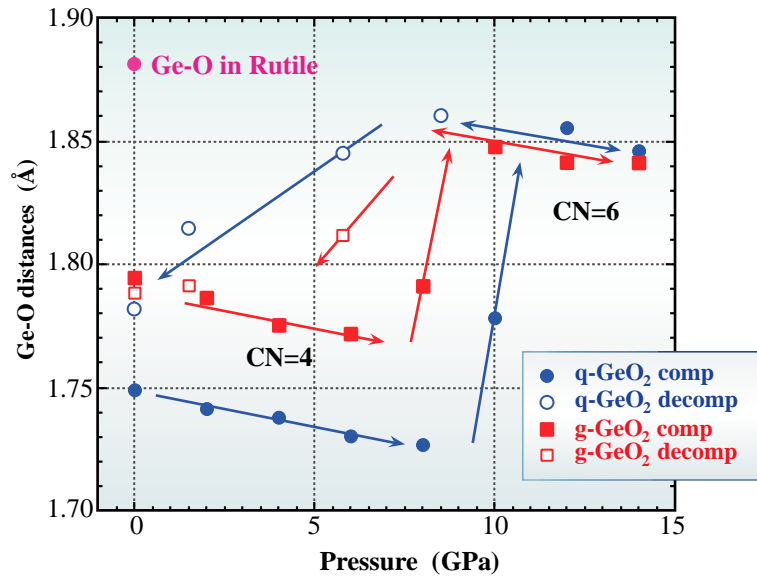


Fig. 2. Variation of Ge-O distance of quartz-type q-GeO₂ and g-GeO₂ by compression (solid symbols) and decompression (open symbols). Circles signify q-GeO₂ while the squares indicate g-GeO₂. Solid lines provide a guide for the eye only.

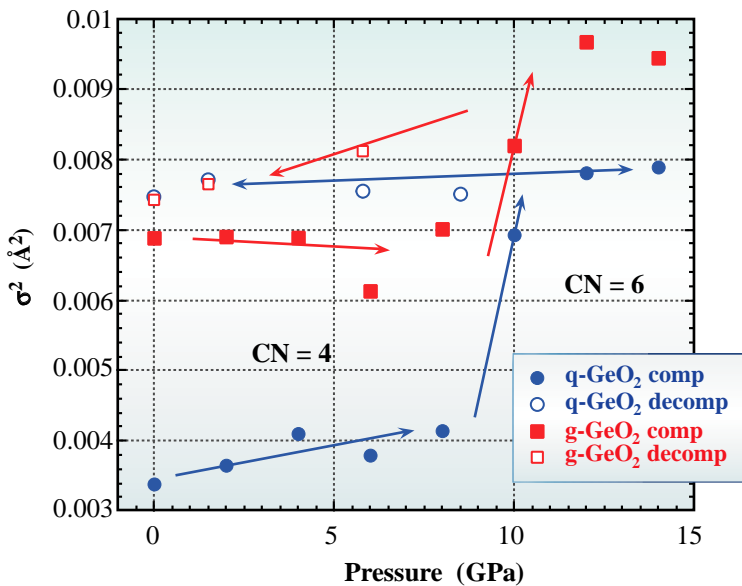


Fig. 3. Variation of Debye-Waller factors, σ^2 of q-GeO₂ and g-GeO₂, by compression (solid symbols) and decompression (open symbols). Circles indicate q-GeO₂ and the squares designate g-GeO₂. Solid lines provide a guide for the eye only.

is completed below 12 GPa. Decompression facilitates a reverse transition, occurring gradually below 6 GPa. Upon complete release of pressure, the Ge-O distance is 1.78 Å, slightly larger than that in the initial q-GeO₂ and similar to that of g-GeO₂. The CN change of g-GeO₂ begins above 6 GPa to finish below 10 GPa, a lower pressure than necessary for q-GeO₂ by 2 GPa. The reversal change of CN occurs below 10 GPa for g-GeO₂, with a smaller hysteresis than q-GeO₂. At the complete release of pressure, the Ge-O distance is 1.79 Å the same as observed for the untreated g-GeO₂. As the g-GeO₂ originally includes a fraction of the Ge possessing a sixfold coordination, we expected a continuous

increase in CN with increasing compression. The Ge-O bond, however, gradually shortens below 6 GPa and elongates within a narrow pressure range only. These results indicate that the compression of the GeO₄ tetrahedron is energetically less costly than CN change, even under circumstances where the GeO₆ octahedron nuclei preexists.

The variation of σ^2 of q-GeO₂ and g-GeO₂ reveals that the initial value of g-GeO₂ is larger than that of q-GeO₂, reflecting the glassy state (Fig. 3). Compression results in the increase of σ^2 for both q- and g-GeO₂, corresponding to the changes in CN [5]. Decompression leaves the once-increased σ^2 of q-GeO₂ at similar values. The reversal change in g-GeO₂ occurs below 10 GPa with hysteresis. Several arguments question whether the high pressure phase is amorphous or

crystalline. Present σ^2 of 0.008 Å² for q-GeO₂ at pressures greater than 10 GPa is considerably larger than the value of 0.004 Å² for rutile-type GeO₂ [5]; it is smaller, however, than that of g-GeO₂ in the same pressure range. This result suggests that the local structure around Ge atoms within the high pressure phase is more random than the rutile phase and less random than g-GeO₂ possessing sixfold coordination. As the CN change occurs at low temperatures during which the thermally activated diffusion process is restrained, the transition likely occurs by a martensitic mechanism. Consequently, we propose that the high pressure phase consists of a fine crystalline domain possessing many defects. The relatively large value of σ^2 in this phase indicates poor crystallization, resulting from defects introduced by a martensitic transition.

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