CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

High-pressure high-temperature transitions in MgCr$_2$O$_4$ and crystal structures of new Mg$_2$Cr$_2$O$_5$ and post-spinel MgCr$_2$O$_4$ phases with implications for ultrahigh-pressure chromitites in ophiolites†

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ABSTRACT

We determined phase relations in MgCr$_2$O$_4$ at 12–28 GPa and 1000–1600 °C using a multi-anvil apparatus. At 12–15 GPa, spinel-type MgCr$_2$O$_4$ (magnesiochromite) first decomposes into a mixture of new Mg$_2$Cr$_2$O$_5$ phase + corundum-type Cr$_2$O$_3$ at 1100–1600 °C, but it dissociates first into MgO periclase + corundum-type Cr$_2$O$_3$ at 1000 °C. At about 17–19 GPa, the mixture of Mg$_2$Cr$_2$O$_5$ phase + corundum-type Cr$_2$O$_3$ transforms to a single MgCr$_2$O$_4$ phase. Structure refinements using synchrotron X-ray powder diffraction data indicated that the high-pressure MgCr$_2$O$_4$ phase has a CaTi$_3$O$_7$-type structure (Cmcm), and that the basic structure of the Mg$_2$Cr$_2$O$_5$ phase is the same as that of recently found modified ludwigite-type Mg$_2$Al$_2$O$_5$ and Fe$_2$Cr$_2$O$_5$ (Pbam). The phase relations in this study may suggest that natural chromitomes in the Luobusa ophiolite regarded as the deep-mantle origin were derived from the mantle shallower than the depths corresponding to pressure of 12–15 GPa because of absence of the assemblage of (Mg,Fe)$_2$Cr$_2$O$_5$ +Cr$_2$O$_3$ in the chromitomes.

Keywords: Post-spinel, Rietveld refinement, crystal structure, high pressure, phase transition, magnesiochromite, calcium titanate, chromite, ophiolite

INTRODUCTION

Chromium-bearing spinel is widely found in igneous and metamorphic rocks as an accessory mineral, and it is accepted as an important indicator for petrogenesis (e.g., Sack and Ghiorso 1991). MgCr$_2$O$_4$ spinel (magnesiochromite) is a major end-member of chromian spinel in mantle-derived peridotites. It is also the commercially available ore mineral of chromium. At ambient conditions, MgCr$_2$O$_4$ spinel has the normal spinel structure (space group Fd$ar{3}$m) in which Mg$^{2+}$ and Cr$^{3+}$ occupy the tetrahedral and octahedral sites, respectively (O’Neill and Dollase 1994).

High-pressure transition of A$^{2+}$B$_2^{3+}$O$_4$ spinel (post-spinel transition) has been extensively studied in various compounds to clarify host phases of trivalent cations such as Al$^{3+}$, Cr$^{3+}$, and Fe$^{3+}$ in the deep mantle. The CaFe$_2$O$_4$(CF)- and CaTi$_2$O$_4$(CT)-structured phases of A$^{2+}$B$_2^{3+}$O$_4$ are major post-spinel phases. Both the CaFe$_2$O$_4$-type structure (Pnma) and CaTi$_2$O$_4$-type structure (Cmcm) consist of double chains of edge-shared B$^{3+}$O$_6$ octahedra running parallel to one of orthorhombic cell axes, in which A$^{2+}$ ions occupy tunnel spaces surrounded by corner-sharing of four double chains, though the CaFe$_2$O$_4$- and CaTi$_2$O$_4$-type structures have different frameworks of B$^{3+}$O$_6$ octahedra. Yong et al. (2012) showed very recently that a cubic-to-tetragonal transition occurred in MgCr$_2$O$_4$ spinel at about 20 GPa and room temperature, based on X-ray diffraction and Raman spectroscopy at high pressure. However, high-pressure and high-temperature behaviors of MgCr$_2$O$_4$ spinel are not still clarified.

We recently found that MgAl$_2$O$_4$ spinel first decomposes into Mg$_2$Al$_2$O$_5$ + Al$_2$O$_3$ at about 20 GPa above 2000 °C and FeCr$_2$O$_4$ chromitite into Fe$_2$Cr$_2$O$_5$ + Cr$_2$O$_3$ at about 14 GPa and 1200 °C, prior to transitions to CF- or CT-phase at higher pressure (Enomoto et al. 2009; Kojitani et al. 2010; Ishii et al. 2014). The Mg$_2$Al$_2$O$_5$ and Fe$_2$Cr$_2$O$_5$ phases have the same structure named modified ludwigite (mLD) structure (Pbam) in which edge- and corner-shared (Mg,Al)$_2$O$_5$ or (Fe,Cr)$_2$O$_5$ octahedra are running parallel to c-axis and tunnel spaces surrounded by the octahedral chains are occupied by six-coordinated Mg$^{2+}$ or Fe$^{3+}$ (Enomoto et al. 2009; Ishii et al. 2014).

In chromitomes composed of MgCr$_2$O$_4$-rich, FeCr$_2$O$_4$-bearing spinel in the Luobusa ophiolite, Tibet, high-pressure minerals such as diamond and coesite were recently discovered (Yang et al. 2007; Yamamoto et al. 2009; Dobrzhinetskaya et al. 2009). Based on the natural observations, the deep-mantle origin of the chromitomes has been discussed (Yang et al. 2007; Araki 2010, 2013; Yamamoto et al. 2009). Ishii et al. (2014) suggested a possible depth limit for origin of the chromitomes of the Luobusa ophiolite, based on phase relations in FeCr$_2$O$_4$ at high pressure and high temperature. However, it would be desirable to discuss the issue using the high-pressure high-temperature phase relations of both MgCr$_2$O$_4$ and FeCr$_2$O$_4$.

In this study, we have investigated in detail the phase rela-