Thermodynamic investigation on phase equilibrium boundary between calcium ferrite-type $MgAl_2O_4$ and $MgO + \alpha\text{-}Al_2O_3$

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ABSTRACT

Calcium ferrite-type $MgAl_2O_4$ is an important endmember of the calcium ferrite phase, which is a high-pressure constituent mineral of mid-ocean ridge basalt at lower mantle conditions. Drop-solution enthalpies of the calcium ferrite-type $MgAl_2O_4$ and a mixture of MgO and $\alpha\text{-}Al_2O_3$ with a mol ratio of 1:1 were measured as 109.18 ± 1.10 and 140.41 ± 0.85 kJ/mol, respectively, by drop-solution calorimetry with $2PbO \cdot B_2O_3$ solvent at 978 K. As determined by differences in the drop-solution enthalpies, the formation enthalpy of calcium ferrite-type $MgAl_2O_4$ from oxides at 298 K ($\Delta_f H^\circ_{298}$) was 31.23 ± 1.39 kJ/mol. To thermodynamically calculate the phase boundary between calcium ferrite-type $MgAl_2O_4$ and $MgO + \alpha\text{-}Al_2O_3$, the $\Delta_f H^\circ_{298}$ was used together with the other thermochemical and thermoelastic data for calcium ferrite-type $MgAl_2O_4$, i.e., heat capacity and entropy estimated by the lattice vibrational calculation, thermal expansivity calculated from the Grüneisen equation, and isothermal bulk modulus and its pressure and temperature derivatives determined by Sueda et al. (2009). The calculated boundary gave a phase transition pressure of 26.6 GPa at 1873 K with a slope of -0.006 GPa/K. This phase boundary is potentially applicable to a high-pressure calibration standard.

1. Introduction

$MgAl_2O_4$ spinel (Sp), a major component of common constituent minerals in the shallow upper mantle, decomposes into MgO periclase $+ \alpha\text{-}Al_2O_3$ corundum at 15–20 GPa (Liu, 1975; Ohtani et al., 1975). Irifune et al. (1991) first reported that $MgAl_2O_4$ with a calcium ferrite ($CaFe_2O_4$)-type crystal structure was synthesized above 25 GPa, hereafter designated as $MgAl_2O_4$ CF. Many high-pressure experimental studies on mid-ocean ridge basalts of oceanic crust subducted into the deep mantle also have reported that an aluminous phase with the calcium ferrite-type structure appears at lower mantle conditions (e.g., Irifune and Ringwood, 1993; Kesson et al., 1994; Hirose et al., 1999; Funamori et al., 2000; Ono et al., 2001; Ricolleau et al., 2008). $MgAl_2O_4$ CF is a major constituent endmember of the calcium ferrite phase (e.g., Guignot and Andrault, 2004). Therefore, an understanding of high-pressure stability relations of $MgAl_2O_4$ CF is important for clarifying the behavior of calcium ferrite phases in the deep mantle.

Akaogi et al. (1999) investigated the phase boundary between $MgAl_2O_4$ CF and $MgO + \alpha\text{-}Al_2O_3$ by high-pressure high-temperature experiments with a quench method. They reported that the boundary has a negative slope and appears between 26 and 27 GPa at 1873 K. Irifune et al. (2002) also determined the phase boundary by both high-pressure in situ and quench experiments, and they proposed a boundary at 25–26 GPa in a temperature range of 1273–1873 K with a slope of -0.002 GPa/K. The pressure of the boundary by Irifune et al. (2002) is 1.5–2 GPa lower than that reported by Akaogi et al. (1999). Very recently, Enomoto et al. (2009) determined the high-pressure high-temperature phase relations in $MgAl_2O_4$ by using the quench method. In addition, more comprehensive phase relations were reported by Kojitani et al. (2010). In both studies, the boundary between $MgAl_2O_4$ CF and $MgO + \alpha\text{-}Al_2O_3$ passes through approximately 27 GPa at 1873 K and shows a steeper negative slope (-0.005 GPa/K) than that observed in previous investigations. Because the results of studies on the $P-T$ boundary are inconsistent, it is desired to determine the stability field of $MgAl_2O_4$ CF with a greater accuracy.

With the availability of a complete set of thermochemical and thermophysical property data, thermodynamics is a powerful tool for calculating the phase boundary independent of the results of high-pressure phase relation experiments. In contrast to the well-constrained thermodynamic properties of MgO and $\alpha\text{-}Al_2O_3$ (Robie and Hemingway, 1995), the thermochemical data of $MgAl_2O_4$ CF are limited because of its stability pressure above 25 GPa (Ono et al., 2009). The heat capacity, entropy, and thermal expansivity can be calculated by using the lattice vibrational properties determined by spectroscopy, the bulk modulus and its temperature derivative for $MgAl_2O_4$ CF determined from high-pressure in situ X-ray dif-

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fraction experiments of Sueda et al. (2009). On the other hand, the formation enthalpy of MgAl$_2$O$_4$ CF was lacking because of the difficulties in preparing sufficient samples for calorimetry. Recently, at Gakushuin University, we modified the Kawai-type high-pressure apparatus system by using tungsten-carbide anvils with a truncated edge length of 2.5 mm to reach a pressure of approximately 28 GPa (Ishii et al., 2011). This method allowed us to synthesize a nearly pure MgAl$_2$O$_4$ CF sample of about 5 mg per run. In this study, drop-solution enthalpies of MgAl$_2$O$_4$ CF and of a mixture of MgO and α-Al$_2$O$_3$ with a 1:1 mol ratio were measured. The difference between the drop-solution enthalpies provided the phase transition enthalpy at ambient conditions for the reaction MgO + α-Al$_2$O$_3$ = - MgAl$_2$O$_4$ CF, which is the same as the formation enthalpy from oxides for MgAl$_2$O$_4$ CF. The phase equilibrium boundary was constrained thermodynamically by using the phase transition enthalpy and other carefully assessed thermochemical and thermophysical properties available for the three materials.

2. Experimental methods

2.1. Sample preparations

Reagent-grade MgO and Al$_2$O$_3$ were heated at 1273 K in air for 5 h in separate Pt crucibles. Powder X-ray diffraction (XRD) measurements (Rigaku RINT2500V) confirmed that the treated MgO and Al$_2$O$_3$ were single phases with rock-salt and corundum structures, respectively. The MgO and α-Al$_2$O$_3$ powders were mixed with a mol ratio of 1:1 and ground under ethanol for 1 h in an agate mortar. The mixture was then heated at 773 K for 3 h to completely remove moisture and ethanol. The prepared mixture sample was used for calorimetry.

MgAl$_2$O$_4$ CF samples were synthesized by using the Kawai-type multi-anvil high-pressure apparatus. The second-stage anvils were 26-mm tungsten carbide cubes with triangular 2.5-mm edge length surfaces. A starting material of MgAl$_2$O$_4$ Sp was prepared by heating a mixture of reagent-grade MgO and Al$_2$O$_3$ at 1673 K for 7 days. The powder XRD measurement and analysis of the synthesized sample through a scanning electron microscope (SEM) (JEOL JSM-6360) with an energy dispersive spectrometer (EDS) (Oxford Instruments INCA energy 300) confirmed that the substance was a single phase of stoichiometric MgAl$_2$O$_4$ spinel. The starting material of the synthetic MgAl$_2$O$_4$ Sp was placed into a cylindrical Re heater in a Cr$_2$O$_3$-doped MgO pressure medium and was kept at 28 GPa and 1873–2173 K for 2–3 h. Recovered samples were identified by using a micro-focus X-ray diffractometer and the SEM-EDS. At both ends of the recovered samples, MgO + α-Al$_2$O$_3$ was observed as the decomposition product of MgAl$_2$O$_4$ Sp on account of the temperature gradient in the sample chamber of ϕ1.6 mm × 2.1 mm height. The MgO + α-Al$_2$O$_3$ regions at the ends were removed by using a diamond file. This removal was confirmed by the micro-focus X-ray diffractometer. Sintered polycrystalline MgAl$_2$O$_4$ CF samples were then divided in two pieces with a diamond disc cutter.

2.2. Drop-solution calorimetry

Drop-solution enthalpy was measured in a Calvet-type twin microcalorimeter (SETARAM HT-1000) with a temperature set at 978 K. A detailed calorimetric setup is described in Kojitani et al. (2009). Samples were dropped into 5 g of 2PbO·B$_2$O$_3$ solvent in a Pt crucible. To enhance dissolution, the solvent was stirred by Ar gas bubbles at a flow rate of 5 cm^3/min. The Ar gas was introduced into the solvent by a thin Inconel tube with a Pt tube tip. The observed heat was calibrated by the drop-solution enthalpy of α-Al$_2$O$_3$ (Kojitani et al., 2009).

The mixture of MgO and α-Al$_2$O$_3$ was compressed into a 2.8–3.3-mg pellet by using a die composed of tungsten carbide. Because pure MgO samples do not readily dissolve in the lead borate solvent, a mixture of MgO and α-Al$_2$O$_3$ was used. In the case of MgAl$_2$O$_4$ CF, polycrystalline samples of 1.7–3.8 mg were dropped directly into and dissolved in the solvent. To prevent possible amorphization and back-transformation of the high-pressure phase, these samples were not ground into a powder at ambient conditions. Corundum and periclase appeared at several grain boundaries in the synthesized MgAl$_2$O$_4$ CF samples; therefore, the drop-solution enthalpies were corrected by the amounts of corundum and periclase, which were estimated through the SEM observation using back-scattered electron images for each sample.

3. Results and discussion

3.1. Enthalpy measurements

Table 1 shows the results of the drop-solution calorimetry. The drop solution enthalpy ($\Delta H°_{d-s}$) for the mixture of MgO and α-Al$_2$O$_3$ was 140.41 ± 0.85 kJ/mol from 12 drops. When the $\Delta H°_{d-s}$ for α-Al$_2$O$_3$ of 106.67 ± 0.51 kJ/mol reported by Kojitani et al. (2009) was used, the $\Delta H°_{d-s}$ for MgO was obtained as 33.74 ± 0.99 kJ/mol. Combining the $\Delta H°_{d-s}$ (MgO) with the $\Delta H°_{d-s}$ (Mg$_2$SiO$_4$ forsterite) of 169.35 ± 2.38 kJ/mol by Akaogi et al. (2007) and the $\Delta H°_{d-s}$ (SiO$_2$ α-quartz) of 40.05 ± 0.36 kJ/mol by Akaogi et al. (1995) yielded a formation enthalpy ($\Delta_f H°_{298}$) from the oxides of −61.82 ± 2.60 kJ/mol for Mg$_2$SiO$_4$ forsterite. This value agrees within the errors with −59.1 ± 2.3 kJ/mol calculated by using $\Delta_f H°_{298}$ values from elements for Mg$_2$SiO$_4$ forsterite, MgO, and SiO$_2$ α-quartz, as reported by Robie and Hemingway (1995). Therefore, our $\Delta H°_{d-s}$ (MgO + α-Al$_2$O$_3$) is consistent with the thermochemical data base values. By using the heat content ($H°_{978} − H°_{298}$) for MgO of 31.72 kJ/mol, calculated from the heat capacity (C_P) equation provided by Robie and Hemingway (1995), a solution enthalpy ($\Delta H°_{sol}$) of MgO at 978 K was obtained to be 2.0 kJ/mol from the following equation:

$$\Delta H°_{d-s} = (H°_{978} - H°_{298}) + \Delta H°_{sol,978} = \int_{298}^{978} C_p dT + \Delta H°_{sol,978}. \quad (1)$$

The $\Delta H°_{sol}$ (MgO) of 4.94 ± 0.33 kJ/mol measured by Charlu et al. (1975) at 970 K in the same solvent is slightly larger than our value.

The $\Delta H°_{d-s}$ of MgAl$_2$O$_4$ CF was 109.18 ± 1.10 kJ/mol from 5 drops. All of the dropped samples contained small amounts of MgO and α-Al$_2$O$_3$ in the grain boundaries, as previously described. Thus the observed $\Delta H°_{d-s}$ values were corrected by using the amounts of MgO and α-Al$_2$O$_3$ determined through the SEM observations. Our $\Delta H°_{d-s}$ of MgAl$_2$O$_4$ CF was larger than 93.3 ± 1.7 kJ/mol estimated by Ono et al. (2009) from the experimentally determined phase boundaries of Akaogi et al. (1999) and Irifune et al. (2002). The enthalpy of the reaction

$$MgO + \alpha\text{-}Al_2O_3 = MgAl_2O_4 CF \quad (2)$$

namely, $\Delta_f H°_{298}$ from the oxides for MgAl$_2$O$_4$ CF, was 31.23 ± 1.39 kJ/mol from the difference between $\Delta H°_{d-s}$ (MgO + α-Al$_2$O$_3$) and $\Delta H°_{d-s}$ (MgAl$_2$O$_4$ CF), as derived from the following equations:

$$H°_{978}(MgO + \alpha\text{-}Al_2O_3, \text{ solution}) - H°_{298}(MgO + \alpha\text{-}Al_2O_3, \text{ cryst.})$$
$$= \Delta H°_{d-s}(MgO + \alpha\text{-}Al_2O_3) \quad (3)$$

$$H°_{978}(MgAl_2O_4CF, \text{ solution}) - H°_{298}(MgAl_2O_4 CF, \text{ cryst.})$$
$$= \Delta H°_{d-s}(MgAl_2O_4CF). \quad (4)$$