Structural characteristics and elasticities of coesite and coesite-II at high pressure

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Abstract
Silica, SiO2, has attracted significant interest as one of the most important compounds in the fields of condensed-matter physics, materials science, and geoscience etc. Here, we theoretically investigate crystal structural characteristics and elastic properties of coesite and its high-pressure polymorph coesite-II at high pressures, which is critical to improve the understanding of densification mechanism of silica at high pressure. The driving mechanism for the pressure-induced transition pathways of coesite comes from both structural features and elastic effect. The phase transition of coesite to cosite-II is triggered by the shortening of Si1–O1 bond distance, and accompanied by elastic instability from a combination of softening elastic constants C_{44} and C_{46}. The structural modulation of coesite-II along the b-axis direction, as proposed experimentally, results from, on the one hand, the bending of Si2–O15–Si3 angles and shortening of Si5–O4 and Si7–O4 distance with increasing pressure and, on the other hand, elastic softening associated with phonon instability. These results provide key insights into the densification mechanism of silica under high pressure.

1. Introduction
Silica (SiO2) as the dominant oxide constituent of the Earth, is of great importance in many fields such as condensed-matter physics, materials, geoscience, and industry [1]. Silica shows rich polymorphism at high-pressure and high-temperature conditions [2], despite its chemical composition is simple. A comprehensive understanding of the transition mechanisms between its polymorphs is essential to understand the structural characteristic and physical properties of silica at elevated pressures and temperatures [3–5].

Coesite, the known densest form of silica with tetrahedral coordination crystallizes in monoclinic crystal system (C2/c, Z = 16) [6]. Since coesite was observed in the laboratory and later discovered in nature [7, 8], its structural behavior under pressure has been extensively investigated by means of experiments and theoretical simulations [9–14]. Static compression experiments and theoretical simulations conclude that coesite undergoes multiple transformation pathways at high pressure [9, 11, 13–15]. Before phase transition to high-pressure polymorph, the structure of coesite presents high anisotropy under pressure. The stiffer direction is along the c-axis, which is the arrangement direction of the tetrahedral chains [10, 12]. Four of the five Si–O–Si angles decrease with increasing pressure, but the Si1–O1–Si1 angle is constrained to 180°.

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due to symmetry requirements [16]. Coesite transforms to coesite-II (P2_1/c, Z = 32) at pressure ~ 22 GPA, possibly resulting from the extreme shortening of the shortest and the most compressible Si1–O1 bond [15]. The crystal structure of coesite-II is a commensurate modulated structure of coesite, with a doubled b-axis parameter. Coesite-II undergoes further structural modulation along the b-axis above 36 GPA, and the long-range ordered crystal structure collapses and starts amorphization beyond ~40 GPA [14]. However, Černok et al [15] and Bykova et al [17] have proposed a transition from coesite-II to a triclinic phase, coesite-III (P −1) above 25 GPA [15]. The framework of coesite-III consists of four-membered rings of [SiO_4] tetrahedra. They also have proposed transitions from coesite-III to coesite-IV (P −1, with [SiO_4], [SiO_3], and [SiO_6] coordination polyhedra) above 30 GPA, and then to coesite-V (P −1, with [SiO_3] and [SiO_6] coordination polyhedra) above 50 GPA. On the contrary, Hu et al [13] have reported a transition from coesite to post-stishovite phase (P2/c, built of only [SiO_6] octahedra) between 26 and 53 GPA through four triclinic intermediate phases. Post-stishovite phase should transform to α-PbO_2-type seifertite eventually [11].

Multiple transformation pathways of coesite at high pressure strongly depend on hydrostatic pressure and stress gradient in the sample chamber. Pressure-induced crystalline-to-crystalline transitions and amorphization result from structural distortion intrinsically and are embodied in elastic instability macroscopically associated with phonon instability [18, 19]. The pressure-induced structural modulations in coesite along its b-axis have been demonstrated to result from phonon instability along the Γ–Y direction of the Brillouin zone [14]. Despite its obvious significance, not much is reported about the single-crystal elasticity of coesite at high pressure, since experimental measurements on elastic constants of coesite with a monoclinic structure are challenging at high pressure condition [20]. A theoretical study on elasticity of coesite up to 15 GPA indicates that coesite exhibits a gradual softening of elastic constant C_44 [21]. However, elasticity of coesite at higher pressure (above 15 GPA) has not yet been depicted calling for further theoretical investigations. First-principles calculations based on density functional theory (DFT) provide an alternative method to study crystal structures and single-crystal elasticities of coesite and its high-pressure polymorph coesite-II at high pressure.

In this study, we perform first-principles calculations of structural relaxations and stress–strain relationships on coesite and coesite-II at high pressures based on DFT. Unit-cell parameters, equation of

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**Figure 1.** Unit-cell parameters of coesite and coesite-II at high pressures. b/2 of coesite-II is calculated and plotted. Literature results from single-crystal x-ray diffraction experiments are plotted for comparison. Solid circles represent coesite and open circles coesite-II. Solid lines are the modified 3rd Birch–Murnaghan equation of state fits through our theoretical data [30].
states, and full sets of elastic constants of two phases are reported and discussed. Structural characteristics, elastic properties, and mechanical stabilities of coesite and coesite-II phases at high pressure, and their relationships to the phase transition between two phases are also discussed in detail. Pressure-induced transition mechanism of coesite is clarified theoretically. These results can shed light on the densification mechanism of silica phases at high pressure.

2. Computational methods

First-principles calculations based on DFT are performed using the Vienna *ab initio* simulation package [22, 23]. The interaction between ions and electrons is described by the projector augmented-wave method [24]. The Ceperley–Alder exchange correlation potential of the local density approximation (LDA) parametrized by Perdew and Zunger is selected [25, 26]. The kinetic energy cut-off is set to 1000 eV and the energy convergence criterion is $10^{-6}$ eV for both coesite and coesite-II phases. The Monkhorst–Pack scheme is used for Brillouin zone sampling [27]. The $k$-points grids are set to $4 \times 2 \times 4$ for coesite and $4 \times 1 \times 4$ for the high-pressure polymorph coesite-II.

Structural relaxations are performed at various unit-cell volumes for coesite and coesite-II phases, where unit-cell parameters and atomic positions are allowed to relax to obtain the minimum total energy. The obtained minimum total energies at different volumes are fitted to the 3rd Eulerian finite strain equation to obtain unit-cell volume ($V_0$), bulk modulus ($K_0$), its pressure derivative ($K_0'$), and energy ($E_0$) at zero pressure [28]. Based on the stress–strain relationships, single-crystal elastic constants ($C_{ij}$) of coesite and coesite-II are calculated. The internal stress in the strained lattice is calculated for two phases by applying positive and negative strains of magnitude of 0.0125. The lattice is deformed with strains in different directions, corresponding to certain elastic constants, and then atomic coordinates are allowed to relax. The crystal structures of coesite and coesite-II are both monoclinic, thus there are 13 independent elastic constants depends on structural symmetry: $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$, $C_{23}$, $C_{15}$, $C_{25}$, $C_{35}$, and $C_{46}$ [29].

3. Results and discussion

3.1. Equation of states and crystal structures

The phase transition of coesite to coesite-II is characterized by the change of structural symmetry from $C2/c$ ($Z = 16$) to $P2_1/c$ ($Z = 32$) (or $P2_1/n$, the same structure but in different setting) and demonstrated experimentally and theoretically [14, 15]. $P2_1/n$ cell setting can be transformed to $P2_1/c$ cell setting by the matrix (100 0 10 0 10 0 10 0 1). In this work, we employed structural models of coesite in $C2/c$ and coesite-II in $P2_1/c$ standard setting for calculations of structural relaxations and elastic constants. The relative enthalpies of coesite and coesite-II are compared in figure S1 (https://stacks.iop.org/NJP/22/093044/mmedia) of the supplementary material. Coesite-II phase has almost identical enthalpy to that of coesite below 15 GPa. Above 15 GPa, coesite-II phase becomes thermodynamically stable over coesite as suggested by its relatively lower enthalpy. The enthalpy difference between coesite and coesite-II increases with increasing pressure,
although the difference is quite small ranging from −0.014 eV/f.u. at 20 GPa to −0.094 eV/f.u. at 35 GPa.

These results provide theoretical support for the phase transition from coesite to coesite-II. For better compare the evolution of unit-cell parameters under pressure with previous experimental results, the obtained coesite-II in P2₁/c setting has been transformed to that in P2₁/n setting as proposed by Černok et al. [15]. Unit-cell parameters of coesite and coesite-II phases at high pressure are plotted in figures 1 and 2 (table S1) and literature experimental results are also plotted for comparison [10, 15, 16]. Compared with experimental data, the LDA calculations generally underestimate unit-cell parameters because of overbinding, zero-point motion and temperature difference. The pressure evolution of unit-cell distances with increasing pressure agrees well with previous experimental results [15]. The smaller Si–O–Si bond angles, Si5–O4–Si7 and Si2–O15–Si3, in coesite-II (figure 3). As demonstrated experimentally, the extreme compression of the shortest Si1–O1 bond (∼1.54 Å at 20–25 GPa) drives the bend of the Si1–O1–Si1 angle. Interestingly, the Si5–O4–Si7 angle (∼177° at 20–25 GPa) in coesite-II is very close to 180° of Si1–O1–Si1 angle in coesite, while the Si2–O15–Si3 angle decreases by 27°–153° at 20 GPa. On the other hand, the lengths of Si5–O4 and Si7–O4 bonds in coesite-II are close to the Si1–O1 bond length in coesite, whereas the Si2–O15 and Si3–O15 lengths are much longer than the Si1–O1 distance.

Thus, phase transition of coesite to coesite-II is associated with bend of the Si2–O15–Si3 angle and elongation of the Si2–O15 and Si3–O15 bonds, resulting in the commensurate modulation along the b-axis direction [14].

With increasing pressure, the Si2–O15–Si3 angle in coesite-II decreases monotonically (∼138° at 35.2 GPa), while the Si5–O4–Si7 angle changes very little (177.6–175.6° at 20–35.2 GPa) and remains close to linear (figure 4(a)). On the other hand, the Si–O distances associated with O4 and O15 also exhibit different pressure evolution. The lengths of Si5–O4 and Si7–O4 in coesite-II decrease gradually with increasing pressure, while the Si2–O15 and Si3–O15 lengths experience relatively small change (figure 4(b)). The pressure evolution trends of Si5–O4–Si7 and Si2–O15–Si3 angles and corresponding Si–O distances shall result in further structural distortion of coesite-II along the b-axis direction, then probably drive a structural modulation in this direction and eventually amorphization as proposed experimentally [14]. Bend of Si–O–Si bond angle and reduction of Si–O bond length at elevated pressure seem to be dominant mechanisms of compression in coesite.

### Table 1. Bulk modulus and its derivative of coesite from this study and previous experimental results.

|            | This study | Angel et al. 2001 [12] | Černok et al. 2014 [15] |
|------------|------------|------------------------|------------------------|
| $K_0$ (GPa) | 87.4(6)    | 93.2(5)                | 95.0(6)                |
| $K_0'$     | 4.96(7)    | 4.3(fixed)             | 4.1(fixed)             |

Energy–volume results from LDA calculations are fitted to the 3rd Eulerian finite strain equation [28],

$$E(V) = E_0 + \frac{9V_0K_0}{16} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 K_0' + \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right],$$

yielding bulk modulus $K_0 = 87.4 \pm 0.6$ GPa and its derivative $K_0' = 4.96 \pm 0.07$ for coesite; $K_0 = 93.7 \pm 1.6$ GPa and $K_0' = 2.53 \pm 0.10$ for coesite-II. The derived equation of state parameters indicate that coesite-II is more compressible than coesite. The energy–volume data from this study are also fixed using experimental $K_0$' [12, 15]. $K_0$ and $K_0'$ are shown in table 1. The bulk modulus of coesite from our DFT calculations is comparable to experimental results considering the trade-off between bulk modulus and its derivative.

The phase transition from coesite to coesite-II is associated with a doubling of the cell parameter along the b-axis. Correspondingly, coesite-II phase has a doubled unit-cell volume and number of formula units. A detailed analysis of structural information based on our DFT calculations is necessary to discuss mechanism of this phase transition. As for coesite, the evolution of Si–O–Si bond angles and Si–O distances with increasing pressure agrees well with previous experimental results [15]. The smaller Si–O–Si bond angle is more compressible and the Si1–O5–Si2 angle is the most compressible. The shortest Si1–O1 bond is the most compressible (figure S3 and table S2). The Si1–O1–Si1 bond angle in coesite is constrained to be 180° due to symmetry requirements. It bends after phase transition, resulting in four non-equivalent Si atoms connected by two non-equivalent O atoms, thus forming two independent bond pairs, Si5–O4–Si7 and Si2–O15–Si3, in coesite-II (figure 3). As demonstrated experimentally, the extreme compression of the shortest Si1–O1 bond (∼1.54 Å at 20–25 GPa) drives the bend of the Si1–O1–Si1 angle. Interestingly, the Si5–O4–Si7 angle (∼177° at 20–25 GPa) in coesite-II is very close to 180° of Si1–O1–Si1 angle in coesite, while the Si2–O15–Si3 angle decreases by 27°–153° at 20 GPa. On the other hand, the lengths of Si5–O4 and Si7–O4 bonds in coesite-II are close to the Si1–O1 bond length in coesite, whereas the Si2–O15 and Si3–O15 lengths are much longer than the Si1–O1 distance.

Thus, phase transition of coesite to coesite-II is associated with bend of the Si2–O15–Si3 angle and elongation of the Si2–O15 and Si3–O15 bonds, resulting in the commensurate modulation along the b-axis direction [14].
3.2. Single-crystal elastic constants

Based on our calculations of stress–strain relationships, we obtain single-crystal elastic constants \((C_{ij})\) of coesite from 0 to 30 GPa, and \(C_{ij}\) of coesite-II from 20 to 35.2 GPa (figure 5 and table S3). Both coesite and coesite-II are monoclinic with the same independent elastic constants plotted together in figure 5. The experimental values at ambient conditions from Brillouin scattering measurements [20] and previous theoretical results from DFT calculations [21] are included in table S3 for comparison. Our obtained elastic constants of coesite at pressures 0–15 GPa agree well with theoretical data reported by Kimizuka et al [21]. They also illustrated the deviation of \(C_{ij}\) (especially \(C_{12}, C_{13}, \) and \(C_{44}\)) at zero pressure between theoretical
Figure 5. Thirteen independent elastic constants ($C_{ij}$) of coesite and coesite-II at high pressures. Solid circles represent coesite and open circles coesite-II.

and experimental values [20]. The elastic constants $C_{11}$, $C_{22}$, and $C_{33}$ reflect the stiffness to axial compression strains along the $a$-, $b$-, and $c$-axes, respectively. The calculated results indicate that $C_{22} > C_{33} > C_{11}$ for coesite (figure 5(a)), suggesting that the $a$-axis of coesite is more compressible than the $b$- and $c$-axes. This result is consistent with the conclusion drawn from the analysis of axial compressibility. The elastic constants $C_{44}$, $C_{55}$, and $C_{66}$, which reflect the stiffness to shear strains along the $b$-axis, the $c$-axis, and the $a$-axis direction, respectively, are smaller than $C_{11}$, $C_{22}$, and $C_{33}$, indicating that coesite is stiffer to axial compression strain than to shear strain.

With increasing pressure to 30 GPa, the elastic constants $C_{11}$, $C_{22}$, $C_{33}$, $C_{12}$, $C_{13}$, $C_{23}$, $C_{15}$, $C_{35}$, and $C_{55}$ of coesite increase significantly, whereas $C_{25}$, $C_{44}$, $C_{46}$, and $C_{66}$ exhibit elastic softening. $C_{25}$ and $C_{66}$ remain positive up to 30 GPa, but $C_{44}$ and $C_{46}$ tend to zero above 22.5 GPa. The gradual softening of $C_{44}$ with pressure up to 15 GPa is also reported theoretically by Kimizuka et al [21]. According to elastic stability criteria [31, 32], the diagonal components, $C_{ii}$, of the conventional elastic constant matrix must be positive for stability, the off-diagonal elements, $C_{ij}$ ($i \neq j$) need not be. The feature of $C_{44}$ tending to zero above 22.5 GPa indicates that coesite exhibits elastic instability and may undergo phase transition beyond this pressure. More often than not, not an individual elastic constant but a combination of elastic constants determines whether an elastic softening or instability develops. Thus, it is essential to discuss the elastic stability limit of monoclinic coesite, $B_1 = C_{44}C_{66} - C_{46}^2 > 0$, at high pressure [31]. Figure 6(a) shows the theoretical pressure dependence of elastic stability limits $B_1$ of coesite and coesite-II. $B_1$ of coesite decreases with increasing pressure and tends to zero above 22.5 GPa. Elastic softening and tendency to zero of $C_{44}$ and $B_1$ are related to shear strains $e_4$ or $e_6$, and it is $e_4$ in this case for coesite. Essentially, the elastic instability of coesite is correlated with its structural distortion along the $b$-axis direction under pressure discussed above, since the elastic constant $C_{44}$ reflects the stiffness to shear strain along the $b$-axis.

Elastic instabilities are related to macroscopic stresses and strains, while intrinsically, the elastic constants are associated with the velocities of acoustic waves. Anomalous variations in the elastic properties are necessarily accompanied by anomalies in the behavior of the acoustic phonons [31]. If an individual elastic constant, or a combination of elastic constants, softens to zero beyond the transition point, the velocity of a related acoustic phonon, the soft acoustic mode, will also tend to zero. We discuss the behavior
Figure 6. (a) Elastic stability limit and (b) soft acoustic mode of coesite and coesite-II at high pressures. Solid circles represent coesite and open circles coesite-II.

of the soft acoustic mode in coesite and coesite-II, as shown in figure 6(b). For monoclinic class, the relation is

$$\rho V^2 = \frac{1}{2} \left\{ (C_{44} + C_{66}) - \left[ (C_{44} - C_{66})^2 + 4C_{46}^2 \right]^{1/2} \right\},$$

where $\rho$ is the density and $V$ is the velocity of soft acoustic mode [31]. We note that $\rho V^2$ of coesite decreases gradually with increasing pressure and tends to zero above 22.5 GPa. Similar trends have been noticed from elastic stability limit $B_i$ (figure 6(a)) and should be associated with the proper ferroelastic transition of coesite to coesite-II. The wave vector $\vec{q}$ and the displacement vector $\vec{u}$ of the soft acoustic mode are restricted to specific directions: $\vec{q} \parallel [010]$, $\vec{u} \perp [010]$ and $\vec{q} [31]$. The pressure points of elastic instability for coesite in this study and phonon instability from our previous theoretical calculations agree very well with the experimental transition pressure from coesite to coesite-II [14].

We also analyze elastic stability of coesite-II under high pressure. At pressure above 37 GPa, the crystal structure after structural relaxation is unstable with the starting model of coesite-II, thus, the corresponding elastic constants of coesite-II based on structural relaxations are only calculated up to ~35 GPa. With increasing pressure, the elastic constants $C_{11}$, $C_{33}$, $C_{13}$, $C_{23}$, $C_{15}$, and $C_{25}$ of coesite-II increase significantly, whereas $C_{22}$, $C_{35}$, $C_{66}$, and $C_{55}$ soften gradually and $C_{33}$ and $C_{44}$ change little. In particular, $C_{66}$ exhibits a trend to zero above 35 GPa. The calculated elastic stability limit ($B_i$ in figure 6(a)) of coesite-II decreases with increasing pressure and tends to zero above 35 GPa. Correspondingly, $\rho V^2$ for the soft acoustic mode of coesite-II decreases gradually with increasing pressure and tends to zero above 35 GPa (figure 6(b)). Likewise, the wave vector ($\vec{q}$) of the soft acoustic mode is parallel to the special [010] direction and perpendicular to its displacement vector ($\vec{u}$) [31]. The elastic softening and tendency to elastic instability of coesite-II above 35 GPa should be related to its structural modulation along the $b$-axis above ~36 GPa observed experimentally [14].

It is also noteworthy that the directions of the soft acoustic modes associated with elastic stability limits of coesite and coesite-II are consistent with the direction of phonon instability (the $\Gamma$–$Y$ direction of the Brillouin zone) proposed in our previous study [14]. The phase transition of coesite to coesite-II results from phonon instability intrinsically and is accompanied by elastic instability with $e_4$ as the symmetry-breaking strain. Additionally, phonon instability and associated elastic softening of coesite-II provide theoretical evidence for its structural modulation along the $b$-axis above ~36 GPa.
3.3. Elastic moduli and velocities

We calculate the isotropic aggregate compressional (P) and shear (S) wave velocities of coesite and coesite-II by following relations:

\[ V_P = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} \quad \text{and} \quad V_S = \sqrt{\frac{G}{\rho}}, \]

where \( \rho \) is the density; \( K \) and \( G \) are the isotropic bulk and shear moduli, respectively, taken from the Voigt–Reuss–Hill approximation theory [33] (figure 7). The isotropic bulk modulus of coesite is predicted to depend strongly on pressure, and it increases systematically with increasing pressure. However, the shear modulus of coesite is nearly independent of pressure and changes very little under pressure. Correspondingly, the compressional wave velocity of coesite increases steadily under high pressure. But, the shear wave velocity exhibits a decreasing tendency with increasing pressure. Our theoretical data are consistent with experimental results from ultrasonic measurements [34]. The decrease of shear wave velocity in coesite is associated with the shear modulus, and intrinsically results from the softening of elastic constants discussed in above section (3.2 single-crystal elastic constants). The anomaly of shear wave velocity is often followed by phase transition or amorphization with further increasing pressure [35–37]. It has been demonstrated that coesite undergoes a structure transition to coesite-II at pressure \( \sim 22 \) GPa. According to our calculations, the isotropic bulk modulus of coesite-II is smaller than that of coesite at the same pressure 20 GPa. This indicates that coesite-II is more compressible than coesite. Consequently, the compressional wave velocity of coesite-II is smaller than that of coesite at 20 GPa. Both shear modulus and shear velocity change little across the phase transition. With further pressure increase, the shear modulus and shear velocity of coesite-II decrease further. The reason is the softening of elastic constants for coesite-II under high pressure discussed above.

3.4. Mechanical stability

The calculated elastic constants of coesite at 0 GPa satisfy the mechanical stability criteria for a monoclinic phase [32, 38]:

\[ C_{ii} > 0 \quad (i = 1, 2, 3, 4, 5, 6), \quad B_2 = C_{11} + C_{22} + C_{33} + 2 (C_{12} + C_{13} + C_{23}) > 0, \]
Both coesite and coesite-II exhibit elastic softening under high pressure. Elastic instability of coesite under pressure comes from both structural features and elastic effect. Calculations in this study demonstrate that the driving mechanism for the transition pathways of coesite become negative. The pressure point of mechanical instability for coesite is in excellent agreement with the phase transitions or amorphization.

If use $C_{ij}$ instead of $\tilde{C}_{ij}$, the criteria of mechanical stability remain valid at high pressure [39]. All conditions given above must be simultaneously satisfied for the structure to be mechanically stable. Tables S4 and S5 list $C_{ij}$ and calculated mechanical stability criteria ($B_2$–$B_7$) of coesite and coesite-II at high pressures. Based on the calculations, the coesite structure becomes mechanically unstable at pressure above 22.5 GPa, as $C_{14}$ and $B_4$ become negative and the mechanical stability criteria get violated. And the coesite-II structure becomes mechanically unstable at pressure about 35 GPa, because $C_{66}$, $B_4$, $B_5$, and $B_7$ become negative. The pressure point of mechanical instability for coesite is in excellent agreement with the experimental transition pressure from coesite to coesite-II [15]. Also, the mechanical instability of coesite-II at ~35 GPa should be correlated with its phonon and elastic softening, indicating further high-pressure phase transitions or amorphization.

For elastic constants at high pressure ($P \neq 0$), Sin’ko and Smirnov [39] derived the pressure-dependent elastic constants $\tilde{C}_{ij}$ as follows:

$$\tilde{C}_{11} = C_{11} - P; \quad \tilde{C}_{22} = C_{22} - P; \quad \tilde{C}_{33} = C_{33} - P; \quad \tilde{C}_{44} = C_{44} - P; \quad \tilde{C}_{55} = C_{55} - P; \quad \tilde{C}_{66} = C_{66} - P,$$

$$\tilde{C}_{12} = C_{12} + P; \quad \tilde{C}_{13} = C_{13} + P; \quad \tilde{C}_{23} = C_{23} + P; \quad \tilde{C}_{15} = C_{15}; \quad \tilde{C}_{25} = C_{25}; \quad \tilde{C}_{35} = C_{35}; \quad \tilde{C}_{46} = C_{46}.$$

If use $\tilde{C}_{ij}$ instead of $C_{ij}$, the criteria of mechanical stability remain valid at high pressure [39]. All conditions given above must be simultaneously satisfied for the structure to be mechanically stable. Tables S4 and S5 list $C_{ij}$ and calculated mechanical stability criteria ($B_2$–$B_7$) of coesite and coesite-II at high pressures. Based on the calculations, the coesite structure becomes mechanically unstable at pressure above 22.5 GPa, as $C_{14}$ and $B_4$ become negative and the mechanical stability criteria get violated. And the coesite-II structure becomes mechanically unstable at pressure about 35 GPa, because $C_{66}$, $B_4$, $B_5$, and $B_7$ become negative. The pressure point of mechanical instability for coesite is in excellent agreement with the experimental transition pressure from coesite to coesite-II [15]. Also, the mechanical instability of coesite-II at ~35 GPa should be correlated with its phonon and elastic softening, indicating further high-pressure phase transitions or amorphization.

4. Conclusions

Phase transitions in materials are governed by a diversity of compressional mechanisms. Theoretical calculations in this study demonstrate that the driving mechanism for the transition pathways of coesite under pressure comes from both structural features and elastic effect.

(a) Both coesite and coesite-II undergo structural distortions along the $b$-axis direction with increasing pressure. The extreme shortening of the shortest and the most compressible Si1–O1 bond in coesite structure results in the phase transition of coesite to coesite-II. The Si1–O1–Si1 angle restricted to be 180° in coesite bends after phase transition, forming two independent bond angles (Si5–O4–Si7 and Si2–O1–Si2) in coesite-II. Different pressure evolutions of two Si–O–Si angles and corresponding four Si–O bond distances in coesite-II indicate that the crystal structure distorts along its $b$-axis with increasing pressure. Further structural modulations along the $b$-axis direction may occurs just as observed experimentally.

(b) Both coesite and coesite-II exhibit elastic softening under high pressure. Elastic instability of coesite above 22.5 GPa derives from a combination of elastic constants $C_{14}$ and $C_{46}$. The wave vector of soft acoustic mode related to elastic instability is along the special [010] direction. This is consistent with the direction of phonon instability (the $\Gamma$–$Y$ direction of the Brillouin zone) proposed in our previous study. Elastic and phonon instabilities of coesite along the special direction provide theoretical evidence for the phase transition of coesite to coesite-II. Likewise, elastic softening in coesite-II is found associated with the softening of acoustic mode along the [010] direction. This may trigger structural modulation of coesite-II along the $b$-axis as proposed experimentally.

To sum up, coesite exhibits dynamical instabilities, elastic instabilities, and mechanical instabilities at pressures above 22.5 GPa, indicating that it will undergo phase transition at high pressure. Either various pressure-induced crystalline-to-crystalline transitions or amorphization results from structural distortion intrinsically and is embodied in elastic instability macroscopically associated with phonon instability. Theoretical calculations in this study help us build up links among structural characteristics, elastic properties, and pressure-induced phase transitions or structural modulations of coesite and coesite-II.
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