Drop-solution enthalpy measurement of MgSiO$_3$ majorite

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Silicate garnet is one of the major Earth's mantle constituent minerals. With increasing depth, pyroxene components dissolve into the silicate garnet. MgSiO$_3$ majorite (Mj) is an important endmember to express such the pyroxene component dissolving in the silicate garnet solid solution. Recently, we experimentally determined isobaric heat capacity and entropy of MgSiO$_3$ Mj. The stability field of MgSiO$_3$ Mj in the MgSiO$_3$ system thermodynamically calculated using these new thermodynamic data of MgSiO$_3$ Mj together with its enthalpy data measured by Yusa et al. (1993) and Saikia (2008) is not consistent with that determined by previous high-pressure phase relation experiments. In this study, the standard enthalpy of MgSiO$_3$ Mj was determined by drop-solution enthalpy measurement and the obtained enthalpy value was applied to examine the phase stability field of MgSiO$_3$ Mj by thermodynamic calculation.

MgSiO$_3$ Mj samples for the drop-solution calorimetry was the same as those used in the heat capacity measurement, which were synthesized at 19 GPa and 2173 K using a high-pressure apparatus at Ehime University, GRC. The sintered polycrystalline samples were crushed into powder. The drop-solution calorimetry was performed using a Calvet-type high-temperature calorimeter (SETARAM, HT-1000). The powdered sample with weight of about 4 mg was compressed into a pellet and it was dropped into the lead borate solvent (2PbO·B$_2$O$_3$) placed in the calorimeter which was kept at 978 K. The summation of heat content from room temperature to 978 K and solution enthalpy at 978 K, namely drop-solution enthalpy (ΔH_{d-s}), was measured. To hasten the solution of the samples, the solvent was stirred by bubbling with Ar gas.

ΔH_{d-s} (MgSiO$_3$ Mj) was determined to be 69.57±0.77 kJ/mol from the average of five data. This value is the middle between 80.0±2.5 kJ/mol (Yusa et al., 1993) and 59.5±3.2 kJ/mol (Saikia, 2008). From the difference between ΔH_{d-s} (MgO) (33.74±0.99 kJ/mol, Kojitani et al. 2012) + ΔH_{d-s} (SiO$_2$ quartz) (40.05±0.36 kJ/mol, Akaogi et al. 1995) and our ΔH_{d-s} (MgSiO$_3$ Mj), the formation enthalpy from the oxides was obtained as 4.2±1.3 kJ/mol. The thermodynamic calculation of the *P-T* phase diagram by adopting the present enthalpy value suggests that the stability field of MgSiO$_3$ Mj would expand to lower temperature region than that determined by previous high-pressure high-temperature experiments and thermodynamic calculations.

Keywords: garnet, majorite, enthalpy, thermodynamic stability, thermodynamic calculation