

The post-stishovite phase transition in hydrous alumina-bearing SiO₂ in the lower mantle of the earth

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Silica is the most abundant oxide component in the Earth mantle by weight, and stishovite, the rutile-structured (P4₂/mnm) high-pressure phase with silica in six coordination by oxygen, is one of the main constituents of the basaltic layer of subducting slabs. It may also be present as a free phase in the lower mantle and at the core-mantle boundary. Pure stishovite undergoes a displacive phase transition to the CaCl₂ structure (Pnmm) at ≈55 GPa. Theory suggests that this transition is associated with softening of the shear modulus that could provide a significant seismic signature, but none has ever been observed in the Earth. However, stishovite in natural rocks is expected to contain up to 5 wt % Al₂O₃ and possibly water. Here we report the acoustic velocities, densities, and Raman frequencies of aluminum- and hydrogen-bearing stishovite with a composition close to that expected in the Earth mantle at pressures up to 43.8(3) GPa [where (3) indicates an uncertainty of 0.3 GPa]. The post-stishovite phase transition occurs at 24.3(5) GPa (at 298 K), far lower than for pure silica at 50–60 GPa. Our results suggest that the rutile-CaCl₂ transition in natural stishovite (with 5 wt % Al₂O₃) should occur at ≈30 GPa or ≈1,000-km depth at mantle temperatures. The major changes in elastic properties across this transition could make it visible in seismic profiles and may be responsible for seismic reflectors observed at 1,000- to 1,400-km depth.

hydrogen | phase transition | silica | high pressure | Brillouin scattering

Stishovite is the lowest-pressure SiO₂ polymorph with octahedrally coordinated silicon. It adopts the tetragonal rutile structure (P4₂/mnm) and is stable from ≈9 GPa to ≈50 GPa at room temperature where it undergoes a displacive phase transition to the orthorhombic CaCl₂ structure (Pnmm), e.g. (1, 2). Estimates for the temperature dependence of this transition (dP/dT) (1, 3, 4) suggested that it might occur at depths of ≈1,500 km or more in the mantle (more than ≈60 GPa), but the expected seismic signatures have never been observed in that depth range. In fact, the phase relations for pure SiO₂ may not be directly relevant to the mantle because they do not include the possible effects of Al₂O₃ and H₂O, which are known to be soluble in stishovite (5, 6). It was previously speculated that impurities might lower the pressure for this transition (7), but clear experimental evidence was lacking. If these effects are significant, they may bring the depth of this phase transition into the region where it could possibly explain seismic reflections observed at 900- to 1,400-km depth (8–11).

Results

Fig. 1 shows the angle-dispersive x-ray spectra of the stishovite and post-stishovite (CaCl₂) polymorphs. Because these single-crystal x-ray diffraction (XRD) spectra were obtained by a rotation of only ±12° on the ω-circle, not all reflections are present. However, the CaCl₂ phase was clearly observed on our x-ray spectra above 24 GPa. The volume change of transition is apparently small (12), and the tetragonal-orthorhombic sym-

metry change can be difficult to resolve. This limitation is a common one among XRD methods of detecting displacive phase transitions, sometimes leading to an uncertainty of >10 GPa in the transition pressure, P_{tr} (13, 14). Here, the MAR-345 images (Fig. 1) clearly show splitting of the (121) and (211) peaks for the orthorhombic higher-pressure phase at 24.8(3) GPa.

Brillouin scattering measurements were performed from nearly the same scattering volume that was probed in the XRD measurements. The orientation of the sample allowed us to collect acoustic velocities close to the [110] phonon direction. In this direction, the elastic shear modulus $V_{SH}^2 \rho = C_{11} - C_{12}$ should vanish approaching P_{tr} (15). Our Brillouin sound velocity measurements show softening of this acoustic mode (Fig. 2), allowing us to bracket the pressure of the phase transition between 20.0(3) and 24.8(3) GPa. In the lower-symmetry CaCl₂ phase, dV_{SH}/dP is larger by the nature of the transition, hence the P_{tr} should be located at a pressure closer to 24.8(3) GPa.

Raman scattering results obtained on pressure decrease (Fig. 2) help to refine further the pressure of the transition. The softening of the mode B_{1g} in the rutile structure is clearly followed by a stiffening of the A_g mode in the CaCl₂ structure. The intersection of linear least-squares fits to the squares of the mode frequencies provides us with a transition pressure $P_{tr} = 24.3(3)$ GPa (15, 16).

Discussion

The post-stishovite phase transition in pure SiO₂ is thought to occur at 50–60 GPa (1, 2, 15, 17). The enormous decrease of transition pressure in aluminous stishovite (which to some extent can be considered a SiO₂-δAlOOH solid solution) (18), compared with the pure end-member, and the pronounced acoustic mode softening documented in our work, opens the possibility of a signature of this phase transition in the upper part of the lower mantle. Our results should be more directly applicable to the Earth mantle because the Al₂O₃ content of natural stishovite in chemically complex mantle assemblages may be as high as 5 wt % (19, 20). If we assume a linear dependence of the transition pressure on aluminum content, $dP_{tr}/dX_{Al_2O_3}$ (Fig. 3), and a Clapeyron slope, $dP_{tr}/dT = 0.004$ GPa/K(1), we estimate a lower bound of $P \approx 36$ GPa for the pressure at which this phase transition would occur in the mantle, corresponding to a depth of ≈1,000 km.

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The authors declare no conflict of interest.

Abbreviations: MORB, mid-ocean ridge basalts; P_{tr} , transition pressure; XRD, x-ray diffraction.

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The crystal was loaded into a symmetric piston-cylinder diamond-anvil cell along with four ruby spheres (29) and two chips of NaCl. Neon served as a pressure-transmitting medium because it provides quasi-hydrostatic conditions to pressures >60 GPa (1, 30). The choice of pressure medium was important because displacive phase transitions are sensitive to nonhydrostatic stress (15, 31).

Simultaneous Brillouin scattering and synchrotron XRD measurements were performed at 13-BMD, GeoSoilEnviroCARS, Advanced Phonon Source (Argonne, IL). We used the recently developed Brillouin scattering system (32) and angle-dispersive x-ray diffraction with an MAR-345 (Mar-USA, Evanston, IL) imaging plate detector. Pressure was increased in small (<1 GPa) increments with a typical spacing of ≈ 5 GPa between Brillouin measurements. After each pressure increase above 20 GPa, the cell was annealed in an oven at 200–300°C for 0.5–24 h or laser-heated at $\approx 1,500^\circ\text{C}$ (CO_2 laser, $\lambda = 10 \mu\text{m}$) to relax deviatoric stresses in the sample chamber. The pressure gradient never exceeded 0.5 GPa in any experiment, as monitored by x-ray diffraction from the pressure medium (neon) and ruby fluorescence.

Raman scattering measurements obtained on decreasing pressure were performed at the University of Illinois. At pressures of 38.4(7) and 28.7(3) GPa, the pressure medium was annealed at 300°C for 30 min.

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