Hardness of polycrystalline SiO$_2$ coesite

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Abstract
We measured elastic moduli and hardness of polycrystalline SiO$_2$ coesite. Translucent polycrystalline bulk coesite with a grain size of about 10 micrometers was fabricated at 8 GPa and 1600°C using a Kawai-type multianvil apparatus. The obtained bulk and shear moduli are 94(1) and 60.2(3) GPa, respectively. The resulting Vickers and Knoop hardness values are 10.9(7) and 9.6(4) GPa, respectively, at an indentation load of 4.9 N. Coesite is as hard as other fourfold coordinated silica materials such as quartz and densified silica glasses. The hardness values of coesite and the fourfold coordinated silica materials are about one-third of those of sixfold coordinated silica materials, stishovite, and seifertite, which are the hardest known oxides.

KEYWORDS
coesite, elastic properties, hardness, mechanical properties, silicates, ultrasonic

1 | INTRODUCTION

Silicon dioxide (SiO$_2$, silica) is the most abundant oxide on the Earth’s surface and this material is heavily used in industry.$^1$ Quartz is used as a crystal oscillator and silica glasses are used as optical components such as lenses and optical fibers. Thus, mechanical properties of quartz and silica glasses including densified silica glasses$^2$ have been extensively studied previously.$^3$

Silica is known to transform to various high-pressure polymorphs with increasing pressure. Quartz is the thermo-dynamically stable phase at ambient conditions and transforms into coesite$^4$ and then stishovite$^5$ with pressure. The quartz-coesite and coesite-stishovite phase boundaries are located at 2-3 and 9-10 GPa, respectively.$^6,7$ All silica phases that are formed below the coesite-stishovite phase boundary$^7$ are composed of SiO$_4$ tetrahedra in which a silicon atom is coordinated by four oxygen atoms (coordination number (CN) of Si is four), whereas stishovite and other high-pressure polymorphs$^8-10$ that are experimentally obtained at pressures higher than this phase boundary are composed of SiO$_6$ octahedra (CN of Si is equal to six). Stishovite, which has the rutile structure, is the hardest known oxide.$^{11}$ The reported Vickers hardness is 29-33 GPa (Ref. 11, 12), which is much higher than those of alumina$^{13}$ and tungsten carbide. It is also known that seifertite$^{14}$ which crystallizes into $\alpha$-PbO$_2$ structure at pressure and temperature conditions higher than 120 GPa and 2200 K (Ref. 9) is as hard as stishovite.$^{15}$

Although mechanical properties of quartz, silica glasses, and the sixfold coordinated high-pressure phases have been extensively studied, knowledge of the mechanical properties of coesite, which has the highest density as a fourfold coordinated silica, has been very limited. Mukhanov et al.$^{16}$
exponentially measured and theoretically calculated the hardness values of coesite to be 20 and 20.8 GPa, respectively, which are comparable to that of alumina.13 More recently, Rakitin et al.17 computed the hardness of coesite and reported two different hardness values of 8.4 and 22.3 GPa by employing the Chen-Niu18 and Lyakhov-Oganov19 models, respectively. This large inconsistency can be explained by different concepts of the models. The latter model is based on microscopic characteristics such as bond strengths and bond topology of the crystal structure. In contrast, the Chen-Niu model is based on the empirical relation between hardness and elastic moduli. The high hardness of coesite by the Lyakhov-Oganov model is attributed to the strong chemical bonding of SiO4 polyhedra. One should also note that the theoretical models do not take the microstructure (e.g., grain size) into account. For these reasons, new experimental data for the hardness of coesite are required.

In this study, we fabricated translucent polycrystalline bulk coesite from pure synthetic silica glass. Using these materials, we measured the density, elastic moduli, and hardness of coesite.

2 | EXPERIMENTAL METHODS

A polycrystalline coesite sample was fabricated at a pressure of 8 GPa and a temperature of 1600°C by the direct conversion from a glass rod (4 mm in diameter and 2 mm in height) made of high-purity synthetic fused silica with OH content less than 1 ppm (SK-1310, Ohara Co., Ltd., Wakayama, Japan). The trace content of other impurities in this starting glass does not exceed 0.01 ppm. The sample fabrication was performed in a Kawai-type multianvil apparatus with a Walker module (mavo press LPR 1000-400/50; Max Vogenreiter GmbH, Mainleus, Germany) installed in Deutsches Elektronen-Synchrotron (DESY), Germany. Tungsten carbide cubes with a truncated edge length (TEL) of 11 mm were used as second stage anvils. We used a Cr-doped MgO octahedron with an edge length of 18 mm as a pressure-transmitting medium. Details of the high-pressure cell assembly were described elsewhere.20 In order to remove absorbed moisture, the whole cell assembly and the starting glass were dried in an oil-free vacuum oven at 8 hPa and 150°C for more than 2 hours before high-pressure and -temperature (high-PT) treatment. During the high-PT treatment, pressure was applied first, and then temperature was gradually increased to the target value. Generated pressure and temperature were estimated using calibrated load-pressure and power-temperature relations.20 After maintaining high-PT conditions (8 GPa and 1600°C) for 1 hour the sample was quenched and decompressed over 12 hours. Then, we recovered the sample at ambient conditions. The second polycrystalline coesite sample was fabricated using the same method to confirm the reproducibility. Densities of the recovered samples were measured using Archimedes principle.

X-Ray diffraction (XRD) measurements for the surfaces of the recovered bulk samples were performed using a benchtop diffractometer with Cu-Kα radiation (MiniFlex600, Rigaku Co. Ltd., Akishima, Japan). High-resolution synchrotron XRD measurements were also carried out for the powdered sample. A small piece of the second sample was ground into a powder using an alumina mortar and pestle. Details of the measurements are given elsewhere.20

In order to measure mechanical properties, the top and bottom surfaces of a recovered sample were polished using diamond pastes down to 1 μm particle size. Compressional and shear wave velocities (Vp and Vs, respectively) were measured by the ultrasonic pulse-echo method using the setup installed in BL04B1, SPring-8, Japan. A LiNbO3 transducer (10° rotated Y-cut) was employed for the measurements, which enables us to measure Vp and Vs simultaneously. A tungsten carbide buffer rod was used.

Both, Vickers and Knoop hardness (HV and HK, respectively) were measured using a microhardness indenter (HM-221; Mitsutoyo, Kawasaki, Japan) installed in DESY, Germany. A hardened steel standard block with 900 HV was employed. Three measurements were made at six different indentation loads of 0.49, 0.98, 1.96, 2.94, 3.92, and 4.9 N. HV and HK values in GPa were calculated using the following equations, respectively: 

\[ H_V = \frac{1854.4Pd}{L^2} \]

\[ H_K = \frac{14229Pd}{L^2} \]

where P is the applied load (N), d is the arithmetic mean of the two diagonals (μm) of a Vickers indentation trace, and L is length of the longer diagonal (μm) of a Knoop indentation trace. The holding time under indentation loads was 15 seconds.

A thin section was prepared from a representative sample for grain size determination and microstructure observations by polarized light microscopy. The observations were carried out using an optical microscope (BX51; Olympus, Tokyo, Japan) installed in DESY.

3 | RESULTS

Figure 1A shows a photograph of a starting silica glass and a recovered translucent sample. A powder XRD pattern of the recovered sample (Figure 1B) demonstrates that the fabricated material is single-phase polycrystalline bulk coesite. The XRD pattern obtained from the bulk sample (Figure S1) indicates that the recovered sample is a randomly oriented polycrystalline bulk material. As it can be seen in Figure 1A, the recovered sample is smaller than the starting glass. This volume reduction is attributed to the fact that the density of coesite (2.92 g/cm³, Ref. 21) is more than 30% higher than that of silica glass (2.20 g/cm³). No
visible cracks or voids were observed in the polycrystalline coesite (Figure 1A). The density value ($\rho$) of this sample measured by Archimedes method is 2.922(5) g/cm$^3$, which agrees to the theoretical density of coesite. This result suggests that the obtained translucent material is pore-free polycrystalline bulk coesite.

Figure 1C and D show optical micrographs of a thin section of the second sample. We observed that polycrystalline coesite exhibits an equigranular texture with an average grain size of ~10 $\mu$m (Figure 1C). We also observed the presence of a few larger grains (>50 $\mu$m) near the surfaces of the coesite sample. This abnormal grain-growth might be related to the formation process of polycrystalline bulk coesite from silica glass via densified silica glass. Masuno et al. reported that density of densified silica glass fabricated at 7.7 GPa and 1200°C is higher than that of $\alpha$-quartz and that the atomic arrangement may be similar to that of coesite. Heterogeneous nucleation of coesite might occur preferentially at the interfaces between the densified glass and the sample capsule.

Results of sound velocity measurements are summarized in Table 1. The present compressional ($V_P$) and shear ($V_S$) velocities as well as derived bulk ($K$) and shear ($G$) moduli show reasonable agreements with results of previous studies. Using the obtained $K$ and $G$, we calculated Young's modulus and Poisson's ratio to be 148.8(7) and 0.24(3) GPa, respectively. These experimental data ensure that the recovered translucent samples are single-phase polycrystalline bulk coesite.

Figure 2A shows indentation load dependences of $H_V$ and $H_K$ of the polycrystalline bulk coesite. The values of $H_V$ are almost independent of applied load, while those of $H_K$ decrease with increasing indentation load. The $H_V$ and $H_K$ values at the maximum indentation load of 4.9 N are 10.9(7) and 9.6(4) GPa, respectively. These values are lower than those experimentally measured and theoretically calculated by Mukhanov et al. Since the main purpose of this previous study was the establishment of a model predicting hardness values of materials from their physical properties, only an experimentally measured hardness value of coesite was listed in a table and no further detail.
regarding the hardness measurement is given in their study. On the other hand, the present hardness values are similar to one reported by Rakitin et al.\textsuperscript{17} where they used Chen-Niu\textsuperscript{18} model based on elastic moduli. When we applied $K$ and $G$ values determined in this study to this model, we obtained a value of $H_v = 10.1(2)$ GPa, which agrees with our measured value within experimental errors.

Figures 2B and C show micrographs of Vickers ($H_v$) and Knoop ($H_k$) hardness of polycrystalline bulk coesite as a function of applied indentation load. Optical photographs (reflective light) of representative (B) Vickers and (C) Knoop indentation traces at applied loads of 3.92 N and 4.9 N, respectively [Color figure can be viewed at wileyonlinelibrary.com]

Figures 2 and 3 show the relationship between normalized density ($\rho/\rho_0$) and Young’s modulus of various silica materials. (A) The relationship between normalized density ($\rho/\rho_0$) and Young’s modulus. (B) The relationship between Young’s modulus and hardness. There is a huge gap between the mechanical properties of fourfold and sixfold coordinated silica materials (indicated by the blue and orange areas, respectively) [Color figure can be viewed at wileyonlinelibrary.com]

Tables 1 and 2 provide sound velocities and elastic moduli of coesite in comparison with results of previous studies.

### Table 1: Sound Velocities and Elastic Moduli of Coesite

<table>
<thead>
<tr>
<th>Method</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$V_p$ (km/s)</th>
<th>$V_s$ (km/s)</th>
<th>$K$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic</td>
<td>2.922 (5)</td>
<td>7.72 (2)</td>
<td>4.54 (1)</td>
<td>94 (1)</td>
<td>60.2 (3)</td>
<td>This study</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>2.92 (2)</td>
<td>7.97 (1)</td>
<td>4.59 (1)</td>
<td>103.6 (4)</td>
<td>61.6 (2)</td>
<td>23</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>2.92$^a$</td>
<td>7.96</td>
<td>4.53</td>
<td>105.1</td>
<td>59.9</td>
<td>Lieberman (1976) see 25</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>2.92$^a$</td>
<td>7.53</td>
<td>4.19</td>
<td>97.2</td>
<td>51.3</td>
<td>24</td>
</tr>
<tr>
<td>Brillouin Scattering$^b$</td>
<td>2.92$^a$</td>
<td>8.19</td>
<td>4.59</td>
<td>113.7</td>
<td>61.6</td>
<td>25</td>
</tr>
<tr>
<td>DFT$^c$</td>
<td>2.96</td>
<td>7.57</td>
<td>4.32</td>
<td>95.9</td>
<td>55.2</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$Theoretical densities.

$^b$Upper and lower values correspond to VRH average from the best and alternate models, respectively.

$^c$Performed for the coesite structure at $T = 0$ K and $P = 0$ GPa. Elastic moduli calculated as VRH average of the elasticity tensor published in Ref. 26.
Figure 3A shows the relationship between the normalized density ($\rho/\rho_0$) and Young's modulus of a series of silica materials\textsuperscript{3,27-32} including coesite. We employed the density of silica glass (2.20 g/cm$^3$) as the reference density ($\rho_0$) to calculate $\rho/\rho_0$ values. In this diagram, the silica materials are divided into two groups. The first group consists of fourfold coordinated silica materials with density of 2.2–2.9 g/cm$^3$. We can see that Young's modulus increases fourfold with density. Coesite is the densest and the elastically stiffest in this group. There is a huge gap between the first and the second group that consists of sixfold coordinated silica materials (stishovite and seifertite). The density increase from coesite to stishovite reaches $\sim$47% and the Young's modulus of stishovite is more than three times larger than that of coesite.

A similar tendency can be seen in Figure 3B showing the relationship between Young's modulus and Vickers hardness.\textsuperscript{3,15,27-35} In the first group, Vickers hardness values are distributed in a narrow range of 10.0 ± 2.5 GPa and coesite is as hard as other fourfold coordinated silica materials. In previous studies, hardness values of quartz were measured using single crystals and the reported values vary from 8.2 to 12.1 GPa (Ref. 33-35). This variation in quartz hardness can be attributed to the crystallographic orientation dependence of quartz hardness. The hardness of silica glasses increases with the degree of permanent densification. Densified silica glasses with densification more than 20% are as hard as coesite. On the other hand, stishovite and seifertite are about three times harder than coesite. The results of this study demonstrate that there is a huge gap between the mechanical properties of four and sixfold coordinated silica materials.

5 | CONCLUSIONS

Translucent polycrystalline bulk coesite materials were fabricated at a pressure of 8 GPa and a temperature of 1600°C. Using these materials, elastic moduli, $H_V$ and $H_K$ of polycrystalline bulk coesite were measured. The present experimental data demonstrate that coesite is as hard as other fourfold coordinated silica materials such as quartz and densified silica glasses. The hardness values of the fourfold coordinated silica materials are about one-third of those of sixfold coordinated silica materials, which are the hardest known oxides.

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REFERENCES


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