

Relation between high-low spin transition and structure transition of Earth's interiors under high pressure

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Major mantle materials such as rock-salts, spinels and perovskites are composed of oxides with transition metal elements. These materials further transforms to high-pressure polymorphs or decomposed to high-pressure structures. Such as post-spinels and post-perovskites have generally higher density materials.

The replacement of Mg by Fe induces changes of the volume of cation sites. X-ray diffraction studies and first-principles calculations show that the cation ordering and spin state affect the phase stability and alter physical properties, such as the equation of state, elasticity, electric band structure and electric conductivity. Cation size effects are largely responsible for these properties. At high pressures above 100 GPa, the spin transition from high-spin state (HS) to low-spin state (LS) reduces ionic radius: about 10 % smaller than the radii at ambient conditions.

The ionic radius at ambient conditions of Fe²⁺ (0.092 nm) is larger than that of Mg²⁺ (0.089 nm) with reference to the empirical ionic radii. The average bond distances of the cation site estimate a larger Fe occupies the larger site than the smaller site and Mg can be located in the smaller site. X-ray powder diffraction study was undertaken for in-situ experiment at beamline 16IDB of HPCAT of the Advanced Photon Source (APS). We found a new Pmcm structure of iron rich post-perovskite (Mg_{0.6},Fe_{0.4})SiO₃ from powder diffraction experiment, X-ray emission study and first-principles calculation. The Pmcm structure has two sites: (Fe_{0.25}, Mg_{0.75}) in the larger M1-site and (Fe_{0.55}, Mg_{0.45}) in the smaller M2 site but the result is against the CaIrO₃ structure, which has only one metal site. The refinement shows the small M2 site is occupied by the larger Fe²⁺ cations and the smaller ion of Mg²⁺ occupies the large M1 site. The solution to this paradox is found by considering the spin state of Fe. Fe in the M2 site is in LS state, this could be explained why the M2 site is smaller than the M1 site.

We executed the XES measurement under the condition where the sample was compressed to over 100 GPa and heated to 2000-3000 K. In XES experiments, the incident x-ray beam first passes through a monochromator which selects an X-ray energy above the Fe K absorption edge. The Fe-K β emission from the sample is collected radial through the gasket to avoid attenuation by the diamond anvils and hits the analyzer (a spherically bent Si (333) crystal), which sits along with the detector on a high resolution (0.5 eV) Rowland-circle spectrometer. XES under high-pressure and high-temperature condition indicate that about three quarter of the Fe²⁺ atom is in the LS state and the rest of the Fe atoms is still in the HS state. This is in excellent agreement with the present Rietveld refinement which found about 70% of the total Fe²⁺ in post-perovskite (Mg_{0.6},Fe_{0.4})SiO₃ occupies the M2 site. Thus we suggest the Fe in M2 is in the LS state but Fe²⁺ in the M1 site is still in the HS state. The spectra can be explained by the mixed spin state of LS and HS in two sites of Fe²⁺ at the M1 and M2 sites.

Keywords: X-ray emission spectra, hi-low spin transition, earth's inetriors, ionic size effect, high-pressure structure transition, transition metal element oxides