FeCr2O4 の高圧相転移と新規ポストスピネル相の結晶構造
High-pressure transitions in FeCr2O4 and crystal structures of new post-spinel phases

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Introduction
FeCr2O4 chromite has the spinel (Sp) structure, and forms the solid solution with MgAl2O4 and MgCr2O4 which occurs in the Earth’s mantle. The chromitite composed of mostly FeCr2O4-rich spinel includes high-pressure minerals such as diamond and coesite, which suggest possible indicators of material cycles in the deep mantle (Arai, 2010; Yamamoto et al., 2009). Chen et al. (2003) reported occurrence of the high-pressure polymorphs of FeCr2O4-rich composition in Suizhou meteorite and synthesized them with diamond anvil cell. They demonstrated that the natural chromite spinel transforms to calcium ferrite (CF)-type at 12.5 GPa and to calcium titanate (CT)-type above 20 GPa. High-pressure transition study of pure FeCr2O4 end-member demonstrated that cubic spinel of FeCr2O4 transforms to tetragonal at high-pressure and room temperature (Kyono et al., 2012). In this study, we report experimental results on the phase relations in FeCr2O4 at high pressure and high temperature and the crystal structure analyses of new post-spinel phases.

Experimantal methods
FeCr2O4 spinel was synthesized from a mixture of Fe2O3 and Cr2O3 with a 1:2 molar ratio by heating at 1200C for 24 h in a controlled oxygen fugacity using a mixture of H2, CO2 and Ar with volume ratios of 1:1:2. High-pressure experiments were made by quenching method at 12-28 GPa and 800-1600C with a Kawai-type 6-8 multianvil high-pressure apparatus at Gakushuin University. Phase identification of each recovered sample was made with powder and microfocus X-ray diffractometers, and compositional analysis was made with a SEM-EDS. The recovered FeCr2O4 sample was observed by a TEM at Geodynamics Research Center of Ehime University. Angle-dispersive synchrotron X-ray diffraction measurements of some recovered samples were made at ambient conditions using the beam line BL02-B2 at SPring-8 for Rietveld analysis with the RIETAN-FP software (Izumi and Momma, 2007).

Results and discussion
Sp-type FeCr2O4 first dissociates into a mixture of Fe2Cr2O5 + Cr2O3 at about 15 GPa, and further transforms to a CF-like phase at lower temperature than 1300C and CT-type FeCr2O4 at higher temperature at around 20 GPa. Although the CF-like phase had the same space group as the CF-type structure from the result of TEM observation, the X-ray diffraction pattern was somewhat different from that of the CF-type structure. Rietveld refinement confirmed that the FeCr2O4 synthesized above about 20 GPa at higher temperature than 1300C has the CT-type structure and that Fe2Cr2O5 phase is isostructural to the high-pressure Mg2Al2O5 phase (Enomoto et al., 2009). The CT-type phase with pure FeCr2O4 composition and the Mg2Al2O5-type Fe2Cr2O5 were synthesized for the first time, and the structure analyses of the phases were carried out.

Keywords: post-spinel, high-pressure, Rietveld analysis, chromite, FeCr2O4, TEM observation