

## High-pressure phase transitions of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ solid solution up to 60 GPa correlated with electronic spin transition

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### 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  $Fd\bar{3}m$  to the tetragonal spinel structure of  $I4_1/amd$  with  $c/a < 1.0$ . The transition is driven by a Jahn-Teller effect of  $^{IV}\text{Fe}^{2+}$  ( $3d^6$ ) on the tetrahedral site. The  $c/a < 1$  ratio is induced by lifting of the degeneracy of the  $e$  orbitals by raising the  $d_{x^2-y^2}$  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  $\text{Fe}_2\text{TiO}_4$  at high pressures confirms the spin transition of  $\text{FeK}\beta$  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  $^{VI}\text{Fe}^{2+}$  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  $Cmcm$  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  $^{VI}\text{Fe}^{2+}$  becomes 20% shortened by the spin transition. At 53 GPa, the structure transforms to another high-pressure polymorph with  $Pmma$  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