

## Atomistic mechanism of Al substitution effects on the post-stishovite transition by high-pressure single-crystal X-ray diffraction

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### ABSTRACT

The influence of Al substitution on the elastic properties of stishovite and its transition to post-stishovite is of great importance for interpreting the seismic wave velocities of subducted mid-ocean ridge basalt (MORB) within the mantle transition zone and the lower mantle. However, atomistic mechanisms of Al substitution effects on the transition and its associated elasticity remain debated. Here synchrotron single-crystal X-ray diffraction measurements have been performed at room temperature on Al<sub>1.3</sub>-SiO<sub>2</sub> [1.3 mol% Al in the chemical formula of Si<sub>0.965(3)</sub>Al<sub>0.041(1)</sub>O<sub>2</sub>H<sub>0.017(4)</sub>] and Al<sub>2.1</sub>-SiO<sub>2</sub> [2.1 mol% Al in Si<sub>0.948(2)</sub>Al<sub>0.064(1)</sub>O<sub>2</sub>H<sub>0.018(3)</sub>] crystals in diamond-anvil cells with Boehler-Almax designed anvils up to 38.0 and 28.5 GPa, respectively. Analyses of the diffraction patterns show that a transformation from stishovite (space group  $P4_2/mnm$ ; No. 136) to CaCl<sub>2</sub>-type post-stishovite (space group  $Pnnm$ ; No. 58) is accompanied by splitting of O coordinates. The Al substitution in stishovite results in a faster decrease in the O coordinate, softer apical (Si,Al)-O bonds, and a softer and less distorted (Si,Al)O<sub>6</sub> octahedron under compression. This leads to reduced adiabatic bulk modulus ( $K_S$ ), shear modulus ( $G$ ), shear wave velocity ( $V_S$ ), and compressional wave velocity ( $V_P$ ) in the stishovite phase, explaining seismic wave perturbations in the mantle transition zone. Together with Raman data, Landau theory modeling shows that Al substitution increases the order parameter and excess free energy, stabilizing the post-stishovite phase at lower pressures. Correlation between elasticity and octahedral distortion index ( $D$ ) reveals that at certain  $D$ , the Al substitution reduces  $K_S$ ,  $G$ ,  $V_S$ , and  $V_P$  of the stishovite phase while increasing  $G$ ,  $V_S$ , and  $V_P$  of the post-stishovite phase. Importantly, the maximum shear reduction is slightly enhanced at  $D = 0.00620(9)$  at the transition point. Our results help explain the seismically observed small-scale  $V_S$  anomalies beneath subduction regions in the shallow lower mantle where Al,H-bearing stishovite undergoes the post-stishovite transition.

**Keywords:** Al,H-bearing stishovite, single-crystal X-ray diffraction, ferroelastic transition, post-stishovite, lower-mantle seismic scatterers, elasticity