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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

$FeCr_2O_4$ chromite has the spinel (Sp) structure, and forms the solid solution with $MgAl_2O_4$ and $MgCr_2O_4$ which occurs in the Earth's mantle. The chromitite composed of mostly $FeCr_2O_4$-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 $FeCr_2O_4$-rich composition in Suizhou meteorite and synthesized them with diamond anvil cell. They demostrated 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 transiton study of pure $FeCr_2O_4$ end-member demonstrated that cubic spinel of $FeCr_2O_4$ transforms to tetragonal at high-pressure and room temperature (Kyono et al., 2012). In this sudy, we report experimental results on the phase relations in $FeCr_2O_4$ at high pressure and high temperature and the crystal structure analyses of new post-spinel phases.

Experimantal methods

$FeCr_2O_4$ spinel was synthesized from a mixture of Fe_2O_3 and Cr_2O_3 with a 1:2 molar ratio by heating at 1200C for 24 h in a controlled oxygen fugacity using a mixture of H_2, CO_2 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 $FeCr_2O_4$ 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 $FeCr_2O_4$ first dissociates into a mixture of $Fe_2Cr_2O_5$ + Cr_2O_3 at about 15 GPa, and further transforms to a CF-like phase at lower temperature than 1300C and CT-type $FeCr_2O_4$ 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 $FeCr_2O_4$ synthesized above about 20 GPa at higher temperature than 1300C has the CT-type structure and that $Fe_2Cr_2O_5$ phase is isostructural to the high-pressure $Mg_2Al_2O_5$ phase (Enomoto et al., 2009). The CT-type phase with pure $FeCr_2O_4$ composition and the $Mg_2Al_2O_5$-type $Fe_2Cr_2O_5$ were synthesized for the first time, and the structure analyses of the phases were carried out.

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