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Thermodynamic re-determination of post-spinel phase transition boundary in Mg2SiO4

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It is widely accepted that the 660-km seismic discontinuity in the deep Earth is caused by the decomposition of $(Mg,Fe)_2SiO_4$ ringwoodite with spinel structure to higher density assemblage of $(Mg,Fe)SiO_3$ perovskite + (Mg,Fe)O ferropericlase. The Clapeyron slope of the post-spinel transition boundary is a very important parameter to discuss pattern of mantle convection. Several previous studies in Mg_2SiO_4 by high-pressure high-temperature experiments and thermodynamic approaches have reported the slope values in a range from -0.4 to -4 MPa/K. However, it has not yet been constrained tightly. Particularly, the phase transition boundary calculated thermodynamically in the previous works included large uncertainty because of less precise thermodynamic data used in the calculations. In this study, we determined more accurately phase transition enthalpy than previous works by measuring drop-solution enthalpies for $MgSiO_3$ perovskite and Mg_2SiO_4 ringwoodite. By using the newly obtained phase transition enthalpy and more reliable thermodynamic data set, containing new data on high-temperature heat capacity of Mg_2SiO_4 ringwoodite by Kojitani et al. (2012a), the phase transition boundary of Mg_2SiO_4 was re-determined thermodynamically.

The drop-solution enthalpy measurements were performed using a Calvet-type twin micro-calorimeter. Samples were dropped from outside of the calorimeter at room temperature into $2PbO.B_2O_3$ solvent at 978 K. High-pressure syntheses of $MgSiO_3$ perovskite and Mg_2SiO_4 ringwoodite samples were made using a Kawai-type high-pressure apparatus. Platinum was used for a heater and sample capsule. $MgSiO_3$ perovskite sample was not ground into powder to avoid possible amorphization. Instead, sintered pieces of $MgSiO_3$ perovskite were used for the enthalpy measurement.

Drop-solution enthalpies for $MgSiO_3$ perovskite and Mg_2SiO_4 ringwoodite were obtained to be 16.47 +/- 0.52, 128.75 +/- 1.99 kJ/mol, respectively. Combining them with drop-solution enthalpy for MgO of 33.74 +/- 0.99 kJ/mol (Kojitani et al.. 2012b), the phase transition enthalpy for the post-spinel transition was determined as 78.54 +/- 2.24 kJ/mol. This value is 10~20 kJ/mol smaller than the previously reported ones. Thermal expansivities and heat capacities for MgSiO3 perovskite and Mg_2SiO_4 ringwoodite were calculated thermodynamically based on the lattice vibrational model calculation. The post-spinel transition boundary calculated in this study passes through 22.7 +/- 0.9 GPa at 1873 K. The obtained Clapeyron slope is -1.2 +/- 0.3 MPa/K at 1873 K, which is gentler than those from the previous thermodynamic calculations, and is consistent with those determined by recent high-pressure in situ X-ray diffraction experiments. The result of this study implies that the post-spinel transition boundary is less effective in impeding mantle convection than previously evaluated.

Keywords: post-spinel phase transition boundary, Mg2SiO4, enthalpy measurement, thermodynamic calculation, Clapeyron slope, mantle convection