High-pressure phase relations and crystal chemistry of calcium ferrite-type solid solutions in the system MgAl$_2$O$_4$-Mg$_2$SiO$_4$

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ABSTRACT

To map the stability field of calcium ferrite-type MgAl$_2$O$_4$–Mg$_2$SiO$_4$ solid solutions, high-pressure phase relations in the system MgAl$_2$O$_4$-Mg$_2$SiO$_4$ were studied in the compositional range of 0 to 50 mol% Mg$_2$SiO$_4$. The calcium ferrite solid solutions are stable above 23 GPa at 1600°C, and the maximum solubility of Mg$_2$SiO$_4$ component in MgAl$_2$O$_4$ calcium ferrite is 34 mol%. Lattice parameters and unit-cell volume of calcium ferrite-type MgAl$_2$O$_4$ (space group Pbnm) determined by Rietveld analysis are $a = 9.9498(6)$ Å, $b = 8.6468(6)$ Å, $c = 2.7901(2)$ Å, and $V = 240.02(2)$ Å$^3$. Lattice parameters for the MgAl$_2$O$_4$–Mg$_2$SiO$_4$ solid solutions with the compositions of 14, 24, and 34 mol% Mg$_2$SiO$_4$ indicated the following compositional dependency of lattice parameters: $a (Å) = 9.9498 + 0.1947 \cdot X_{Mg_2SiO_4}$, $b (Å) = 8.6468 - 0.1097 \cdot X_{Mg_2SiO_4}$, and $c (Å) = 2.7901 + 0.0086 \cdot X_{Mg_2SiO_4}$, where $X_{Mg_2SiO_4}$ is the mole fraction of Mg$_2$SiO$_4$ component. A linear extrapolation of the composition-molar volume relationship gave an estimated volume of 36.49(2) cm$^3$/mol for the hypothetical calcium ferrite-type Mg$_2$SiO$_4$. This value is larger than that of the isomorphous mixture of MgSiO$_3$ perovskite and MgO, 35.72(1) cm$^3$/mol. This implies that the mixture of MgSiO$_3$ perovskite and MgO is more stable than the hypothetical calcium ferrite-type Mg$_2$SiO$_4$ under the lower mantle conditions.

Keywords: MgAl$_2$O$_4$, Mg$_2$SiO$_4$, calcium ferrite, high pressure, phase relation, Rietveld refinement

INTRODUCTION

MgAl$_2$O$_4$ spinel is an important mineral in the Earth’s upper mantle. The spinel decomposes to MgO periclase + Al$_2$O$_3$ corundum at about 15 GPa (e.g., Akaogi et al. 1999). Irifune et al. (1991) first reported that the oxide mixture reacts to form a phase with the calcium ferrite-type structure at about 25 GPa. Because the calcium ferrite structure has tunnel-like large cation sites suitable for alkali ions, it has been proposed as a possible structure for a high-pressure AB$_2$O$_3$ compound that could host alkali elements in the Earth’s deep mantle (e.g., Ringwood et al. 1967). Recent high-pressure and high temperature experiments of mid-oceanic ridge basalt (MORB) considering subducted oceanic crust into deep mantle showed existence of aluminous phases with the calcium ferrite-type structure at lower mantle conditions (Kesson et al. 1994; Hirose et al. 1999; Funamori et al. 2000; Ono et al. 2001a, 2002). Chemical analyses of these phases indicated that they consisted mainly of NaAlSiO$_4$ and MgAl$_2$O$_4$ components. Guignot and Andrault (2004) noticed that the calcium ferrite phase in the high-pressure phase assemblage of MORB also contained a relatively large amount of Mg$_2$SiO$_4$ component. In general, it is convenient to treat the calcium ferrite phase as a solid solution among MgAl$_2$O$_4$, NaAlSiO$_4$, Mg$_2$SiO$_4$, and other minor end-members. However, detailed information of the calcium ferrite solid solutions is limited to the MgAl$_2$O$_4$-CaAl$_2$O$_4$ system (Akaogi et al. 1999).

Considering the coupled substitution, 2Al$^{3+}$ = Mg$^{2+}$ + Si$^{4+}$, which has been observed in various solid solutions such as majorite garnet solid solution in the system Mg$_3$Al$_2$Si$_3$O$_12$, it is likely that the same substitution occurs in MgAl$_2$O$_4$ calcium ferrite, resulting in a solid solution between MgAl$_2$O$_4$ and Mg$_2$SiO$_4$. Therefore, it is interesting from crystal chemical and geochemical points of view to determine how much Mg$_2$SiO$_4$ component can be incorporated into MgAl$_2$O$_4$ calcium ferrite.

In this study, the stability field of the calcium ferrite phase in the MgAl$_2$O$_4$–Mg$_2$SiO$_4$ system was established at pressures up to 27 GPa. The maximum solubility of Mg$_2$SiO$_4$ component was of particular interest. Only lattice parameters at ambient and high pressure have been determined for the calcium ferrite-type MgAl$_2$O$_4$ (Irifune et al. 1991, 2002; Yutani et al. 1997; Funamori et al. 1998). In this study, the structure was refined using the Rietveld method to determine the atomic positions and displacement parameters. Lattice parameters of some members of MgAl$_2$O$_4$–Mg$_2$SiO$_4$ solid solution were also determined to establish changes in the lattice parameters as a function of composition. Instability of the hypothetical calcium ferrite-type Mg$_2$SiO$_4$ is also discussed using its volume estimated by extrapolation from those of the known solid-solution members.

EXPERIMENTAL METHODS

High-pressure phase relations

High-pressure phase relation experiments in the system MgAl$_2$O$_4$-Mg$_2$SiO$_4$ were done with a Kawai-type multi-anvil high-pressure apparatus at Gakushuin University. The truncated edge length of tungsten carbide anvils was 1.5 mm. The pressure medium was a semi-sintered MgO octohedron. A cylindrical Re heater was put into the pressure medium together with a LaCrO$_3$ sleeve for thermal insulation. The powder sample was placed directly in the Re heater. Temperature was measured with a Pt/Pt-13% Rh thermocouple whose hot junction was positioned in the central part of the heater. Pressure was calibrated at room temperature using...