Structure analyses including spin state of the D zone materials and newly developed diffractometry at HPCAT, APS

Takamitsu Yamanaka[1]

[1] Carnegie Inst. Geophysical Lab.

Numerous high-pressure experiments on post-perovskite (ppv) $MgSiO_3$ in the deep lower mantle have been undertaken from the powder X-ray diffraction patterns and fist-principles calculation to explain the seismic velocity in the region of the Earth core boundary. Additionally, their structural simulation has reported many experiments of ABO_3 compounds with the ppv structures. High-pressure studies of material sciences attract a large attention in order to understand strong electronic correlation such as the charge transfer, electron hopping, electron high-low spin transition, Jahn-Teller distortion and charge desiproponation in the lower mantle or subduction zone by X-ray emission spectra studies or synchrotron Meossbauer studies. However, very few precise structure analyses have been performed based on in situ single-crystal and even powder X-ray diffraction studies at pressures above 100 GPa and about 2000K, because of the experimental difficulties. Characterizing and understanding the Fe and Mg cation distribution and ordering in ppv-(Mg,Fe)SiO_3, is crucial for constraining chemical equilibrium of lower mantle (i.e. element partitioning and the equation of state). Cation size effects are largely responsible for these properties due to spin configuration. The partial replacement of Mg by Fe changes the site volume of the structure.

We newly developed a high-pressure single-crystal diffraction system and micro-size particle diffraction system in powder sample using narrow beam of 0.5 micron above megabar region at HPCAT APS. Perovskite structure with ferroelectric property has been performed up to 60GPa. XES experiments of post-spinels of $CaMnO_3$ and iron-rich post-perovskite (Mg,Fe)SiO_3 have been carried out above 100 GPa.

In the present experiment we also performed precise X-ray powder diffraction measurements of iron-rich post-perovskite of $(Mg_{0.6}\ Fe_{0.4})SiO_3$ with Rietveld profile fitting analysis. We first determined the most reliable structures of the post-perovskite polymorph of (Mg,Fe)SiO_3 based on structure models proposed by the Monte Carlo calculations using the diffraction intensities. Rietveld refinement of post-perovskite $(Mg_{0.6}\ Fe_{0.4})SiO_3$ was performed using data taken from the average of twenty patterns collected from the different positions in the sample under a pressure of 137 GPa with laser heating to about 2000 K in order to avoid the non-uniformity in diffraction patterns due to grain growth which is caused by laser heating the sample in the gasket. Monte Carlo calculation was applied after the indexing to find the possible candidates for the structure of the ppv-En60. The calculation presented three reasonable structure models with different cation distributions characterized by three space groups: *Pmmn* (*Pmnm*) for (M1,M2) SiO_3 *Pmcm* (*Pmma*) for (M1, M2)(Si1,Si2)O_3 and *Cm2m* for (M1, M2)SiO_3. All three models belong to the non-isomorphic subgroups of Cmcm. We carried out the Rietveld profile fitting analysis for all three models including a variable parameter of site occupancy of Fe and Mg in the M1 and M2 sites with the chemical constraint

Recently two jumps of seismic velocity in the deep lower mantle or near core boundary region have been reported . This can be related to structure deference including the spin state.