European Mineralogical Conference
Vol. 1, EMC2012-15, 2012
European Mineralogical Conference 2012
© Author(s) 2012

Correlation between structure transition and electron spin state of earth's interiors under high pressure

T. Yamanaka (1), S. Kharlamova (2), A. Kyono (3), Y. Nakamoto (4), V. Struzhkin (1), H. Mao (1), and R. Hemley (1)

(1) Geophysical Laboratory, Carnegie Institution of Washington, USA, (2) High Pressure Synergetic Consortium Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois, USA, (3) Division of Earth Evolution Sciences, Graduate School of Life and Environment Sciences, University of Tsukuba, Japan, (4) Center of quantum science and technology under extreme conditions Osaka University, Japan

Motivation To elucidate the correlation between structure transitions and spin state is one of the crucial problems for understanding the geophysical properties of earth interiors under high pressure. High-pressure studies of iron bearing spinels attract extensive 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 disproponation in the lower mantle or subduction zone.

Experiment Structure transitions of Fe3-xSixO4, Fe3-xTixO4 Fe3-xCrxO4 spinel solid solution have been investigated at high pressure up to 60 GPa by single crystal and powder diffraction studies using synchrotron radiation with diamond anvil cell. X-ray emission experiment (XES) at high pressure proved the spin transition of Fe-Kβ from high spin (HS) to intermediate spin state (IS) or low spin state (LS).

Jahn-Teller effect A cubic-to-tetragonal transition under pressure was confirmed by Jahn-Teller effect of IVFe2+ (3d6) in the tetrahedral site of Fe2TiO4 and FeCr2O4. Tetragonal phase is formed by the degeneracy of eg orbital of Fe2+ ion. Their c/a ratios are c/a<1 due to dx2-y2 orbital of the electronic tetrahedral configuration. However, Fe3O4 (I), Fe2SiO4 (N), do not have a tetragonal polymorph because of no IVFe2+ ion.

Spin transition HS-to-LS transition starts from 15.6GPa in Fe3O4, 19.6 GPa in Fe2TiO4, 17GPa in Fe2SiO4. The transition is more capable due to VIFe2+ in the octahedral site, than Fe ion in the 4-fold or 8-fold coordinated site. The extremely shortened octahedral bonds result in a distortion of 8-fold cation site. This structure change is accelerated at higher pressure due to HS-LS transition of Fe2+ in the 8-fold coordination site. This transition is induced by the 20% shrinkage of ionic radius of VIFe2+at the low sin state.

Post spinel transition The transition to orthorhombic post-spinel structure with Cmcm has been confirmed in the whole compositional range of Fe3-xTixO4 and Fe3-xCrxO4 . There are two octahedral cation sites: M1 and M2 in the orthorhombic phase. Fe2+ and Ti4+ are disordered in the M2 site. At pressures above 53 GPa, the Fe2TiO4 structure transforms to Pmma. This structure change results from the order-disorder transition.

Rhombohedral Fe2SiO4 The spin transition exerts an influence to Fe2SiO4 spinel structure and triggers two distinct curves of the lattice constant in the spinel phase. The reversible structure transition from cubic to rhombohedral phase (R-Fe2SiO4) was observed at about 45 GPa. R- Fe2SiO4 structure has R m space group symmetry with Z=6, D=5.867 g/cm3 about 5% larger than D=5.584 g/cm3 of spinel at 39 GPa. R- Fe2SiO4 structure has two alternated octahedral layers of Fe1 and Fe2 perpendicular to the c axis. Laser heating experiment at 1500 K has confirmed the decomposition from R- Fe2SiO4 to two oxides of FeO and SiO_2.