Low temperature heat capacities and enthalpies of high-pressure magnesium silicates with high-pressure phase equilibria

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High-pressure phase equilibria in Mg2SiO4 and MgSiO3 have been studied extensively because of their importance for phase transitions of mantle minerals. To calculate phase relations at high pressure, thermodynamic data, in particular, enthalpy and entropy of transition are indispensable. The enthalpies of transitions in magnesium silicates have been measured by high temperature calorimetry (e.g. Akaogi et al., 1989; 2002). Entropy is obtained by heat capacity measurement at low temperatures. A widely used method for the low temperature heat capacity measurement is an adiabatic method which requires a sample of one to several grams. Therefore, entropies of high pressure minerals have not yet been directly measured except for some low-pressure phases such as coesite. However, recently a thermal relaxation method that requires only a sample of several miligrams has been able to apply to high pressure mantle minerals. In this study, we have synthesized beta- and gamma-Mg2SiO4 and MgSiO3 ilmenite of sufficient amounts for calorimetry, and have measured heat capacities at low temperatures by the thermal relaxation method. Enthalpies of transitions of Mg2SiO4 have also been measured by high temperature calorimetry. Combing both of the data, we have calculated equilibrium phase relations of alpha-beta-gamma transitions in Mg2SiO4.

The samples of beta- and gamma-Mg2SiO4 and MgSiO3 ilmenite were synthesized in the stability fields using a multianvil apparatus. Heat capacities of the sintered samples of 6.1-7.3mg were measured at 1.8-305K using a PPMS apparatus. Enthalpies of drop-solution in 2PbO.B2O3 at 978 K were measured using a Calvet-type microcalorimeter. Heat content of beta-Mg2SiO4 was also measured by drop calorimetry.

The measured heat capacity showed that Cp decreases in the order of olivine, beta and gamma of Mg2SiO4, and entropies for the olivine-beta and beta-gamma transitions are -7.7 and -3.6 JK-1mol-1, respectively. High temperature calorimetry experiments indicated that enthalpies for the olivine-beta and beta-gamma transitions at 298 K are 28.9 and 12.9 kJmol-1, respectively.

The entropies and enthalpies of transitions have been used to calculate equilibrium transition boundaries. Although the calculated boundaries depend in part on high temperature heat capacity equations adopted, the olivine-beta transition boundary has a slope between those by Morishima et al. (1994) and Akaogi et al. (1989), and the beta-gamma boundary slope is close to that by Akaogi et al. (1989).