High-pressure phase transitions of $\text{Fe}_2-x\text{Ti}_x\text{O}_4$ solid solution up to 60 GPa correlated with electronic spin transition

TAKAMITSU YAMANAKA,1,* ATSUSHI KYONO,1,2 YUKI NAKAMOTO,1,3 YUE MENG,4 SVETLANA KHALAMOVA,5 VICTOR V. STRUZHGIN,1 AND HO-KWANG MAO1,4,5

1Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, U.S.A.
2Division of Earth Evolution Sciences, Graduate School of Life and Environment Sciences, University of Tsukuba, Tsukuba 3058-572, Japan
3Center of Quantum Science and Technology under Extreme Conditions Osaka University, Osaka 560-8531, Japan
4High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.
5High Pressure Synergetic Consortium, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.

ABSTRACT

The structural phase transition of the titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) solid solution under pressures up to 60 GPa has been clarified by single-crystal and powder diffraction studies using synchrotron radiation and a diamond-anvil cell. Present Rietveld structure refinements of the solid solution prove that the preferred cation distribution is based on the crystal field preference rather than the magnetic spin ordering in the solid solution.

The Ti-rich phases in $0.734 \leq x \leq 1.0$ undergo a phase transformation from the cubic spinel of $\text{Fd}_{3} \text{m}$ to the tetragonal spinel structure of $\text{I}_{4}/\text{amd}$ with $c/a < 1.0$. The transition is driven by a Jahn-Teller effect of $\text{Fe}^{2+}$ ($3d^6$) on the tetrahedral site. The $c/a < 1$ ratio is induced by lifting of the degeneracy of the $e$ orbitals by raising the $d_{2z}$ orbital below the energy of the $d_{z^2}$ orbital. The distortion characterized by $c/a < 1$ is more pronounced with increasing Ti content in the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ solid solutions and with increasing pressure. An X-ray emission experiment of $\text{Fe}_x\text{Ti}_o$ at high pressures confirms the spin transition of FeKβ from high spin to intermediate spin (IS) state. The high spin (HS)-to-low spin (LS) transition starts at 14 GPa and the IS state gradually increases with compression. The $\text{VI}^{2+}$ in the octahedral site is more prone for the HS-to-LS transition, compared with $\text{Fe}^{2+}$ in the fourfold- or eightfold-coordinated site.

The transition to the orthorhombic post-spinel structure with space group $\text{Cmcm}$ has been confirmed in the whole compositional range of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$. The transition pressure decreases from 25 GPa ($x = 0.0$) to 15 GPa ($x = 1.0$) with increasing Ti content. There are two cation sites in the orthorhombic phase: M1 and M2 sites of eightfold and sixfold coordination, respectively. $\text{Fe}^{2+}$ and $\text{Ti}^{4+}$ are disordered on the M2 site. This structural change is accelerated at higher pressures due to the spin transition of $\text{Fe}^{2+}$ in the octahedral site. This is because the ionic radius of $\text{VI}^{2+}$ becomes 20% shorter by the spin transition. At 53 GPa, the structure transforms to another high-pressure polymorph with $\text{Pnma}$ symmetry with the ordered structure of Ti and Fe atoms in the octahedral site. This structure change results from the order-disorder transition.

Keywords: Phase transition, crystal structure, high-pressure study, XRD data

INTRODUCTION

High-pressure phase transitions of many spinel compounds in the Earth’s crust have attracted much attention from the geophysical community. Many spinels decompose directly or indirectly to ilmenite+B1, rutile+B1, and perovskite+B1 with increasing pressure. However, some spinels transform to the high-pressure post-spinel phases without decomposition. High-pressure studies of spinels are also motivated by the need to understand strong electronic correlations such as charge transfer, electron hopping, electron high-low spin transition, Jahn-Teller distortion, and charge disproportion in the lower mantle or subduction zone.

The solid solution of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) between magnetite ($\text{Fe}_3\text{O}_4$) and ulvöspinel ($\text{Fe}_2\text{Ti}_4\text{O}_8$) is one of the principal magnetic substances used for the investigation of rock magnetism. Its magnetic property changes from ferrimagnetic magnetite $\text{Fe}_3\text{O}_4$ to antiferromagnetic ulvöspinel $\text{Fe}_2\text{Ti}_4\text{O}_8$ with increasing Ti content. Several studies of the cation distribution in the solid solution have been carried out and the Fe/Ti distribution has been examined (Akimoto 1954; Neel 1955; Chevallier et al. 1955; O’Reilly and Banerjee 1965; Lindsley 1976; Kakol et al. 1992; Pearce et al. 2006). Models were proposed based on X-ray and neutron diffraction studies, magnetic susceptibility measurements and X-ray absorption. They are described by cation site preference based on crystal field, relative cation size and magnetic moment. Wechsler et al. (1984) reported almost the same result as the Akimoto model from their X-ray-neutron studies. Bossi et al. (2009) discussed the crystal chemistry of the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ solid solutions as a function of Ti composition by X-ray single-crystal diffraction study.

* E-mail: tyamanaka@ciw.edu