Pressure-induced drastic collapse of a high oxygen coordination shell in quartz-like $\alpha$-GeO$_2$

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Abstract
With the combination of a single crystal diamond anvil cell and a polycapillary half-lens, the local structural evolution around germanium in tetrahedrally networked quartz-like $\alpha$-GeO$_2$ has been investigated using extended x-ray absorption fine structure spectroscopy of up to 14 GPa by multiple-scattering analysis method. While the first shell Ge–O bond distances show a slight contraction with increasing pressure, the third shell Ge–O bond distances are found to decrease dramatically. The sluggish lengthening of the first shell Ge–O bond distances, initiated by coordination increase from fourfold to sixfold, occurs in the 7–14 GPa range just when the third shell Ge–O bond distances fall in the region of the second shell Ge–Ge bond distances. Moreover, these features are accompanied by the closing of intertetrahedral Ge–O–Ge angles and the opening of two intratetrahedral O–Ge–O angles, whose topological configuration surprisingly exhibits a helical chirality along the c axis that is opposite to the double helices of the corner-linked GeO$_4$ tetrahedra. These results suggest that the high-pressure phase transitions in quartz and quartz-like materials could be associated with a structural instability that is driven by the drastic collapse of the next-nearest-neighbour anion shell, which is consistent with the emergence

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of high-symmetry anion sublattice. Our findings provide crucial insights into the densification mechanisms of quartz-like oxides, which would have broad implications for our understanding of the metastability of various post-quartz crystalline phases and pressure-induced amorphization.

1. Introduction

The high-pressure behaviour of the silica polymorph $\alpha$-quartz, which is one of the most abundant minerals in the Earth’s crust and is an important engineering material, has drawn considerable attention from both experimental and theoretical perspectives [1–5]. Knowledge of its high-pressure structural stability trends and the underlying mechanisms can help to understand chemical bonding, glass formation, phase transitions and geological processes in the Earth’s interior. At ambient conditions, $\alpha$-quartz forms tetrahedrally networked structure. $\alpha$-quartz was found to undergo pressure-induced amorphization transition at pressures of around 18–35 GPa [6–8]. This phenomenon has also been observed in a variety of quartz-like oxides (e.g. $\alpha$-GeO$_2$ [9–14], $ABO_4$ ($A = \text{Al, Ga and } B = P, \text{As}$) berlinites [15, 16] and ice Ih [17]) and even in polyhedron-based borides like boron carbide B$_4$C [18, 19], and it has been extensively investigated. The initiation mechanism behind amorphization transition is usually associated with mechanical instability via violation of the Born stability criteria due to elastic softening coupled with acoustic phonon branch collapse [20–22]. The negative pressure derivatives of one of the elastic moduli in these materials generally suggests that pressure-induced amorphization is driven by an intrinsic structural instability [20, 23]. In $\alpha$-quartz, several structural parameter evolutions with pressure, such as intertetrahedral angle bending [24–28], tetrahedral distortion [24, 29], intertetrahedral O–O compression [28, 30] and movement of O atoms towards high-symmetry packing [31–33], have been used to characterize the densification process. However, the driving forces that could destabilize the original phase are still not well understood. While rotations of the tetrahedral units arising from intertetrahedral angle bending were predicted to induce the volume collapse [25, 26, 28], first-principles calculations suggested that the amorphization transition was triggered by a lattice shear instability that was related to the presence of an O body-centred-cubic (bcc) sublattice [22]. Subsequent molecular dynamics have also shown that the shear instability can be attributed to the intertetrahedral O–O compression, which would cause tetrahedral distortion and facilitate low-activation passageways for Si movements [33]. However, to our knowledge, most of the published experimental works have focused on the nearest intratetrahedral Si–O and intertetrahedral Si–Si coordination shells [12–14, 24–27], and a systematic clarification of the effect of intertetrahedral O–O compression on tetrahedral distortion which involves the next-nearest-neighbour Si–O interactions has not been available. Additional complexity is revealed regarding the metastability of various competing post-quartz crystalline phases that precede or coexist with the full amorphization [21, 34–36], indicating that the structural transformation pathways are highly dependent on the origin and nature of the samples as well as the degree of nonhydrostaticity [14, 33, 37], which have remained elusive. Accurate measurement of the local structural evolutions, including high anion shells and intertetrahedral and intratetrahedral angles around the cations, in quartz under hydrostatic pressure is thus extremely desirable. These results are of great interest, not only for
understanding the high shell densification behaviour, which has not yet been studied, but also for clarifying the driving forces of structural instability as well as for understanding the nature of metastability in quartz and quartz-like compounds.

Extended x-ray absorption fine structure (EXAFS) spectroscopy is a very powerful tool for the characterization of local atomic structure around the selected element of materials and it has been extensively applied in condensed matter physics and materials science [38, 39]. However, measurement of EXAFS spectra by a conventional energy-scanning method in such high-pressure devices as diamond anvil cell (DAC) remains challenging. A major difficulty arises from the DAC-produced severe distortions on the EXAFS spectra due to the Bragg reflections of single crystal diamond anvils. When the Bragg law is satisfied at certain energies and orientations of the diamonds, the transmitted x-ray intensity is drastically reduced and sharp spike-like peaks are often superimposed on the original spectrum. These Bragg glitches result in limited glitch-free energy range and thus low quality and reduced free parameters for the quantitative EXAFS analysis that have hindered a precise evaluation of the Debye–Waller factors as well as the inclusion of high coordination shells and multiple-scattering (MS) effects [40]. Diamond anvils are also transparent only to high-energy absorption edges (e.g. Ge K-edge), which impedes measurement at low-energy absorption edges (e.g. Si K-edge). Several methods to avoid Bragg glitches and obtain good quality EXAFS data have been proposed [41–46]. Recently, we have shown that the combination of single crystal DAC and polycapillary half-lens (PHL) refocusing optics is effective to suppress the DAC glitches from single crystal diamond anvils, and have obtained glitch-free spectra from −200 to 800 eV relative to the Ge K-edge energy for crystalline Ge [47]. This large glitch-free range extends the possibility of considering both high shells and MS effects in high-pressure EXAFS research. Therefore, in the present paper we address the aforementioned densification issues with MS EXAFS study on \(\alpha\)-GeO\(_2\), which initially attracted attention as the closet structural isotype of \(\alpha\)-quartz. It was also shown that \(\alpha\)-quartz and \(\alpha\)-GeO\(_2\) have a common sequence of high-pressure structural transformations [3]. We have collected long glitch-free spectra for \(\alpha\)-GeO\(_2\) up to post-edge 750 eV under hydrostatic pressure to 14 GPa, and performed MS EXAFS analysis up to the third shell distances to investigate the pressure evolution of high shell bond distances and bond angles. Besides the intertetrahedral Ge–O–Ge angle bending and GeO\(_4\) tetrahedral distortion, the drastic collapse of the next-nearest-neighbour oxygen shell is revealed, and their possible roles in understanding the densification mechanisms of \(\alpha\)-GeO\(_2\) are discussed. The MS EXAFS results are supported by x-ray absorption near edge structure (XANES) simulations.

2. Experiment

The Ge K-edge EXAFS spectra of \(\alpha\)-GeO\(_2\) under pressure up to 37 GPa were recorded at beamline 4W1B of the Beijing Synchrotron Radiation Facility (BSRF) in China with the transmission mode using a Si(111) double crystal monochromator. The pressure was generated using a piston-type DAC having a pair of 300 \(\mu\)m flat culet single crystal diamonds. The \(\alpha\)-GeO\(_2\) sample of 99.999% purity was loaded into a hole of about 100 \(\mu\)m in diameter and 40 \(\mu\)m in thickness that was drilled in a Re gasket with LiF as hydrostatic pressure-transmitting medium. The mass ratio between \(\alpha\)-GeO\(_2\) and LiF was 1.67 to guarantee that the edge jump of Ge was around 1 during the compression process. One small ruby sphere was loaded into the sample chamber for pressure calibration according to its \(R1\) fluorescence peak position.
The pre-focused x-ray beam by the toroidal mirror was re-focused down to a spot of about 50 µm FWHM by PHL optics. A considerable reduction in the number of DAC glitches by PHL [47] made it very convenient to reject the remaining glitches from the energy range (−150 to 750 eV relative to the edge energy) by adjusting the DAC orientation relative to the incident x-ray beam. Due to the limited PHL tip-to-focus distance (21 mm) and the large divergence of the emergent beam (15 mrad), both the incident and transmitted x-ray intensities were measured using Si photodiodes that consist of Si chips of 5 µm in thickness as substitute for the ionization chambers [47]. The EXAFS raw data were background-subtracted, normalized and Fourier transformed by the standard procedures with the ATHENA analysis software [48].

3. Data analysis and results

Figures 1(a) and (b) show the pressure dependence of Ge K-edge EXAFS oscillations $\chi(k)$ and their Fourier transforms acquired by the combination of single crystal DAC and PHL, respectively. The EXAFS function $\chi(k)$ and Fourier transform at 0.8 GPa are comparable to that of $\alpha$-GeO$_2$ standard obtained outside DAC at ambient pressure, and the Bragg glitches from the single crystal diamond anvils are completely removed up to $k$ = 14 Å$^{-1}$, implying that there are enough numbers of free parameters for the qualitative MS EXFAS analysis. Under hydrostatic condition, $\alpha$-GeO$_2$ undergoes transition to a monoclinic $P2_1/c$ phase built up of edge-sharing GeO$_6$ octahedra [37]. Pronounced changes to the EXAFS functions $\chi(k)$ and Fourier transforms are observed above 7.4 GPa, which finishes up to 14.1 GPa. The EXAFS
oscillation peaks from the initial hexagonal $\alpha$-quartz-like phase are found to disappear and several new oscillation peaks emerge in the $k$ range of 4.0–8.5 Å$^{-1}$, as shown in the yellow-hatched region in figure 1(a). In the Fourier transform profiles in the real space (figure 1(b)), correlated changes can also be identified. The Fourier transform curve in the $\alpha$-quartz-like phase at ambient pressure is characterized by three peaks. While the first peak at 1.4 Å corresponds to the first shell Ge–O bonds, the other two peaks spreading from 2.5 to 3.4 Å can be attributed to the second shell Ge–Ge and the third shell Ge–O bonds and MS contributions [12]. On compression, the first peak moves slightly towards lower $R$ directions and grows in intensity owing to the contracted first shell Ge–O bond distances and suppressed thermal disorder. Further compression at 7.4 GPa yields a positive shift in its $R$ position and a sudden decrease in its intensity, which indicates a severe distortion of the GeO$_4$ tetrahedra near the onset of phase transition. Meanwhile, the shoulder peak gradually drops in intensity and moves to lower $R$ directions. At 7.4 GPa it merges with the second peak at 2.6 Å, signifying the significance of taking account of high shells and MS effect to understand the densification process of the $\alpha$-quartz-like phase. Above 14.1 GPa, the Fourier transform curves of the $P2_1/c$ phase are featured by three main peaks located at 1.4, 2.6, and 3.3 Å, respectively, and show small changes with increasing pressure. The $P2_1/c$ phase persists up to 36.5 GPa. These results agree well with previous diffraction studies and EXAFS measurements on $\alpha$-GeO$_2$ in this pressure range [12, 37, 49].

To obtain quantitative structural parameters during the densification of $\alpha$-quartz-like phase, a least-squares curve fit including MS contributions was carried out for EXAFS analysis using the ARTEMIS program [48]. The theoretical scattering amplitude functions and phase shifts for all single-scattering (SS) and MS paths, as well as the photoelectron mean free path, were calculated self-consistently by FEFF9.05 code [39, 50] based on the known crystalline structure for $\alpha$-GeO$_2$ [27]. The Hedin–Lundqvist self-energy and simple final-state rule core hole were used. This calculation accounts for charge transfers between Ge and O atoms and gives an accurate determination of Fermi level, enabling us to do the fit with a single energy shift $\Delta E_0$. A single energy scale for the theoretical signals has also been applied in the framework of another EXAFS analysis package GNXAS [51] for various systems. The passive electron reduction factor $S_0^2$ was fixed to 1.1 [12]. Three SS paths for the first three shells were included corresponding to the four Ge–O1, four Ge–Ge1, and four Ge–O2 bonds, respectively. The Ge–Ge1 bond distances were constrained by the intertetrahedral geometry of the triangular scattering (TS) path Ge $\rightarrow$ Ge1 $\rightarrow$ O1 $\rightarrow$ Ge (see figure 2). The intertetrahedral Ge–O–Ge angle bending was proposed to be the predominant bulk compression mechanism in $\alpha$-GeO$_2$. At ambient pressure, Giangrisostomi et al [52] pointed out that it might be difficult to distinguish between the slightly different intratetrahedral O–Ge–O angles ($\sim$5$^\circ$) as predicted by diffraction studies; however, large splitting of the O–Ge–O angles near the onset of phase transition ($\sim$13$^\circ$ at 5.57 GPa) was shown [11, 24, 27], as confirmed in $\alpha$-SiO$_2$ [24, 27]. Therefore, we considered two independent intratetrahedral TS paths Ge $\rightarrow$ O1 $\rightarrow$ O1 $\rightarrow$ Ge with their total coordination number fixed. The fit was done in $R$ space 0.8–3.4 Å with $k$ range of 3.4–13.6 Å$^{-1}$ and $k$-weight of 2. Above 9.8 GPa, higher shell peaks in $R$ space are attributed to a mixing behaviour of Ge–O and Ge–Ge bonds, and only the first shell peak was taken into account. A comparison between the experimental spectrum collected at 0.8 GPa and the best-fit result is shown in figure 3.

5 EXAFS calculation, http://leonardo.phys.washington.edu/feff/wiki/index.php?title=EXAFS_calculation.
Figure 2. Schematic scattering paths of $\alpha$-GeO$_2$ in the first three shells. The O1, Ge1 and O2 denote the first, second and third shell atoms around the central absorber Ge atom, respectively. Three SS paths (SS1, SS2 and SS3), an intertetrahedral TS path (TS1), and two intratetrahedral TS paths (TS2 and TS3) are described.

Figure 4 shows the pressure dependence of the best-fit bond distances, bond angles and mean square relative displacements. The fitting results reveal that, when moving from $\alpha$-quartz-like to $P2_1/c$ phase, the GeO$_4$ tetrahedra undergo severe distortion, as manifested by the large splitting of the intratetrahedral angles $\theta_{\text{O1-Ge-O1}}$ into two groups. With $\theta_{\text{O1-Ge-O1(min)}}$ and $\theta_{\text{O1-Ge-O1(max)}}$ changing, respectively, from 107.8° and 112.8° at ambient pressure to 105.7° and 117.3° at 7.4 GPa, the number of $\theta_{\text{O1-Ge-O1(min)}}$ increases from 3 to 4, while the number of $\theta_{\text{O1-Ge-O1(max)}}$ decreases from 3 to 2, which is in good agreement with the results obtained by diffraction experiments [11, 24, 27, 31]. The first shell Ge–O bond distances remain nearly constant at low pressures and show a sluggish lengthening of about 0.1 Å in the 7–14 GPa range, which is associated with a coordination change from fourfold to sixfold and a rough increase of about 0.004 Å$^2$ for $\sigma^2_{\text{Ge-O1}}$. This agrees well with the pressure dependences of $R_{\text{Ge-O1}}$ and $\sigma^2_{\text{Ge-O1}}$ as obtained in [12–14] by EXAFS measurements on $\alpha$-GeO$_2$ up to 14 GPa. In compressed $\alpha$-SiO$_2$, a similar distortion behaviour for the SiO$_4$ tetrahedra was observed in the 0–18 GPa [26, 27]. This confirms that the distortion of tetrahedral units in quartz and quartz-like materials is relaxed mainly through intratetrahedral angle deviation, whereas the bond distance changes are secondary. In this process, the third shell bond distances $R_{\text{Ge-O2}}$ are found to decrease dramatically and fall in the range of the second shell bond distances $R_{\text{Ge-Ge1}}$ at 7.4 GPa, implying a possible correlation between the GeO$_4$ tetrahedral distortion and the drastic shortening of the third shell bond distances $R_{\text{Ge-O2}}$. In contrast, the decrease rate of the second shell bond distances $R_{\text{Ge-Ge1}}$ that is geometrically related with the intertetrahedral angle $\theta_{\text{Ge-O1-Ge1}}$ is reduced with increasing pressure, which could suggest an increasing stiffness of the Ge–O–Ge angle bending. An increasing stiffness for the Si–O–Si angle in $\alpha$-SiO$_2$ above...
Figure 3. Comparison between the experimental EXAFS spectrum collected at 0.8 GPa and the best-fit result. Comparisons are reported for (a) the extracted $k^2\chi(k)$ signal and for (b) the fourier-transformed magnitude and imaginary part (in the inset).

10 GPa was also reported [30]. In addition, the O arrangement in $\alpha$-SiO$_2$ was pointed out to move towards a bcc framework under compression, which was further suggested to be responsible for the shear instability of quartz structure [22]. To examine the formation of an O bcc arrangement and its relation with the GeO$_4$ tetrahedral distortion in our present study of $\alpha$-GeO$_2$, we reconstructed the crystal structure variations as a function of pressure. $\alpha$-GeO$_2$ has a hexagonal $P3_21$ symmetry, and the unit cell is defined by two lattice constants ($a$, $c$) and four atomic coordinates ($u$, $x$, $y$, $z$), with Ge at Wyckoff 3$a$ ($u$, 0, 2/3) and O at 6$c$ ($x$, $y$, $z$) positions. Based on the local structural parameters from EXAFS analysis, the lattice constants and atomic coordinates were obtained by minimizing the objective function

$$f = \sum_{i=1,Nb} [d_i(a, c, u, x, y, z) - d_i(\text{EXAFS})]^2 + \sum_{j=1,Na} [\theta_j(a, c, u, x, y, z) - \theta_j(\text{EXAFS})]^2$$

using a conjugate gradient algorithm, where $i$ denotes the $i$th bond distance, $j$ the $j$th bond angle. As shown in figure 5, the refined structural parameters in the $\alpha$-quartz-like phase, such as $a$, $c/a$ ratio, cell volume and fractional parameters, follow a nice evolution path that compares satisfactorily well with the point from diffraction experiments [11, 24, 27, 53]. A fit of third-order Birch–Murnaghan equation of state yields a bulk modulus $K_0$ of 41.6 (9.7) GPa and its pressure derivative $K'_0$ of 5.8 (3.4) GPa, which is in good agreement with previous experimental data [24, 27, 53, 54] where the bulk modulus is found in the range of 32.8–42 GPa. It is also noted that the pressure dependence of the lattice constants and cell volume measured through present EXAFS study is systematically stiffer than most of the diffraction data in the literature.
Figure 4. Change of (a) the best-fit bond distances, (b) bond angles and (c) mean square relative displacements with increasing pressure. In the insets, the coordination numbers for the first shell Ge–O bond distance and the O–Ge–O angles are shown. The vertical dashed lines denote the phase boundaries.

This discrepancy is partially due to the different sensitivity of these two techniques to the correlation of interatomic vibrations perpendicular ($\sigma_{\perp}^2$) to a given bond direction [55], with the consequence that the EXAFS interatomic distances are slightly longer than the diffraction distances $R_c$ by a magnitude of $\sigma_{\perp}^2 / 2R_c$. On the other hand, it may result from the effects of the different pressure-transmitting media used in the high-pressure EXAFS (e.g. LiF, h-BN [12] and a-B [14]) and earlier diffraction (a mixture of methanol and ethanol) [11, 24, 27, 53] experiments. For the ideal bcc arrangement of O ions and ideally centred GeO$_4$ tetrahedra, the atomic coordinates are $u = 5/12$, $x = y = 1/3$, $z = 0.75$ and $c/a = \sqrt{3}/\sqrt{2} \approx 1.225$ as indicated by the dashed dot lines in figure 5(d) [32]. The structural parameters obtained from our EXAFS results change from $u = 0.4466$, $x = 0.3992$, $y = 0.3072$ and $z = 0.7572$ at ambient pressure to $u = 0.4274$, $x = 0.3807$, $y = 0.3306$ and $z = 0.7501$ at 7.4 GPa, consistent with the prediction of the ideal bcc model. However, it is worth noting that the structural parameters do not fully converge to the ideal bcc model (especially for the atomic coordinate y), which indicates that the high-pressure intermediate state remains significantly distorted from an ideal bcc framework. The phase transition probably takes place before an ideal bcc sublattice is fully realized.

The Ge K-edge XANES spectra as a function of pressure are presented in figure 6(a). A large increase (~1 eV) in the edge shift is shown in the transition region at about 7–14 GPa, which happens because of a structural transition from a tetrahedrally coordinated $\alpha$-quartz-like phase to an octahedrally coordinated $P2_1/c$ phase. A similar energy shift of about 1.2 eV between the $\alpha$-quartz-like and the sixfold coordinated rutile-type phases of GeO$_2$ was
Figure 5. Pressure evolution of the reconstructed structural parameters for $a$, $c/a$ ratio, cell volume and fractional coordinates in $\alpha$-GeO$_2$ based on the EXAFS results. The solid curve is the best-fit Birch–Murnaghan equation of state with parameters $K_0 = 41.6(9.7)$ GPa and $K'_0 = 5.8(3.4)$, where $K_0$ and $K'_0$ denote the zero pressure bulk modulus and its pressure derivative, respectively. The diffraction experiment data points are from [24] (solid circles), [11] (solid triangles), [54] (solid stars) and [27] (solid diamond).

observed [56]. However, our Bader charge analysis [57], which is based on the charge density from the VASP code [58] with the local density approximation [59] exchange-correlation potential, showed that the electron population of Ge in the fourfold and sixfold coordinations differs by only 0.04$e$, and the energy shift cannot be attributed to Ge 4p transfer, which is in good agreement with the theoretical calculations of Bertini et al [56]. At ambient conditions, the spectrum of $\alpha$-quartz-like phase (figure 6(a)) exhibits six well-defined features (white line and peaks A–E). Upon compression, peak A progressively gains intensity and moves to a higher energy, while peak B decreases in intensity with energy shift to higher energy and is smoothed into a shoulder at 7.4 GPa. The most outstanding features are the strong intensity increase of peak C and the energy shift of peak D to higher energy that finally merges together with peak E. The spectrum at 14.1 GPa shows only two broadened features.
Figure 6. (a) The experimental Ge K-edge XANES spectra of compressed α-GeO$_2$. In the inset, the edge shift with respect to the ambient point is shown. (b) The calculated XANES spectra at each pressure based on the local atomic parameters obtained by MS EXAFS analysis. The spectrum at 9.8 GPa is the average of the calculated signals for the α-quartz-like phase at 7.4 GPa and the $P2_1/c$ phase under ambient condition.

(peaks F and G), which is consistent with the large structural disorder of the $P2_1/c$ phase [37]. To confirm the compatibility of the MS EXAFS results with the measured XANES spectra, we calculated XANES spectra for the α-quartz-like phase with the best-fit lattice constants and atomic coordinates based on the local atomic structural parameters by MS EXAFS analysis. For the monoclinic $P2_1/c$ phase, the structural parameters reported by Haines et al [37] was used, and the resulting theoretical spectrum is the weighted average of contributions from each nonequivalent Ge site. The calculations were carried out with the FDMNES code [60], and the muffin-tin effects were avoided by finite difference method. Figure 6(b) shows the calculated XANES spectra at each pressure. This demonstrates that the simulated trends of the energy positions and relative intensities for the six features (especially for peaks C and D) of the α-quartz-like phase are in excellent agreement with the experimental results, fully supporting the validity of the structural parameters of α-GeO$_2$ obtained by our MS EXAFS analysis. The well reproduction of the overall profile of the experimental XANES spectrum at 14.1 GPa by using the $P2_1/c$ phase structure also confirms the α-quartz-like→$P2_1/c$ phase transition, although various pressure-induced amorphizations have been reported to occur in α-GeO$_2$ [9–11].
4. Discussion

Rotations of SiO$_4$ tetrahedra arising from the decrease in the Si–O–Si angles were proposed to control the densification in $\alpha$-SiO$_2$ before the amorphization transition occurring at pressures of around 18–35 GPa [25, 26, 28]. At pressures below 10–15 GPa, it was found that both the bulk volume and the Si–O–Si angles evolved in an approximately linear way with increasing pressure, and small volume compression (<1%) was accounted for by the SiO$_4$ tetrahedral distortion. Hazen et al [26] attempted to correlate the Si–O–Si angle bending with the structural stability trend, and suggested that it would result in a sharp increase of the strain energy when these angle values fell below 120°. This was in accordance with previous conjecture that the structural transformation in $\alpha$-SiO$_2$ was initiated by rotations of SiO$_4$ tetrahedra that caused the volume collapse [36]. However, using first-principles calculations, Chelikowsky et al [30] argued that the Si–O–Si angles were well above 125° near the amorphization transition pressure of 18 GPa and did not fall below 120° until a pressure of about 40 GPa, which is at variance with the suggestions of Hazen et al. We can further test the suggestion with MS EXAFS measurements of $\alpha$-GeO$_2$ under pressure. Due to the chemical pressure introduced by Ge cations (the ratio of ionic radii $R$(Ge$^{2+}$)/$R$(Si$^{2+}$) = 1.26) [3], $\alpha$-GeO$_2$ at low pressures represents a high-pressure model of $\alpha$-SiO$_2$. Our MS EXAFS fitting shows that the Ge–O–Ge angles are around 122.9° near the onset of phase transition at 7.4 GPa, which is in agreement with the result of Chelikowsky et al. This indicates that the predominant role of intertetrahedral angle bending in controlling the densification of quartz and quartz-like structures might be suppressed at high pressures, which can be attributed to the stiffening of the Ge–O–Ge angles by the Ge–Ge repulsions as manifested by the significantly reduced decreasing rates of the Ge–O–Ge angles and the second shell Ge–Ge bond distances above 4.5 GPa (figure 4). It was also pointed out that the intertetrahedral angles could be stiffened by the increasing repulsions between the nearest intertetrahedral O–O anions [28].

Because of the slight contribution of tetrahedral distortion to the significant bulk volume compression in quartz, tetrahedral distortion was scarcely considered as a compression mechanism. However, given the relatively strong cation–anion bonding in quartz and quartz-like structures, it was argued that tetrahedral distortion could lower the high kinetic barriers associated with the transitions to stable phases containing octahedrally coordinated cations at high pressures [33]. We can gain further insight into this point from the MS EXAFS analysis. To this end, we track the structural evolution of the first three shells of Ge as a function of pressure based on the reconstructed crystal structures of compacted $\alpha$-GeO$_2$ (figure 7(a)). As pressure increases, the two O–Ge–O angles having O atoms along the b’ and c’ axes are opened. The two opened O–Ge–O angles are cross to each other, which effectively amounts to a flattening of GeO$_4$ tetrahedra. Moreover, figures 7(b) and (c) surprisingly show that the topology of the opened O–Ge–O angles adopts a helical configuration parallel to the c axis that is of opposite handedness to the double helices of corner-linked GeO$_4$ tetrahedra. With two cross opened O–Si–O angles, similar SiO$_4$ tetrahedral distortion helices along the c axis in $\alpha$-SiO$_2$ are confirmed by examining the existing high-pressure diffraction data [24–27], even though the SiO$_4$ tetrahedra of $\alpha$-SiO$_2$ are relatively more rigid than these of $\alpha$-GeO$_2$ and compression of $\alpha$-SiO$_2$ at low pressures occurs mainly via rotations of SiO$_4$ tetrahedra [5]. Low-activation passageways for the displacement of cations along the bisectors of the opened intratetrahedral angles are consequently established. Under further compression or thermal activation, such deformation will shift the cations towards the edges of tetrahedral, which can
result in an abrupt coordination change from fourfold to sixfold. Qualitatively, this peculiar tetrahedral deformation behaviour is consistent with the movements of Si atoms along the eigenvector of the soft \( K \)-point phonon mode, as shown in \( \alpha \)-SiO\(_2\) at 19 GPa \[22\]. Meanwhile, in compressed \( \alpha \)-SiO\(_2\) \[20–22\] and \( \alpha \)-GeO\(_2\) \[61\], it is coupled with the violation of the Born mechanical criterion arising from the softening of the shear modulus \( C_{44} \) with increasing pressure, indicating that the softening of acoustic branch and loss of elastic stiffness and stability may be closely linked to the deformation of the tetrahedral building blocks. Recently, icosahedra-based boron carbide \( B_4C \) was reported to undergo a similar amorphous transition at high pressure as in quartz, which was ascribed to the disassembly of the deformed icosahedral units, driven by shear stresses \[18, 19\]. In addition, the helix-type tetrahedral deformation in \( \alpha \)-SiO\(_2\) and \( \alpha \)-GeO\(_2\) constitutes an essential intermediate state that precedes the pressure-induced transitions to an amorphous form or a post-quartz crystalline phase, thus providing us with a context to elucidate the structural characteristics and metastability of the final structures. For instance, by small perturbation of this intermediate state, the high-density amorphous form produced on compression of \( \alpha \)-SiO\(_2\) and \( \alpha \)-GeO\(_2\) may be generated from fractional persistence of the helical low-energy passageways provided by the opened intratetrahedral angles in which cations are disordered over the octahedral sites. This may explain the short- and intermediate-range order in the dense amorphous form, as suggested by Teter \textit{et al} \[34\]. Upon release of the pressure, quartz remains amorphous, but the material is elastically anisotropic with ‘memory’ of the quartz crystallographic orientation \[6\], which may be partially due to the recovery of the helical order. Furthermore, the transition of the quartz phase to various metastable post-quartz crystalline structures rather than directly to the stable stishovite phase can be imposed by the helices of the opened intratetrahedral angles, since the post-quartz crystalline structures (e.g. quartz-II \[21\], the \( P3_2 \) phase \[36\]) also exhibit chiral configurations, despite their mixed polyhedral building blocks. This is further evidenced by the fact that the transition from \( \alpha \)-quartz to post-quartz \( P2_1/c \) phase (characterized by \( 3 \times 2 \) kinked chains of octahedra) and then to stishovite phase (characterized by straight chains of octahedra) can be realized by undergoing a gradual elimination of the kinking of octahedral chains, unless a large kinetic is exerted to diffuse the cations with direct reconstructive transition from \( \alpha \)-quartz to stishovite phase \[62\]. Despite the similarities in the high-pressure compression behaviour and structural transformation sequence between \( \alpha \)-SiO\(_2\) and \( \alpha \)-GeO\(_2\), no intermediate phase, analogous to the quartz-II for SiO\(_2\), has been observed to occur prior to or coexist with the amorphous or \( \alpha \)-quartz \( \rightarrow \) \( P2_1/c \) transition for \( \alpha \)-GeO\(_2\) in our and other studies \[3, 37\], which was ascribed to the different sizes and mobility of cations within oxygen network \[3\]. Hence, the real phase transition pathway can be dependent on several factors such as the origin and nature of samples, the degree of nonhydrostaticity, duration of high-pressure treatment, cation sizes and so on, which can affect the shear stress conditions and the coupling of the soft phonon modes in the helical intermediate state near the critical transition pressure.

The above results indicate that the driving forces that destabilize the quartz and quartz-like structures can be associated with changes leading to the flattening of tetrahedral units or the opening of the two cross intratetrahedral angles, which may correlate with the phonon softening together with shear instability. Rigid unit mode analysis showed that tetrahedral distortion might be independent of intertetrahedral angle bending \[63\]. On the other hand, tetrahedral distortion was linked to the O sublattice rearrangement, because SiO\(_4\) and GeO\(_4\) tetrahedra in \( \alpha \)-SiO\(_2\) and \( \alpha \)-GeO\(_2\) was found to became more and more flattened when O atoms moved towards a bcc framework \[31\], which is in good agreement with our present study (figure 5(d)).
Figure 7. (a) Local atomic arrangement of $\alpha$-GeO$_2$. The distorted bcc unit cell is shown in dashed dot lines. The two opened intratetrahedral angles $\theta_{O1-Ge-O1(max)}$ are described. (b) Side view and (c) perspective view (along the c axis) of the topology of the opened O–Ge–O angles. The helices of opened O–Ge–O angles are left-handed, whereas the double helices of corner-linked GeO$_4$ tetrahedra adopt right-handed configuration.
Sowa [31] showed that tetrahedral flattening was consistent with the trend of O bcc packing which contains only flattened tetrahedral voids with two nominal cross opened intratetrahedral angles of about 126.9°. However, in [22], the presence of an O bcc array was shown to trigger a lattice shear softening that would elongate the O bcc sublattice in the c’ direction (figure 7(a)), giving rising to the opening (closing) of the O–Si–O angles having the O atoms along (perpendicular) the elongation axis. This is inconsistent with the tetrahedral flattening, which might be due to the occurrence of phase transition prior to an ideal bcc sublattice is fully realized. Using Sommerville tetrahedra rather regular tetrahedra to characterize tetrahedral distortion in α-SiO₂, recently, Thompson and Downs [28] proposed that tetrahedral distortion could be attributed to the shortening of the nearest intertetrahedral O–O distances, which may drive the lattice shear instability [33]. However, they did not relate their results to the change of O–Si–O angles. Consequently, the relationship between intertetrahedral O–O compression and tetrahedral distortion is still not fully understood. We find that the third shell O atoms of the Ge sites are just neighboured to first tetrahedral shell O atoms, providing us with an opportunity to clarify the effect of intertetrahedral O–O interactions on tetrahedral distortion. Our MS EXAFS results on α-GeO₂ show a drastic shortening of the third shell Ge–O distances. The phase transition occurs when the third shell Ge–O distances fall in the range of the second shell Ge–Ge1 bond distances, which suggests that the opening of the O–Ge–O angles can be caused by the drastic shortening of the third shell Ge–O distances. In particular, as shown in figure 7(a), the two third shell O2 atoms in [0′20’] plane drive the opening of the O1–Ge–O1 angle having O1 atoms along b’ direction, and the other two O2 atoms in [0′0’1] plane drive the opening of the O1–Ge–O1 angle having O1 atoms along c’ direction. This process benefits mainly from the strong intertetrahedral O1–O2 repulsions. Moreover, the drastic shortening of the third shell Ge–O2 distances can maximize the Ge–O2 attractions and further facilitate the movement of Ge atoms. These results are consistent with the theoretical calculations by Teter et al [34] and Martoňák et al [62], who found that α-SiO₂ can undergo a diffusionless transformation to the post-quartz P2₁/c phase without kinetic activation. They are also in agreement with the concept of eutaxy conjectured by O’Keeffe [64], which states that the densification is dominated by a balance between maximizing cation–anion attractions and minimizing anion–anion and cation–cation repulsions, while simultaneously maximizing the density. As shown by the converging fractional coordinates (figure 5(d)), the densification process is accompanied by the emergence of O bcc framework, which can be responsible for the distortion as described above. This picture is consistent with the two-step densification mechanism for networked oxides proposed by Huang et al [33], which has been confirmed in the high-pressure transformations of α-SiO₂, cristobalite SiO₂, and α-AlPO₄ berlinite [65]. A compact high-symmetry anion sublattice is first formed, and then followed by the redistribution of cations onto newly created interstices. For the high-pressure behaviour of other tetrahedrally networked systems without ordered anion sublattice, such as polyamorphous transitions occurring in vitreous SiO₂ and GeO₂ [12], drastic shortening of next-nearest-neighbour cation–anion distances can also play a key role in inducing the coordination transformation.

5. Conclusions

In conclusion, using Ge K-edge in situ high-pressure EXAFS spectra with long glitch-free k range, we have been able to perform MS analysis up to the third shell range to resolve the pressure evolution of high shell bond distances and bond angles of α-GeO₂ with a high
accuracy. We find that the drastic collapse of the next-nearest-neighbour anion shell plays a crucial role in inducing the structural instability in quartz and quartz-like materials. It not only drives the opening of the intratetrahedral angles, owing to the strong anion–anion repulsions, but it also simultaneously maximizes the next-nearest-neighbour cation–anion attractions, which facilitates a low-activation pathway for the displacement of cations onto the newly octahedral interstices created by anion sublattice. Furthermore, in $\alpha$-quartz and $\alpha$-GeO$_2$, the topology of the opened intratetrahedral angles reveals helical chirality along the $c$ axis, which may be responsible for the ‘memory’ effect of the amorphous state produced on releasing pressure [6] and the chiral and metastable properties of various post-quartz crystalline structures. These findings provide deep insights into the densification mechanism of the four to six coordinated cation transformations in quartz and quartz-like compounds, which could have important implications for illuminating problems ranging from the amorphization and loss of elastic stiffness on impact or the development of high-toughness ceramics [33], to the seismic discontinuities in the crust–mantle transition zone [21].

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