Post-perovskite Phase Transition in $MgSiO_3$

$MgSiO_3$ is a representative chemical composition of the Earth's mantle. The upper/lower mantle boundary is marked by the formation of orthorhombic $MgSiO_3$-rich perovskite (space group: *Pbnm*). The $MgSiO_3$ perovskite was first synthesized at 30 GPa in 1975 [1]. Later, the conservation of perovskite structure was confirmed up to 127 GPa [2]. It has been believed that the perovskite-type $MgSiO_3$-rich phase is a predominant mineral in the lower mantle and is stable to 135 GPa a condition corresponding to the bottom of the mantle. However, phase transition of $MgSiO_3$ perovskite was once suggested from the seismic anomalies near the base of the mantle around 2700-km depth [3].

In order to investigate the stability and possible phase transition of $MgSiO_3$ perovskite, we performed *in situ* X-ray observation of pure $MgSiO_3$ composition at high pressure and temperature up to 134 GPa and 2600 K corresponding to the conditions of the lowermost mantle [4]. Angle-dispersive X-ray diffraction spectra were collected at beamline **BL10XU**. High pressure and temperature conditions were generated in a laser-heated diamond anvil cell (LHDAC). Temperature was measured by the spectroradiometric method. Pressure was determined from the unit-cell volume of platinum mixed with the sample using *P-V-T* equation of state.

Results demonstrate that the *Pbnm* perovskite structure is stable at least to 114 GPa and 2300 K (Fig. 1). Above 127 GPa and 2500 K, fifteen new peaks were observed in the diffraction pattern. These new peaks from a new $MgSiO_3$ polymorph (post-perovskite phase) can be indexed by an orthorhombic cell with lattice parameters of a = 2.456(0) Å, b = 8.042(1) Å, and c = 6.093(0) Å. In order to determine the crystal structure that possesses these lattice parameters, molecular dynamics (MD)-aided crystal structure design was performed. The appropriate number of atoms (8 Mg + 8 Si + 24 O; Z=8) were positioned randomly in a double unit cell because of the small a-parameter. Classical MD calculations were carried out with the (NTV) ensemble of this system at high temperature (5000 K), and then the system was quenched to 0 K. The calculations were repeated, each time checking and correcting the atomic positions until the crystal structure became consistent with the crystal chemistry and the calculated XRD pattern matched the observed one. The result revealed a crystal structure of a new phase (post-perovskite phase) with a space group of *Cmcm* (Fig. 2). This is isostructural with $UFeS_3$ or $CaIrO_3$. The post-perovskite phase is denser than perovskite by 1.0-1.2 % at 121 GPa and 300 K.

The post-perovskite phase has six-fold Si and

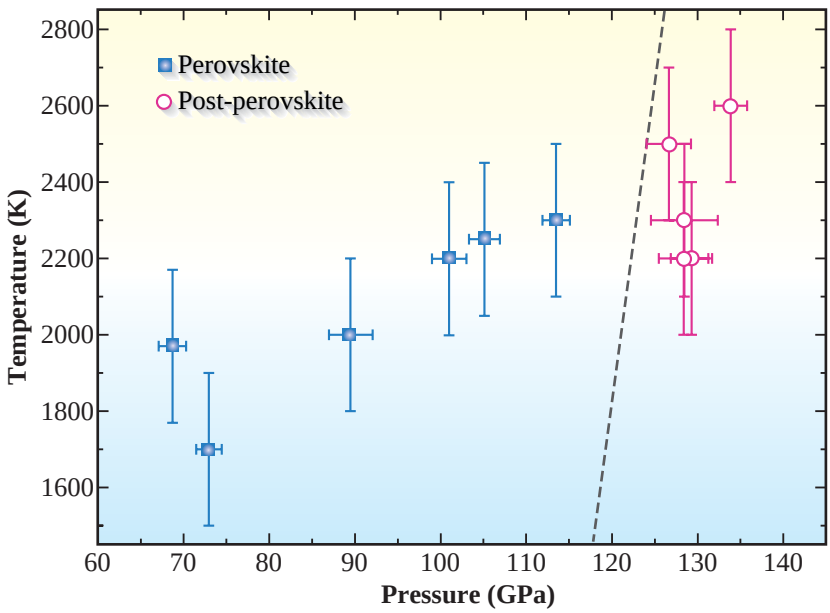

Fig. 1. Phase diagram of $MgSiO_3$. Solid squares and open circles indicate the stabilities of *Pbnm* perovskite and post-perovskite phase, respectively. A broken line shows the transition boundary.

eight-fold Mg coordination, and the SiO_6-octahedra share the edges to make an octahedral chain like rutile-type structure. These chains run along *a*-axis and are interconnected each other by apical oxygen atoms in the direction of *c*-axis to form edge and apex shared octahedral sheets. The octahedral sheets are stacked along *b*-axis with interlayer Mg^{2+} ions. This crystal structure was further optimized by the first-principles calculations [5]. The calculations also indicated that the post-perovskite phase stabilizes relative to perovskite above 98 GPa and 0 K.

These results show that the $MgSiO_3$ post-perovskite is a predominant mineral in the Earth's lowermost mantle (D" region) at 2700 to 2900-km depth. Phase transition can cause large seismic heterogeneities. The D" seismic discontinuity is observed in many regions around the world about 200-300-km above the core-mantle boundary (119-125 GPa). The post-perovskite phase transition occurs at depths matching those of the D" discontinuity (Fig. 1) and is most likely responsible for the cause of seismic velocity increase up to 3%. A large S-wave polarization anisotropy ($V_{SH} > V_{SV}$) is also observed below the D" discontinuity. It can be explained by a strong preferred orientation of the post-perovskite phase under the strong horizontal shear flow [5]. The D" region has long been the most enigmatic region in the Earth's interior. The newly discovered $MgSiO_3$ post-perovskite phase provides a consistent way to explain a number of seismic anomalies observed in this region.

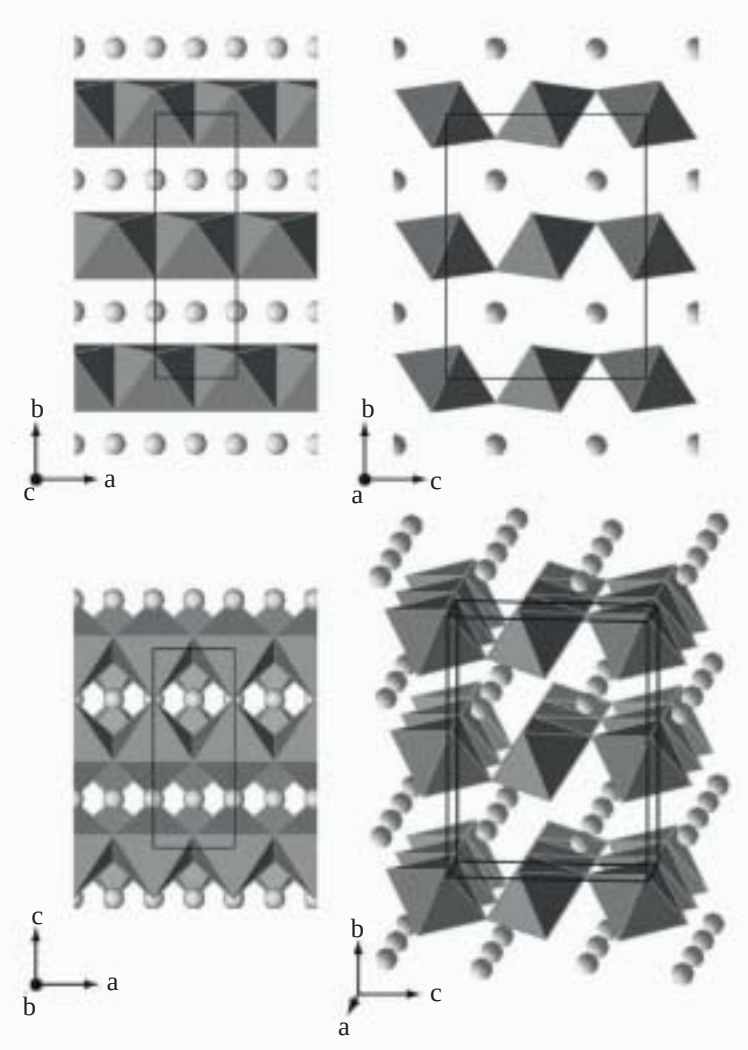

Fig. 2. Crystal structure of the post-perovskite phase projected along [001], [100], and [010] directions, and a stereoscopic view showing the layer stacking structure. Coordination polyhedra of oxygen atoms around Si atoms are shown as octahedra, and the Mg^{2+} ions are shown as balls. Bold line indicates the unit cell.

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References

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