High-pressure syntheses and crystal structure analyses of a new low-density CaFe$_2$O$_4$-related and CaTi$_3$O$_4$-type MgAl$_2$O$_4$ phases

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**Abstract**

Three single crystals of CaTi$_3$O$_4$ (CT)-type, CaFe$_2$O$_4$ (CF)-type, and new low-density CaFe$_2$O$_4$ (LD-CF) related MgAl$_2$O$_4$ were synthesized at 27 GPa and 2500 °C and also CT-type MgAl$_2$O$_4$ at 45 GPa and 1727 °C using conventional and advanced multi-anvil technologies, respectively. The structures of CT-type and LD-CF related MgAl$_2$O$_4$ were analyzed by single-crystal X-ray diffraction. The lattice parameters of the CT-type phases synthesized at 27 and 45 GPa were $a = 2.7903(4)$, $b = 9.2132(10)$, and $c = 9.3968(12)$ Å, and $a = 2.7982(6)$, $b = 9.2532(15)$, and $c = 9.4461(16)$ Å, respectively, ($Z = 4$, space group: $Cnmc$) at ambient conditions. This phase has an AlO$_6$ octahedral site and an MgO$_6$ bicapped trigonal prism with two longer cation-oxygen bonds. The LD-CF related phase has a novel structure with orthorhombic symmetry (space group: $Pnma$), and lattice parameters of $a = 9.207(2)$, $b = 3.0118(6)$, and $c = 9.739(2)$ Å ($Z = 4$). The structural framework comprises tunnel-shaped spaces constructed by edge- and corner-sharing of AlO$_6$ and a $4+1$ AlO$_6$ trigonal bipyramid, in which MgO$_6$ trigonal bipyramids are accommodated. The CF-type MgAl$_2$O$_4$ also has the same space group of $Pnma$ but a slightly different atomic arrangement, with Mg and Al coordination numbers of 8 and 6, respectively. The LD-CF related phase has the lowest density of 3.50 g/cm$^3$ among MgAl$_2$O$_4$ polymorphs, despite its high-pressure synthesis from the spinel-type phase (3.58 g/cm$^3$), indicating that the LD-CF related phase formed via back-transformation from a high-pressure phase during the recovery. Combined with the previously determined phase relations, the phase transition between CF- and CT-type MgAl$_2$O$_4$ is expected to have a steep Clapeyron slope. Therefore, CT-type phase may be stable in basaltic- and continental-crust compositions at higher temperatures than the average mantle geotherm in the wide pressure range of the lower mantle. The LD-CF related phase could be found in shocked meteorites and used for estimating shock conditions.

**Keywords:** Single-crystal X-ray diffraction, crystal structure, high pressure, phase transition, spinel, post-spinel, calcium titanate, calcium ferrite

**Introduction**

MgAl$_2$O$_4$ spinel (Sp) is a minor but common mineral in lherzolite xenoliths from 20–50 km depths and in meteorites. The high-pressure polymorphs of MgAl$_2$O$_4$ with calcium ferrite (CF)- and calcium titanate (CT)-type structures are considered important and abundant components that are stable under lower-mantle conditions in Al$_2$O$_3$-rich rocks, such as basalt, upper continental crust, and sediment (e.g., Irifune and Ringwood 1993; Irifune et al. 1994; Ono et al. 2005; Ishii et al. 2012, 2019a). High-pressure transitions in MgAl$_2$O$_4$ thus have been an important subject for understanding hosts of aluminum in the Earth’s mantle.

High-pressure and high-temperature phase transitions in MgAl$_2$O$_4$ have been investigated for more than four decades (Liu 1978; Irifune et al. 1991, 2002; Funamori et al. 1998; Akaogi et al. 1999; Ono et al. 2006; Enomoto et al. 2009; Kojitani et al. 2010, 2012). At temperatures of 1200 to 1600 °C with pressures of 15 to 16 GPa, MgAl$_2$O$_4$ Sp decomposes to MgO periclase (Pe) + Al$_2$O$_3$ corundum (Cor) at pressures of 15 to 16 GPa. They react at pressures of 25 to 27 GPa to form CF-type MgAl$_2$O$_4$ (Akaogi et al. 1999; Irifune et al. 2002; Kojitani et al. 2012). At temperatures above 2000 °C and pressures of 20 to 26 GPa, Sp first dissociates to modified ludwigite-type Mg$_5$Al$_2$O$_7$ + Cor (Kojitani et al. 2010). The dissociated phases again form a single phase with MgAl$_2$O$_4$ composition at pressures above 26 GPa, and this single phase has been recovered as an unknown phase at ambient conditions (Enomoto et al. 2009; Kojitani et al. 2010). Above 40 GPa, the CF phase transforms to a CT-type phase in a wide temperature range of 1200 to 3000 °C (Funamori et al. 1998; Ono et al. 2006). The structure of CT-type MgAl$_2$O$_4$ has not yet been analyzed due to difficulty in collecting data suitable for analyzing the structure. It is important to analyze the structure for clarifying that the phase transformed from CF phase is CT phase. It was also reported that a poorly characterized orthorhom-