High-pressure phase transitions in FeTiO₃, Fe₂TiO₄ and FeTi₂O₅

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Introduction

Iron titanium oxides are of considerable importance in earth science as magnetic minerals and indicators of oxidation state. FeTiO₃, Fe₂TiO₄ and FeTi₂O₅ are Fe-Ti endmembers of natural ilmenite, spinel and pseudobrookite, respectively. Although several high-pressure investigations on the Fe-Ti oxides have been made with a diamond anvil cell, the results are still controversial, particulary at pressure above 20 GPa.

Experimental methods

We have examined detailed phase relations in FeTiO₃, Fe₂TiO₄ and FeTi₂O₅ up to 35 GPa and 1600 °C, using multianvil apparatus with tungsten carbide anvils. The quenched samples were examined by microfocus and powder X-ray diffractometers, and composition analysis was made using SEM-EDS. Insitu X-ray diffraction experiments on FeTi₂O₅ were performed with a laser-heated DAC at SPring-8.

Results and discussion

FeTiO₃ ilmenite (Ilm) transforms at 14 GPa and 1200 °C to perovskite (Pv) which changes to LiNbO3type phase on release of pressure [1]. In contrast to Pv-postPv transition in MgSiO₃, FeTiO₃ Pv dissociates at 27 GPa into two phases: calcium titanate (CT) type $Fe_2TiO_4 + O1$ -type TiO_2 below 1100 °C and Fe₂TiO₄ CT + a new FeTi₂O₅ phase above 1100 °C. The in-situ X-ray studies at 35 GPa showed that the new FeTi₂O₅ phase has orthorhombic symmetry and is 7 % denser than the low-pressure assemblage of FeTiO₃ Pv + TiO₂ O1. Fe₂TiO₄ ulvospinel dissociates into FeTiO₃ Ilm + wustite at 4 GPa, which changes into Pv + wustite at 14 GPa, and further they combine into Fe_2TiO_4 CT at 17 GPa. These results indicate that Fe2TiO4 CT, TiO2 O1 and the new orthorhombic $FeTi_2O_5$ phase are stable phases in the $FeO\text{-}TiO_2$ system in the upper part of lower mantle. A LiNbO3-type FeTiO3 phase recently discovered in shocked gneiss in the Ries Crater, Germany, was interpreted to be the retrograde transformation product of FeTiO₃ Pv [2]. Based on the phase relations in this study, we estimate that the phase occurred at shock pressure between 14 and 27 GPa.

[1] Leinenweber et al. (1991) Phys. Chem. Min., 18, 244-250.
[2] Dubrovinsky et al. (2009) Meteorit. Planet. Sci., 44, A64.