High-pressure phase relations in the MgAl2O4-Mg2SiO4 system

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High-pressure and high-temperature experiments on MORB have reported the existence of an Al-rich phase in its high-pressure phase assemblage. Calcium ferrite-type MgAl2O4 is regarded as the most likely candidate of the Al-rich phase. Tiny amount of the calcium ferrite-type MgAl2O4 can be synthesized due to a synthesis pressure which is almost the upper limit of a Kawai-type high-pressure apparatus with tungsten carbide anvils. Furthermore, a negative slope of the phase boundary between the calcium ferrite–type MgAl2O4 and MgO + Al2O3 makes a single phase synthesis difficult. From these reasons, detailed crystal structure of the calcium ferrite-type MgAl2O4 has not been researched very well. In this study, the Rietveld refinement of the calcium ferrite-type MgAl2O4 was performed to determine lattice parameters and fractional atomic coordinates. Since calcium ferrite-type MgAl2O4 containing Mg2SiO4 component was found in our high-pressure experiments in the system MgO-Al2O3-SiO2, we investigated high-pressure phase relations in the MgAl2O4-Mg2SiO4 system to know the stability field for the MgAl2O4-Mg2SiO4 calcium ferrite solid solutions. Effect of Mg2SiO4 solubility on lattice parameters was also obtained.

High-pressure and high-temperature experiments were performed using a Kawai-type high-pressure apparatus with tungsten carbide anvils (TEL 1.5 mm) at Gakushuin University. Samples were heated by a Re heater. Temperature was measured by a Pt/Pt-13%Rh thermocouple. Starting materials for the phase relation experiments were the mixture of MgO, Al2O3 and SiO2. Six kinds of starting materials with the bulk composition of MgAl2O4:Mg2SiO4 = 95:5, 90:10, 78:22, 70:30, 50:50 and 20:80 were prepared. They were heated at 1600 C and at 21, 22, 23, 25 or 27 GPa for three hours. Pure calcium ferrite-type MgAl2O4 for the Rietveld refinement was synthesized by heating MgAl2O4 spinel at 27 GPa and about 2200 C for one hour. Recovered samples were cooled to the liquid nitrogen temperature and then crashed into very small peaces for a powder XRD measurement (Cr K-alpha, 45 kV, 250 mA). XRD data were measured by a step-scanning method with a step of 0.02 degree and a 2 theta range of 20-140 degree. Obtained XRD profiles were used to identify phases and to determine lattice parameters by the least squares method. Composition analyses were made using a SEM-EDS. The Rietveld analysis was performed using the RIETAN-2000 program.

The minimum pressure in the stability filed of the MgAl2O4-Mg2SiO4 calcium ferrite solid solutions is about 23 GPa. The maximum solubility of Mg2SiO4 component is about 25% at 1600 C and at the pressure range of 23-27 GPa. Lattice parameters for calcium ferrite-type MgAl2O4 were determined to be a = 9.9495(6) A, b = 8.6466(5) A, c = 2.7901(2) A (space group Pbnm) by the Rietveld analysis. Obtained fractional atomic coordinates for all of sites are almost the same as those for CaFe2O4 calcium ferrite. This is consistent with that an ionic radius ratio of 8 coordinate Mg2+ to 6 coordinate Al3+ is very similar to that of 8 coordinate Ca2+ to 6 coordinate Fe3+ (high spin). Lattice parameters for MgAl2O4-Mg2SiO4 calcium ferrite solid solutions were obtained as a = 9.9495(6) A, b = 8.6466(5) A, c = 2.7901(2) A for the MgAl2O4: Mg2SiO4 = 90:10 solid solution, and a = 9.9495(6) A, b = 8.6466(5) A, c = 2.7901(2) A for the MgAl2O4:Mg2SiO4 = 78:22 solid solution. The composition-lattice parameters relation indicates that increase of Mg2SiO4 component results in increase of the a-axis and decrease of the b-axis. The c-axis indicates no change with increasing Mg2SiO4 component. A linear extrapolation of the obtained volumes provides a volume for a hypothetical calcium ferrite-type Mg2SiO4 of 35.82(7) cm3/mol. It is larger than that for MgO + MgSiO3 perovskite (35.72(2) cm3/mol).