Structure transition of Fe$_{3-x}$Ti$_x$O$_4$ solid solution under pressures

Takamitsu YAMANAKA$^{1,2}$, Yuki NAKAMOTO$^2$, Atsushi KYONO$^1$, Svetlana KHARLAMOVA$^1$, Muhtar AHART$^1$, Viktor STRUZHKIN$^1$, Bjorn O. MYSEN, Ho-kwang MAO$^1$ and Russell J. HEMLEY$^1$

$^1$Carnegie Institution of Washington  Geophysical Laboratory
$^2$Center for Quantum Science and Technology under Extreme Conditions, Osaka University

The solid solutions between magnetite (Fe$_3$O$_4$) and ulvöspinel (Fe$_2$TiO$_4$) are principal magnetic substance for the rock magnetism in the crust. Their electron conductivity and magnetic properties are very similar to Fe$_{3-x}$Si$_x$O$_4$ (Yamanaka et al., 2001a, b). Fe$_3$O$_4$ is ferrimagnetic and Fe$_2$TiO$_4$ is antiferromagnetic. A number of previous studies have examined the cation distribution. Several models of the cation distribution in Fe$_{3-x}$Ti$_x$O$_4$ solid solutions have been proposed. In this experiment, electron spin states of these solid solutions have been investigated by X-ray powder diffraction, X-ray emission, Raman spectra and Mössbauer studies under high pressures.

Diffraction study of high-pressure transition of the Fe$_{3-x}$Ti$_x$O$_4$ solid solution

Powder diffraction experiments of Fe$_{3-x}$Ti$_x$O$_4$ at pressures up to 60 GPa using DAC and synchrotron radiation indicates their lattice constants, oxygen positional parameter and volumes of the tetrahedral (A) and octahedral site (B) as functions of composition and pressure. High-pressure transition from cubic spinel (Fd$\bar{3}$m, z=8) to orthorhombic post-spinel structure (Cmcm, z=4) is found in the whole compositional range. The transition pressure decreases from 27 GPa (x=0.0) to 12 GPa (x=1.0). The solid solutions with $0.734 \leq x \leq 1.0$ show the transformation from cubic to tetragonal spinel structure (I4$_1$/amd Z=4) with c/a$<$1.0 below the transition to the orthorhombic phase. The transition pressures are 12 GPa at x=0.734 and 8 GPa at x=1.0. This transition can be explained by Jahn-Teller effect of Fe$^{2+}$ at the A site or high-low spin transition of one of Fe$^{2+}$ ion in the A or B site.

X-ray emission study of Fe$_2$TiO$_4$

There are two Fe$^{2+}$ (3$d^6$) in the A and B site of Fe$_2$TiO$_4$ ulvöspinel. X-ray emission study at BL16-ID-D APS confirms mixed spin state of high spin ($e_g^2t_2g^4$) and low spin state for two ions or intermediate spin state of both ions at such much lower pressure as 5 GPa compared with Fe$_3$O$_4$. The ionic radii change by the high-low spin transition induced the cubic-to-tetragonal transition and may bring the first order transition. The spin transition pressure is a little lower than found by X-ray diffraction. The emission spectra does not show any spectra change up to 15GPa. The spin configuration of the orthorhombic phase has two iron position sites at 6-fold and 8-fold.

Bond distance and site volume

With increasing Ti$^{4+}$ substitution for Fe$^{3+}$ in the octahedral site, simultaneously inducing the substitution of Fe$^{2+}$ for Fe$^{3+}$ in the tetrahedral site, Rietveld profile fitting indicates that A-O and B-O bond distances reflect the cation distribution. The almost linear site volume change is induced by the substitution of Fe$^{2+}$ (0.63Å) for Fe$^{3+}$ (0.49Å) in the A site and the replacement of Ti$^{4+}$ (0.605Å) for Fe$^{3+}$ (0.63Å) in the B site.

Raman Spectra Measurement

Three clear bands were obtained at ambient conditions. The observed bands are associated with the following modes: 780 cm$^{-1}$ ($A_1g$) with stretching mode of the A site, 680 cm$^{-1}$ ($F_2g$) with bending mode of the B site, and 480 cm$^{-1}$ ($F_2g$) with bending mode of the B site. The peak positions of the last two peaks continuously shift toward to the higher energy sides with increasing pressure up to 19 GPa. Their FWHM values of the spectra remain almost unchanged up to about 7 GPa, where cubic and tetragonal spinels are stable, but start to increase rapidly at about at above 10 GPa. The results suggest the construction of the B-O bond distances and the phase transformation toward a lower-symmetry structure due to more than one band.

Key word: Fe$_{3-x}$Ti$_x$O$_4$ solid solution, High pressure, Powder diffraction, X-ray emission, Raman spectra.

tyamanaka@ciw.edu, t.yamanaka@kce.biglobe.ne.jp