High-pressure transformation of CaFe2O4 (post-spinel)

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[Introduction] Studies about spinel structure and physical properties are very important for Earth's science under high-pressure and -temperature conditions, since spinel and spinel-type materials exist in the Earth crust or the upper Mantle.

In the previous studies CaMn2O4-type, CaFe2O4-type, and CaTi2O4-type structures are proposed as the candidates of the high-pressure phases of spinel-type materials, so-called post-spinel phase. It is suggested MgAl2O4 (spinel) transformed from post-spinel phase with CaFe2O4-type structure (Pbnm) to CaTi2O4-type structure (Cmcm) at 40 GPa (Funamori et al. 1998).

In this study, we investigated the further transformation of post-spinel phase under high pressure and the structure of the higher-pressure phase. We investigated CaFe2O4, which performs the same pressure-induced phase transition sequence as MgAl2O4 spinel, but their transition pressures are much lower than those of the latter.

[High-pressure powder diffraction] Synchrotron powder diffraction experiment under high pressure was carried out using lever-type diamond anvil cell (with 0.3 mm diameter culets) at PF (in KEK) BL18C at room temperature. An incident X-ray beam with a wavelength of 0.6095 A was collimated to 0.04 mm in diameter.

The powdered CaFe2O4 sample and pressure-transmitting media of 16:3:1 methanol:ethanol:H2O mixture were placed in a sample chamber, drilled in a Re gasket. Pressure was determined by ruby fluorescence method.

New diffraction peaks appeared at 40.1 GPa. In the process of pressure reduction, diffraction patterns returned to those of CaFe2O4 structure. Hence we could assume decomposition had not occurred. These indicate a phase transition from CaFe2O4 to high-pressure phase at 40.1 GPa.

We calculated V0 (volume at 0.01 GPa) = 299.53(A^3). The Birch-Murnaghan equation of state, with K'0 fixed to 4, yields K0 = 181 GPa.

[Structure at high-pressure] We tried the structure analysis of high-pressure phase using powder diffraction. At the first stage, indexing and determination of the lattice parameters have been performed by DICVOL04 (A. Boultif et al. 2004). We picked several models as candidates of lattice parameters.

Secondary, with applying the parameters, searching model of the unknown structure mentioned above was undergone using crystal structure model-assembly program SMAP (H. Miura et al. 1999) that uses the Monte Carlo method.

[Single-crystal structural analysis] The synthesis of single-crystal of CaFe2O4 under high-temperature and -pressure was carried out using 5000t multi anvil press at Institute for Study of the Earth's Interior, Okayama University. We used multi anvil of tungsten carbide with 3mm truncate edge length. The cell assembly was composed of pressure-transmitting media of MgO, heater of Re, heat insulation material of ZrO2, and buffer of Fe2O3. We compressed up to 15 GPa and then heated the sample up to 1500 degree Celsius. The sample was kept for 55 minutes. After that, it was quenched and the sample was recovered at ambient condition. As a result, a black and platy single-crystal was obtained.

X-ray fine focused powder diffraction measurement was conducted with thus obtained single-crystal sample. The diffraction patterns of the sample were confirmed to be CaFe3O5. In addition, the composition was CaFe3O5 by EPMA analysis.

The diffraction intensity measurement by four-circle X-ray diffractometer was conducted with a wavelength of 0.71969 A, scan method of omega-2theta scan, scan width of 0.5 degree, scan rate of 2 degree / min. As a result, 923 reflections were obtained and the lattice parameters were determined, a = 3.03 A, b = 10.01 A, and c = 12.73 A.

We refined the structure of the single crystal as CaFe3O5 with ABSORB software package (R. J. Angel 2004) for absorption correction and RADY software package (Sasaki 1989) for full matrix least-squares refinement. We applied the structure parameters reported by Evrard O. et al. (1980) as the initial parameters.