

## High-pressure phase relation in Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>TiO<sub>4</sub> solid solution and structure of titanomagnetites

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Titanomagnetites Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub> in the solid solution between Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>TiO<sub>4</sub> have an inverse spinel structure (space group Fd-3m, Z=8) with a mixed valence iron. Ti ions exclusively occupy octahedral (B) sites and Fe ions occupy both tetrahedral (A) sites and octahedral (B) sites. Magnetite Fe<sub>3</sub>O<sub>4</sub>, end-member in the solid solution, is interested from the industrial usage. Also the high-pressure studying of titanomagnetites, which are the most abundant mineral responsible for magnetic and electric properties in crust, is crucial for geophysics. It has been suggested that most of spinel transforms into high-pressure phase with orthorhombic symmetry, CaMn<sub>2</sub>O<sub>4</sub>-type (Pbcm), CaTi<sub>2</sub>O<sub>4</sub>-type (Bbmm), or CaFe<sub>2</sub>O<sub>4</sub>-type (Pnma) structure. However, these structures are very similar, therefore previous high-pressure studies of magnetite Fe<sub>3</sub>O<sub>4</sub> are inconsistent about orthorhombic structure: CaMn<sub>2</sub>O<sub>4</sub>-type or CaTi<sub>2</sub>O<sub>4</sub>-type.

In this study, we performed high-pressure X-ray powder diffraction measurements of titanomagnetites with x=0, 0.1, 0.25, 0.5, 0.6, 0.7, 0.8, 1.0 at room temperature and investigated the compositional dependence of phase transition pressure and the structures of their polymorphs.

### Experiments

The samples were prepared by sintering technique at 1450C in Ar atmosphere or at 1350C in H<sub>2</sub>/CO<sub>2</sub> gas with powder mixture of reagent-grade Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The spinel structure and compositional uniformity were verified by X-ray powder diffraction and EPMA, respectively. The high-pressure experiments were carried out using lever or box-type diamond anvil cell (DAC) at KEK BL13A, BL18C, and Mo rotating anode X-ray generator at room temperature. The powdered titanomagnetites sample and pressure-transmitting media of 16:3:1 methanol:ethanol:H<sub>2</sub>O mixture or He (only for x=1.0) were placed in a sample chamber, drilled in a preindented Re gasket. Pressure was determined from ruby fluorescence method. Rietveld refinement has been carried out using the RIETAN2000 program.

### Results and Discussion

The composition(x)-pressure phase diagram for titanomagnetites at room temperature was clarified.

We observed a second-order phase transition for specimens with x=0.7-1.0. With increasing Ti content(x), the transition pressure from cubic to tetragonal phase decreased: 16GPa for x=0.7, 11GPa for x=0.8, and 6GPa for x=1.0. This second-order transition may be induced from tetragonal distortion due to the Jahn-Teller effect of Fe<sup>2+</sup> (3d<sup>6</sup>) at A site and does not take place for specimens with less than x=0.6, which contain lower amount of Fe<sup>2+</sup> at the A site.

In the whole solid solution range, cubic or tetragonal spinel transforms to orthorhombic phase. We tried powder structure analysis of Fe<sub>2</sub>TiO<sub>4</sub> (x=1.0) diffraction pattern at 30GPa by Reitveld analysis to determine the orthorhombic structure. The structure parameters of CaMn<sub>2</sub>O<sub>4</sub>-type, CaTi<sub>2</sub>O<sub>4</sub>-type, and CaFe<sub>2</sub>O<sub>4</sub>-type structure were applied as initial structure model. The R-factor for CaFe<sub>2</sub>O<sub>4</sub>-type was clearly larger than that of other two models proving that this structure should not be a candidate. Besides, the converged structure with starting from CaMn<sub>2</sub>O<sub>4</sub>-type model was identical to that for CaTi<sub>2</sub>O<sub>4</sub>-type model. This indicate that the orthorhombic phase adopts CaTi<sub>2</sub>O<sub>4</sub>-type structure. The transition pressure to orthorhombic phase also decrease with increasing Ti content(x).

In addition, we found a new higher-pressure form for specimens with x=0.8, 1.0 at 59GPa and 45GPa, respectively. We named it phase X. We could not confirm phase X for specimens with less than x=0.7 in the present experimental pressure range. The phase X is originated from the phase transition not from decomposition. This was probe by the back transformation. At this moment the structure has not been completed.