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Acoustic velocity measurements for stishovite across the post-stishovite phase transition under deviatoric stress: Implications for the seismic features of subducting slabs in the mid-mantle

Yuki ASAHARA*,†,‡, Kei HIROSE§, Yasuo OHISHI¶, Naohisa HIRAO®, Haruka OZAWA®, Motohiko MURAKAMI*

1Osaka University, Toyonaka 560-0043, Japan (*correspondence: asahara.y@m.tohoku.ac.jp)
2Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
3IFREE/JAMSTEC, Yokosuka, Kanagawa 237-0061, Japan
4JASRI/SPring-8, Sayo, Hyogo 679-5198, Japan
5Tohoku University, Sendai 980-8578, Japan

#Present address; Tohoku University, Sendai 980-8578, Japan
ABSTRACT

The acoustic velocity in polycrystalline stishovite across the post-stishovite phase transition was measured by Brillouin scattering in the pure SiO$_2$ system at room temperature under deviatoric stress. High-pressure synchrotron X-ray diffraction data were also collected at SPring-8. A linear fit to the symmetry-breaking strain values and the pressure of the transverse velocity minimum indicate a transition pressure between 25 and 35 GPa, which is about 20 GPa lower than that under hydrostatic conditions. The transverse velocity dropped by about 3% at around 25 GPa in this study. This is much smaller than the prediction from ab initio calculations that a transverse velocity reduces by approximately 60% at around 50 GPa under hydrostatic conditions. The results of the present study indicate that the deviatoric stress lowers transition pressure and reduces acoustic velocity change associated with the post stishovite phase transition. Sedimentary and mid ocean ridge basalt (MORB) layers in a subducting slab are likely sites for finding stishovite and its high-pressure polymorphs in the deep earth. Seismic observations of deep earthquakes occurring in subducting slabs indicate the existence of considerable stress in downgoing slabs. This study suggests that nonhydrostatic deviatoric stress is one of the possible reasons for the absence of general seismic features in subducting slabs corresponding to
1500 km depth that can be directly related to the post-stishovite phase transition. The phase
transition of stishovite under deviatoric stress, which occurs at shallower depths, can affect
the local seismic scattering structures and the rheological behavior of a subducting slab in
the mid-lower mantle region.

Keywords: HIGH PRESSURE STUDIES: stishovite, acoustic velocity, post-stishovite
transition, deviatoric stress, subducting slab
INTRODUCTION

Silica (SiO$_2$) is one of the major constituents of the earth’s crust, and significant amounts of silica and silicates are transported to the deep earth by subducting slabs. Stishovite, a six-coordinated high-pressure polymorph of silica, is considered to be an important constituent of subducted oceanic basalts and sediments in the earth’s deep interior. Stishovite exhibits the tetragonal rutile structure and transforms to the orthorhombic CaCl$_2$ structure above 50 GPa in the pure SiO$_2$ system (e.g., Tsuchida and Yagi 1989; Kingma et al. 1995; Andrault et al. 1998; Hemley et al. 2000; Andrault et al. 2003). This has been thought to be a classic displacive transition. According to theoretical models, the phase transition is triggered by the lattice instability of the soft transverse acoustic mode associated with the shear elastic constant; ($c_{11}$-$c_{12}$)/2. A strong change in elastic properties is expected across the transition (e.g., Cohen 1992). Karki et al. (1997) reported that the shear wave velocity ($V_3$) decreases by 60% and the anisotropy increases by a factor of five prior to the transition from the tetragonal rutile structure to the orthorhombic CaCl$_2$ structure based on athermal first-principle calculations. They reported that the post-stishovite phase transition may cause discontinuous change in the shear wave velocity. Conversely, using a
Landau free energy expansion, Carpenter et al. (2000) suggested that the variation in the transverse and longitudinal velocities might exhibit a dip instead of a discontinuity in the vicinity of the transitional pressure. For this considerable expected character, the nature of the post-stishovite phase transition has been the focus of much research in condensed-matter physics and earth science.

The reported values for the transition pressure widely ranges from 40 to 90 GPa. Such scattering possibly resulted from the difficulty in phase identification and the choice of pressure scales, and the effect of deviatoric stress. It is known that the deviatoric stress affects the phase transformation pressures of crystals (e.g., Akaogi and Akimoto 1977); in particular, the effect of deviatoric stress is considered to be strong for the post-stishovite phase transition. Dubrovinsky and Belonoshiko (1996), using molecular and lattice dynamics, suggested that deviatoric stress of about 1.5–2.5 GPa is sufficient to trigger structural transformation occurred at much lower pressures than that under hydrostatic conditions. Hemley et al. (2000) conducted high-pressure experiments using single-crystal stishovite in a hydrogen pressure medium and observed hysteresis of transition; the transition between stishovite and the CaCl₂-structured phase occurred at 58 GPa along the compression path and at 40 GPa along the decompression path. The hysteresis of transition
indicates weak first-order character, and it may indicate a finite value of C_{11}-C_{12} at
transition pressure. It is also possible that the hysteresis was a result of small deviatoric
stress remained in the sample. Andrault et al. (2003) conducted powder X-ray diffraction
experiments for SiO_2 up to 130 GPa using the laser annealing technique and a NaCl
pressure medium. They synthesized stishovite at around 12 GPa in the diamond anvil cell
and annealed the sample before conducting all measurements at 2300 K, and checked the
full width at half maximum (FWHM) of the X-ray diffraction lines to confirm whether the
stress was relaxed. They observed the transition pressure around 60 GPa. They also
suggested that the post stishovite transition is essentially second order from strain and
thermal energy analysis. Radial X-ray diffraction experiments and stress analyses across the
post-stishovite phase transition under nonhydrostatic compression were conducted by Shieh
et al. (2002). They used synthesized stishovite powder as a starting material and no pressure
medium. The differential stress of stishovite was observed to be 4.5 GPa below 40 GPa,
and was found to decrease in a pressure range of 40–50 GPa. They also observed that the
difference between the volumes obtained across the maximum and minimum strain axes
increased above 20 GPa. It indicates that lattice deformation of stishovite started around 20
GPa, although the differential stress in the sample reached a minimum around 50 GPa.
From inversion of measured lattice strains, they suggested that elastic instability occurs in stishovite near 50 GPa.

The elastic constants of stishovite were measured at ambient conditions (Weidner et al. 1982; Brazhkin et al. 2005), and up to 12 GPa (Jiang et al. 2009) by Brillouin spectroscopy. However, there are no experimental acoustic velocity data for pure stishovite across the transition. Lakshtanov et al. (2007) conducted simultaneous Brillouin scattering and synchrotron X-ray diffraction measurements for hydrous alumina-bearing stishovite across the post-stishovite transition. The transition pressure for stishovite with impurities of 6 wt% Al$_2$O$_3$ and 0.24 wt% H$_2$O dropped to approximately 25 GPa. The acoustic shear velocity near the [110] phonon direction decreased by approximately 11%. In this phonon direction, the elastic shear modulus should vanish approaching the transition pressure, i.e., $V_s$ becomes zero. The deviation from the [110] direction and the presence of impurities may be the reasons for the shear velocity not completely reaching zero at the transition pressure.

In this study, we measured acoustic velocities in pure, polycrystalline stishovite samples under nonhydrostatic conditions. In principle, acoustic velocity measurements under hydrostatic conditions should be performed to clarify the nature of the post-stishovite transition in the pure SiO$_2$ system. However, this is technically challenging and the
experimental pressure has been limited to 12 GPa (Jiang et al. 2009). A method of measuring the acoustic velocities of stishovite and other lower-mantle phases under quasi-hydrostatic conditions at high temperatures and high pressures is required. With this in mind, we conducted acoustic velocity measurements of stishovite under nonhydrostatic conditions in process of developing method. Sedimentary and MORB layers in the subducting slab are plausible sites for high-pressure silica polymorphs to exist in the deep earth. Deep earthquakes reveal that subducting slabs are under considerable stress in the mantle. The present study may give insight on the seismic features and physical properties of subducting slabs.

EXPERIMENTAL PROCEDURE

We synthesized a polycrystalline stishovite sample for Brillouin acoustic velocity and X-ray diffraction measurements by sintering SiO₂ reagent powder at 20 GPa and 1500 K using a Kawai-type multi-anvil apparatus. The sample was sufficiently transparent for Brillouin scattering. The synthesized pellet was analyzed using a scanning electron microprobe equipped with an electron dispersive spectrometer, and with an infrared
spectrometer. The pellet consists of pure SiO$_2$ and has an OH concentration of approximately 20 ppm. X-ray diffraction was measured with a microfocused X-ray diffractometer (Rigaku) with an anticathode of Cu; a wavelength of 1.5418 Å. The average grain size of the sintered pellet is about 1 μm. The pellet was double-side polished to a final thickness of about 40 μm, and cut with a diamond saw to about 80 μm square. The polycrystalline chip was loaded between thin NaCl pellets in a hole in a pre-indentated rhenium gasket and confined in a symmetric diamond anvil cell with a 60° angular aperture. Two beveled diamonds with 200 μm culets were used as anvils. A photograph of the sample is shown in Figure 1. The diameter of the sample chamber was about 100 μm. NaCl was used as the pressure medium and as a pressure gauge. The sample was compressed at 2–3 GPa intervals and was heated at 423 K in a vacuum oven to reduce the deviatoric stress in the sample chamber to below 10 GPa. Above 10 GPa, the compressed sample was heated using a CO$_2$ laser with an injected power of 20–30 W for about 60 s to reduce the deviatoric stress. We heated the sample to temperatures well below the condition at which irradiation started to prevent grain growth because the Brillouin signal is sensitive to crystallographic orientation (e.g., Shimizu et al. 1995; Baer et al. 1998). After heating, the pressure was measured using the Raman peak shift of diamond (Akahama and Kawamura 2006), and
then the Brillouin scattering data were collected.

Brillouin scattering was performed with the system installed at SPring-8/ BL10XU (Ohishi et al. 2008). A six-path tandem Fabry-Perot interferometer was used to collect the Brillouin spectra. A diode-pumped laser with a wavelength of 532 nm was used as the incident probe beam, and was focused on the sample to a spot size of approximately 20 μm in diameter. All measurements were performed in a symmetric scattering geometry with an external scattering angle (θ) of 49.0–50.7°, which was calibrated with a borosilicate crown optical glass (BK7; Yoneda and Song 2005) before measurements. Three separate series of experiments were conducted for the Brillouin scattering and X-ray diffraction measurements. The first series were performed along the compression path, and the second along both the compression and decompression paths. Two chips of polycrystalline stishovite were used for the first and second series respectively. These were cut from the same sintered pellet. NaCl was used as a pressure medium. The collection of Brillouin scattering spectra was conducted at 1–65 GPa in the first and second series of experiments. The X-ray diffraction measurements were conducted at pressures of 1, 40, and approximately 60 GPa after the Brillouin scattering measurements on the same loading conditions respectively. The chip recovered from the second set of experiments was loaded
with a small ruby sphere and a mixture of methanol–ethanol–water (in proportions of 16:3:1 by volume) for the third set of experiments to examine the effect of deviatoric stress on the sample during the high-pressure experiment. X-ray diffraction measurements were performed at pressure ranged 4.7–15.6 GPa along the compression path in the third series of experiments. We conducted Brillouin scattering measurements on the recovered sample only at 4.7 GPa. The recovered sample was partly deteriorated by the green laser injection, therefore, we didn’t measure Brillouin scattering of the sample at higher pressures.

We collected Brillouin spectra from three or four different positions and $\chi$ angles ($\chi$ angle: the angle rotated around the compression axis of the diamond anvil cell) at fixed pressure conditions. The number of grains probed at a given pressure is roughly estimated about 1800–3200 from diameter of incident laser (20 $\mu$m) and sample thickness (30–40$\mu$m) under pressure, and number of measurements. We averaged the data at the same pressure conditions from the first and second series of experiments to ensure a representative average of acoustic velocity in the polycrystalline sample. The uncertainties of the individual velocity data were $\pm$120 m/s (less than 1%) for $V_p$ and $\pm$80 m/s for $V_s$ (less than 1.2%).

The X-ray diffraction measurements were conducted in four different experimental
periods, and the experimental conditions and results are summarized in Table 1. The angle-dispersive X-ray diffraction spectra were collected using a CCD camera or an imaging plate. The incident X-ray beams were monochromized to wavelengths of 0.4130, 0.4135, 0.4136, and 0.4157 Å respectively for each experimental period. The X-ray beam was collimated to 15 or 30 μm in diameter. The collection time for each X-ray diffraction measurement was about 120–240 s.

The pressure deviations of the different pressure scales, i.e., Raman frequency shift of the diamond and NaCl volume (Brown 1999, for B1 structure; Sakai et al. 2011, for B2 structure) and ruby fluorescence (Mao et al. 1978), were within ±3 GPa above the pressure of 15 GPa. This includes the uncertainty of the pressure determination and the pressure gradient in the sample chamber. The relationship between the pressures obtained with the diamond Raman scale and those obtained using the other scales are shown in Figure 2. Only the (110) diffraction from the B2-structured NaCl was observed. Therefore, we did not use B2-structured NaCl as a pressure scale but used as a pressure gauge showing the pressure gradient within the sample chamber. We used the B1-NaCl and the ruby scale below 20 GPa, and the diamond Raman scale above 20 GPa to determine the experimental pressure.
RESULTS

The fine circular two-dimensional X-ray diffraction image obtained in this study indicates that the sample was initially an isotropic aggregate with no preferred orientation (see supplementary figure). The variations in measured acoustic velocity along χ angles were about 5.2% for longitudinal velocity ($V_p$) and 3.8% for transverse velocity ($V_s$) at 1 GPa (NaCl-B1 pressure gauge). These variations were less than 1.4% for $V_p$ and less than 1.1% for $V_s$ at higher pressures. There was no clear correlation between velocity variation and χ angle. Relatively large variations in velocity at 1 GPa might indicate that the sample was not compacted well yet at that pressure. A representative Brillouin spectrum is shown in Figure 3. The longitudinal acoustic velocities and transverse acoustic velocities obtained as a function of pressure are shown in Figure 4. It is observed that the transverse velocity reaches a minimum between 20 GPa and 30 GPa, whereas this is not observed for longitudinal velocity. The $V_p$ signal of stishovite always overlapped the $V_s$ signal of single-crystal diamond, and therefore, the peak fitting has rather large uncertainties (less than 1%). The standard deviation of an average of measured velocities obtained from
different series of experiments with NaCl pressure medium was less than 2% except for the
value obtained at 20 GPa along compression paths (2.7% for $V_s$). Measured velocities
obtained during compression and decompression were comparable. It indicates that grain
size reduction under pressure did not occur to a level that causes velocity reduction
(Marquardt et al. 2011) in the present experiments. When a mixture of
methanol–ethanol–water was used as a pressure medium, the measured velocity for the
recovered sample was comparable with those obtained at first and second series of
experiments. The sample was deteriorated by the green laser at the first Brillouin scattering
measurement, and therefore the Brillouin spectrum was collected only at 4.7 GPa for the
third series of experiment.

The representative integrated X-ray diffraction profiles collected at the pressures of 1, 16,
39, and 60 GPa are shown in Figure 5. The (211) of stishovite splits into two peaks above
30 GPa (i.e., (121) and (211) of the CaCl$_2$-structured phase), which indicates that the
rutile-type structure is distorted to the CaCl$_2$-type structure (e.g., Andrault et al. 1998). A
NaCl-B2 pressure gauge indicated that the pressure difference between the center and the
edge of the stishovite pellet was about 2 GPa at 39 GPa. The broad FWHM in the X-ray
diffraction profiles (Fig. 5) also indicate that a certain amount of stress remained after
annealing.

It is known that the identification of the rutile-type structured phase and the CaCl₂-type structured phase is difficult from an X-ray diffraction profile due to the similarity and small splitting. Therefore, we calculated the symmetry-breaking strain (Carpenter et al. 2000) to determine the transition pressure. The spontaneous strains \( e_1 - e_3 \) for the tetragonal \( \rightarrow \) orthorhombic transition are defined as \( e_1 = (a - a_0)/a_0 \), \( e_2 = (b - a_0)/a_0 \), and \( e_3 = (c - c_0)/c_0 \), where \( a \), \( b \), and \( c \) are the lattice parameters of the orthorhombic phase, and \( a_0 \) and \( c_0 \) are the lattice parameters of the tetragonal phase, extrapolated into the stability field of the orthorhombic phase \( [a_0 = (a \times b)^{0.5}] \). The symmetry-breaking strain is \( (e_1 - e_2) = (a - b)/a_0 \).

The square of the measured symmetry-breaking strain is shown as a function of pressure in Figure 6 along with previous results (Andrault et al. 2003). The linear fit to the data, \( (e_1 - e_2)^2 \), are greater than zero, gives a transition pressure of 35 GPa. This transition pressure is considerably lower than the values which reported in previous X-ray diffraction studies for single crystal SiO₂ (stishovite) under quasi-hydrostatic conditions (Hemley et al. 2000); about 50 GPa, and for polycrystalline SiO₂ (stishovite) using the laser annealing method (Andrault et al. 2003); about 60 GPa. The unit cell volume and lattice parameters as a function of pressure determined in this study as well as in previous studies are shown in
Figure 7. The unit cell volume measured in this study deviated by approximately 3.2% over 30 GPa from the compression curve of stishovite, which was previously reported under hydrostatic conditions. This indicates that the nonhydrostatic effect became severer over 30 GPa. The compressibility of the c-axis measured in this study is almost comparable (within 0.3%) to that under hydrostatic conditions, whereas the a-axis is less compressible than that under hydrostatic conditions. The linear fit to the symmetry-breaking strain and the transverse velocity minimum indicate that the transition pressure is in the range of 25–35 GPa in the present study.

We conducted the line breadths analyses to get information about microstress with following procedure. Similar analyses have been conducted on energy dispersion X-ray profiles (e.g., Gerward et al. 1976; Weidner et al. 1998). The line breadths due to particle size, $\beta_S$, and distortions, $\beta_D$, in angle-dispersive diffraction are expressed with following equations (Klug and Alexander 1974):

\[
\beta_S(2\theta) = \frac{K\lambda}{L \cos \theta}
\]

(1)

\[
\beta_D(2\theta) = 4e \tan \theta
\]

(2)

where $K$ is the Sherrer constant, $\lambda$ is the X-ray wavelength, $\theta$ is the scattering angle, $L$ is the average crystalline size, and $e$ is the approximate upper limit of strain.
With the assumptions as to the shape of the broadening profile due to crystalline size and strain, the observed breadths, \( B \), in the case of Lorentzian (Cauchy type) profiles is given by

\[
B(2\theta) = \beta_L(2\theta) + \beta_o(2\theta)
\]  

(3)

The effect of grain size of 1 \( \mu \)m, which obtained by SEM analyses in present study, is small and it is easily hidden in the effect of instrumental contribution. If we apply equation 1 (Sherrer equation) to estimate grain size of around 1 \( \mu \)m, we need a careful evaluation of instrumental broadening. Brillouin scattering result suggests that apparent grain size reduction didn’t occur in present experiment. Therefore, we use this equation for the evaluation of instrumental contribution in present study. We assume instrumental broadening can be included in the term of \( \beta_o \) as a constant, and crystalline size \( L \) is a constant in present study, then equation 3 can be written

\[
B(2\theta) = \frac{a\lambda}{\cos\theta} + 4e\tan\theta
\]  

(4)

, where \( a \) is a constant including the effects of instrumental reflection and crystalline size.

Figure 8 shows the observed breadths of stishovite plotted against 2 theta at 1.1 GPa obtained in this study. We used a FWHM as for a peak breadth in present study. We
obtained $a = 9.8 \times 10^6 \pm 0.8 \times 10^6$ m$^{-1}$, and average upper limit of strain $e = 9.0 \times 10^{-4} \pm 0.7 \\
\times 10^{-4}$ by fitting the FWHM data with equation 4. We can obtain upper limits of strain from independent peaks with the obtained value of $a$ and equation 4. Figure 9a and 9b show upper limits of strain from independent diffraction peaks plotted against $d$ value and pressure respectively. Uncertainty of the values is approximately 9%. Large deviation of the strain values from hkl = (101) compared to those from the other directions are the result of contamination of hkl = (011) above 30 GPa. Except for the contaminated hkl = (101), the deviation between the strain values of hkl = (110) and (111) increases with increasing pressure above 30 GPa. The deviation may indicate that the deviatoric stress in the polycrystalline stishovite increases severely with increasing pressure above 30 GPa. To be exact, we need strain data and elastic constants for all independent orientation to obtain deviatoric stress. We note the values of the average upper limit of strain multiplied bulk modulus because the value may indicate deviatoric stress range on the sample: The values are 2.3 GPa, 4.4 GPa, and 7.0 GPa at the experimental pressures of 16 GPa, 39 GPa, and 64 GPa, respectively. The bulk modulus of polycrystalline stishovite was obtained using acoustic velocity and density which were measured in this study.

Figure 10 shows the acoustic velocity data for stishovite obtained in this and previous
studies. The acoustic velocities of polycrystalline stishovite under nonhydrostatic conditions are comparable to the aggregate velocity obtained from the measured acoustic velocity of single-crystal stishovite under hydrostatic conditions by Jiang et al. (2009) and to predictions by Karki et al. (1997) and Carpenter et al. (2000) before the transition. The transverse velocity drop around 25 GPa in this study is about 3%, which is much smaller than the velocity reduction of 60% that is predicted under hydrostatic conditions at 50 GPa by ab initio calculations.

As for a confirmation of present result, we conducted a preliminary experiment using diamond anvils with 450 μm culets without X-ray diffraction measurements. Transverse velocity was measured with Brillouin scattering in a pressure range of 15–40 GPa. The transverse velocity minimum was observed at around 27 GPa with 1.6% velocity reduction (see supplemental figure 2). The absolute values of measured transverse velocity are approximately 100 m/sec higher than those of present experiments. It might be due to the difference of stress conditions and/or grain size in the sample.

**DISCUSSION**

A linear fit to the symmetry-breaking strain values and the pressure of the transverse
velocity minimum indicate a transition pressure between 25 and 35 GPa in present study. This transition pressure is considerably lower than the values which reported in previous X-ray diffraction studies for single crystal SiO$_2$ (stishovite) under quasi-hydrostatic conditions (Hemley et al. 2000) and for polycrystalline SiO$_2$ (stishovite) using the laser annealing method (Andrault et al. 2003). The lower transition pressure observed in the present study might be caused by relatively large deviatoric stress in the sample, although the laser annealing method used in the present study was similar to that of Andrault et al. (2003). A stress condition is estimated as a pivotal pressure gradient (2 GPa/50 µm at 39 GPa with a NaCl-B2 pressure gauge) in present study. The estimated pressure gradient is a lower bound due to the low shear strength of NaCl. The high shear strength of SiO$_2$ may allow higher shear stress to be stored than that inferred from NaCl. Sintered polycrystalline stishovite, which was synthesized and recovered from a high-pressure and high-temperature experiment, was used as a starting material in the present study, whereas in situ synthesized stishovite was used in Andrault et al. (2003). It is plausible that the difference in sample preparation methods caused the difference in stress distribution in the sample because of the high shear strength of stishovite. Furthermore, Andrault et al. (2003) conducted laser annealing at 2300 K to attain almost hydrostatic conditions, whereas, in the present study,
laser annealing was conducted below the temperature threshold at which irradiation started,
in order to prevent grain growth. The post-stishovite transition is known to be strongly
affected by a deviatoric stress (e.g., Tsuchida and Yagi 1989), and the high shear strength of
stishovite causes large deviatoric stresses under nonhydrostatic conditions (e.g., Hemley et
al. 2000). Dubrovinsky and Belonoshko (1996) showed that even small deviatoric stress
could affect the post-stishovite phase transition. The method of identification of transitional
pressure in the present study was the same as that in Andrault et al. (2003). Therefore, the
difference in a stress condition is likely to be one of the main sources for lower transition
pressure obtained in this study.

The results of this study are also inconsistent with the results of a radial X-ray
diffraction experiment conducted under nonhydrostatic conditions by Shieh et al. (2002).
They reported that the differential strain in the sample was around 4.5 GPa below 40 GPa
and decreased to a minimum at around 48 GPa. Therefore, the displacive transition
occurred at approximately 48 GPa, although the volume began to deviate from the values
under nonhydrostatic conditions at around 20 GPa in the case of Shieh et al. (2002). We
consider that the differences between the present study and that by Shieh et al. (2002)
resulted from different stress distributions in the samples. This is plausible, because Shieh
et al. (2002) used synthesized powder without a pressure medium and did not conduct laser
annealing, whereas the present study used a sintered pellet with a NaCl pressure medium
and moderate laser annealing. Volume differences between the values obtained under
hydrostatic conditions and under deviatoric stress were approximately 3% in present study,
and approximately 2% in Shieh et al. (2002). It may imply that deviatoric stress condition
in present study is relatively larger than the value of 4.5 GPa observed in the experiment by
Shieh et al. (2002). Acoustic velocity measurements under controlled stress conditions with
dense X-ray diffraction data, hopefully with a radial X-ray diffraction method, should be
conducted to examine this inference.

If the observed velocity minima at around 22 GPa marks the beginning of transition, it
takes about 18 GPa for the CaCl$_2$ phase to reach a transverse velocity value comparable to
the one of the stishovite before softening. This pressure range is much larger than that
reported by previous studies; 0 GPa reported with ab initio calculation for pure SiO$_2$ by
Karki et al. (1997), around 5 GPa for experimental observation on hydrous alumina bearing
SiO$_2$ by Lakshmanov et al. (2007), around 11 GPa suggested using a Landau free energy
expansion for pure SiO$_2$ by Carpenter et al. (2000). In the present study, the acoustic
velocity of polycrystalline SiO$_2$ was measured. Therefore, the obtained velocity is an
average of each SiO₂ grain. The small velocity drop observed in the present study may
indicate that the phase transition was gradual and corresponded to heterogeneous stress
distribution at intergranular contacts in the sample; as a result, the strong elastic softening
feature of post-stishovite transition was suppressed. The relatively large pressure interval of
velocity rebound might also be a result of overlapping of velocity minima in individual
grains. Partial dislocations associated with the shear induced phase transition may also
affect the reduction of velocity change across the transition (e.g., Putonis 1992). There is no
clear difference between the data measured along compression path and decompression
path in present result. Consistent absolute values might imply that grain size in the sample
didn’t change apparently during compression. However, the hysteresis of transition
pressure might exist at least for the difference of stress condition between compression path
and decompression path. When we examine the data on compression and decompression
separately, compression data indicates that velocity minima may exist between 20 GPa and
30 GPa and decompression data indicates velocity minima may exist between 10 GPa and
20 GPa. In present study, deviatoric stress seems to suppress clear transition features of the
post-stishovite phase transition. To discuss about hysteresis and the change of elastic
properties accompanying by the post-stishovite phase transition, hydrostatic experiments
should be conducted with dense X-ray diffraction and acoustic velocity measurements.

It is predicted that even a few volume percent of free silica can provide observable seismic reflections in the mid-lower mantle because of the anomalous reduction in shear velocity associated with the post-stishovite phase transition (Karki et al. 1997). A basaltic layer in the subducting slab contains about 10–25 vol% of free SiO₂ in the deep mantle region (e.g. Ono et al., 2001). Therefore, a seismic anomaly could be observed as a general feature where subducting or upwelling oceanic crust exists. In fact, there are several seismic reflectors at 800–1800 km depth which may be related to the post-stishovite phase transition (Kawakatsu and Niu 1994; Le Stunff et al. 1995; Kaneshima and Helffrich 1999, 2010; Vinnik et al. 2001; Niu et al. 2003; Kaneshima 2009; Vinnik et al. 2010). Several individual groups have investigated the phase boundary between stishovite and the CaCl₂-structured phase at high temperature, and the results were rather controversial due to difficulties in phase determination and choice of pressure scales, and the effect of deviatoric stress (e.g., Kingma et al. 1995; Ono et al. 2002; Tsuchiya et al. 2004; Nomura et al. 2010). Most recently, Nomura et al. (2010) determined the phase boundary at temperatures of 300–2500 K using a laser-heated diamond anvil cell experiment; they determined the phase boundary to be at 50 GPa at 300 K with a positive Clapeyron slope of 11.1 MPa/K. The
transitional pressure in the pure SiO$_2$ system was found at 56–70 GPa for typical slab and mantle geotherms, which corresponds to the reflectors at a depth of around 1500 km (Kaneshima and Helffrich 1999, 2010) in the mantle and is still higher than the pressure corresponding to the reflectors at 800–1200 km depth. The effect of impurities such as Al and H in the SiO$_2$ phases is one of the possible explanations for the seismic reflectors at 800–1200 km depth (Lakshtanov et al. 2007), but this explanation does not exclude other possibilities such as compositional layering or decomposition of phase D (e.g., Kawakatsu and Niu 1994). A reduction in shear velocity across the post-stishovite transition as a result of Al or H impurities in stishovite is about 11% at a direction near [110] (Lakshtanov et al. 2007). The transition might be visible in seismic profiles if a subducting slab is under hydrostatic conditions. However, seismic observations indicating the occurrence of the post-stishovite transition accompanied with strong $V_s$ reductions have only been observed locally, despite the large influence expected (Kaneshima and Helffrich 2010). Experimental investigation of the acoustic velocity in stishovite under hydrostatic conditions at high temperatures and pressures should be undertaken to clarify the nature of the post-stishovite phase transition. However, the present results may suggest that nonhydrostaticity in the subducting slab is one of the possible reasons for the absence of general seismic features in
the subducting slabs that clearly relate to the post-stishovite phase transition accompanied by extremely low shear velocity anomalies. The present study reveals that nonhydrostatic deviatoric stress reduces the transitional pressure and velocity change. Therefore, if the post-stishovite phase transition occurs at lower pressures under nonhydrostatic stress, the phase transition of stishovite containing some or no impurities does not occur at transitional pressures with expected velocity reductions under hydrostatic conditions in the downgoing slab. Silica-bearing layers such as basalts and sediments are likely to be stretched and folded in the mid-lower mantle; therefore, a velocity change of less than 3% due to the phase transition of stishovite might be obscured by anomalies caused by temperature differences or chemical and structural heterogeneity. However, this phase transition of stishovite under deviatoric stress could affect the generation of scattering objects in the mid-lower mantle (e.g., Kaneshima and Helffrich 2010) and also could influence the rheological behavior of a subducting slab, such as slab thickening observed in the mid-lower mantle (Van der Hilst 1995; Shellard et al. 2009; Zhao 2004).

The deviatoric stress in the present study was estimated to be 2 GPa from pressure distribution in the sample obtained using NaCl-B2 pressure gauge. However, the difference between the volumes of stishovite obtained in this study and in previous studies under
hydrostatic conditions and under deviatoric stress implies that stress condition in stishovite
was larger than a value about 4.5 GPa. This is in the possible stress range for a subducting
slab based on the stress capacity of major constituent minerals (Chen 2010), although the
actual stress conditions in the subducting slab are not known. According to the stress
measurements for mantle phases (e.g. Weidner et al. 1998; Chen et al. 2010), differential
stress decreases with increasing temperature. Weidner et al. (1998) demonstrated that
microstrain in stishovite decreased to 80% of initial strain with increasing temperature up
to 1273 K at experimental pressure of 12 GPa. The experimental condition is close to the
coesite-stishovite phase boundary (Akaogi et al. 1995). Stishovite has a wide stability field
from 8 GPa to 60 GPa along the cold slab geotherms (e.g. Kirby et al. 1996) which
corresponding to the range from the transition zone to the mid-lower mantle region of the
earth, The stress capacity of stishovite under higher pressures is still unclear. Although the
value depends on the mineral phases, the rate of reduction was estimated to be 60% and
20% at 20 GPa and 1073 K for ringwoodite and perovskite, respectively (Chen et al. 2010).
This implies that the stress capacity of minerals is small under mid-lower mantle conditions.
In the mid-lower mantle region, the stress conditions might be weaker than that in the
region shallower than 700 km depth because of stress-reducing processes such as seismic
energy release and recrystallization annealing across the perovskite-forming reaction (e.g., Bina 2010). However, it is plausible that a certain deviatoric stress exists in silica-rich layers even in the mid-lower mantle region, as a result of the high shear strength of stishovite. The results presented here suggest the possibility that the post-stishovite phase transition under deviatoric stress explains the lack of general seismic features of extreme reductions in shear velocity related to the post stishovite transition in the mid-lower mantle. The post stishovite transition which occurs at lower pressures under nonhydrostatic conditions may affect the local seismic scattering structures and the rheological behavior of subducting slabs, as displayed by slab-thickening features observed in the mid-mantle region. The effect of stress on the transitional pressure and the elasticity change of stishovite at high temperatures should be investigated with accurate stress estimation for further discussion.

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Figure captions

Figure 1. Photograph of a SiO₂ sintered pellet confined within the NaCl pressure medium in the diamond anvil cell at 300 K and 40 GPa.

Figure 2. The relation between pressures obtained with the internal pressure scales of ruby and NaCl against the pressure obtained with the Raman edge frequency shift of a diamond culet.

Figure 3. A representative Brillouin spectrum corrected at 56 GPa and room temperature.

Figure 4. Acoustic velocities in polycrystalline stishovite measured in this study as a function of pressure: A) longitudinal velocities; B) transverse velocities. Filled circles and open squares represent acoustic velocities measured along compression and decompression paths, respectively. The uncertainties of the obtained velocity were calculated from uncertainty of peak fitting and standard deviation of averaged data.
Figure 5. Representative integrated X-ray diffraction profiles of the sample (SiO$_2$ and NaCl) at room temperature and pressures of (a) 1 GPa, (b) 16 GPa, (c) 39 GPa, and (d) 60 GPa. Abbreviations of peaks are as follows: R, Rutile-type SiO$_2$; C, CaCl$_2$-type SiO$_2$; B1, B1-type NaCl.

Figure 6. Square of the symmetry-breaking strain through the transition. Open and filled circles, the data obtained in this study for the rutile-structure phase and the CaCl$_2$-type phase, respectively; crosses and open squares, the data obtained by Andrault et al., (2003) for the rutile-structure phase and the CaCl$_2$-type phase, respectively. The bold dashed line and the solid line are a fit to the data for the CaCl$_2$-structured phase obtained in this study and Andrault et al., (2003), respectively; the thin dashed line is a horizontal line for zero.

Figure 7. Volumes (A) and lattice parameters of SiO$_2$ phases as a function of pressure for a and b axes (B), and for c axes (C). Open circles, lattice parameters for the rutile-type phase obtained in this study; filled diamonds and filled circles, lattice parameters for the CaCl$_2$-type phase obtained in this study; Crosses and gray filled triangles, lattice parameters for the rutile-type phase obtained by Andrault et al., (2003) and Ross et al., (1990),
respectively. Open triangles and open squares, lattice parameters for the CaCl$_2$-type phase
obtained by Andrault et al. (2003).

Figure 8. The FWHM of polycrystalline stishovite as a function of 2 theta at 1 GPa. The
curve shows a fitting result on these data to equation 1? with the weighted least square
method.

Figure 9. The approximate upper limit of strain obtained from the FWHM analysis a) as
a function of pressure, b) as a function of d value. Relatively large values of upper limit of
strain for hkl = (101) corresponding to the d-value of around 2.2 Å are due to
contamination of hkl = (011) above 30 GPa.

Figure 10. Acoustic velocities in SiO$_2$ phases as a function of pressure. Filled circles and
open squares, longitudinal velocities measured in this study along compression and
decompression paths, respectively; open circles and filled squares, transverse velocities
measured in this study along compression and decompression paths, respectively; open
diamonds and open triangles, longitudinal and transverse velocities for aggregate obtained
from the measurement data for single crystal SiO$_2$ by Jiang et al., (2009); solid triangles, acoustic velocities close to the [110] phonon direction of hydrous alumina bearing stishovite measured by Lakshtanov et al. (2007); gray dashed lines, aggregate velocity predicted by a Landau free energy calculation by Carpenter et al. (2000); solid lines, polynomial fit to the longitudinal velocities and transverse velocities measured in this study, respectively. Polynomial fits were made separately on transverse velocity at pressures below and above 25 GPa. The longitudinal velocities didn’t treat separately as transverse velocity because the data were not sufficient due to overlapping with diamond transverse velocity (see text): the gray dotted line is a visual guide for the measured velocities for Al- and H-bearing SiO$_2$.

Supplementary figure 1. A representative 2-dimensional X-ray diffraction image obtained at 1 GPa and room temperature.

Supplementary figure 2. Transverse acoustic velocities in polycrystalline stishovite measured in this study as a function of pressure: The values obtained in an additional experiment are plotted as gray circles. The velocity minimum is observed around 27 GPa.
Fig. 1
Fig. 2
Fig. 3
Fig. 4a
Fig. 4b
Fig. 5 r2
Fig. 6
Fig. 7a
Fig. 7b
Fig. 7c
Fig 8 r2
Fig 9a r3
Fig 9b r3
Fig. 10 r2