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Redetermination of high-temperature heat capacity of Mg2SiO4 ringwoodite

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It is accepted that (Mg, Fe)$_2$SiO$_4$ ringwoodite is an major constituent mineral in the mantle transition zone. Since Mg_2SiO_4 ringwoodite is a dominant endmember of the ringwoodite phase, its physical and thermochemical properties are very important to discuss the deep mantle. In a thermodynamic calculation, heat capacity at constant pressure (C_P) is used to calculate enthalpy and entropy at given temperature and 1 atm. Measured high-temperature C_P data of Mg_2SiO_4 ringwoodite have been already reported by Watanabe (1982) and Ashida et al. (1987). However, the C_P calculated by several theoretical studies were not consistent with them. In this study, the high-temperature $C_P$of Mg_2SiO_4 ringwoodite was remeasured using differential scanning calorimetry (DSC) in a temperature range of 298-850 K. At temperatures above about 900 K, the C_P data were not available due to the back transformation to Mg_2SiO_4 forsterite. Therefore, the C_P at temperatures higher than 850 K were calculated using a lattice vibrational model calculation.

A Mg_2SiO_4 ringwoodite sample for the C_P measurement was synthesized using a Kawai-type multi-anvil high-pressure apparatus at GRC, Ehime University. A starting material of Mg_2SiO_4 forsterite was heated at 22 GPa and 1473 K for one hour, and then quenched and decompressed to ambient pressure. Powder XRD and SEM-EDS measurements confirmed that the recovered sample was single phase of stoichiometric Mg_2SiO_4 ringwoodite. The C_P measurement was performed using a differential scanning calorimeter. In a temperature range from 300 to 573 K, a heating rate was 10 K/min and data were obtained with a step of 5 K. In a range of 553-843 K, the step was 20 K with the heating rate of 20 K/min. Observed heat data were calibrated by corundum based on the C_P of Ditmars et al. (1982). The 3-7 data were averaged at each temperature. For the lattice vibrational model calculation, the Kieffer model with the vibrational density of states model for Mg_2SiO_4 ringwoodite, which well reproduces the low-temperature C_P from 1.8 to 304.7 K reported by Akaogi et al. (2007), was used.

The C_P data measured in this study are about 3-5% larger than those reported by Watanabe (1982) and Ashida et al. (1987) over the measurement temperature range and are very consistent with those determined from the vibrational model calculation by Chopelas et al. (1994) and from the ab initio calculation by Ottonello et al. (2009). The C_P calculated by the Kieffer model shows very good agreement with those measured in this study. The re-determined C_P of Mg_2SiO_4 ringwoodite is represented as C_P = 164.30 + 1.0216x10^{-2}T + 7.6665x10^{3}T^{-1} - 1.1595x10^{7}T^{-2} + 1.3807x10^{9}T^{-3} (J/mol K) in a range of 250-2500 K. The result gives a larger entropy at high temperature than those calculated using the C_P measured in the previous works, suggesting more gentle, negative slope of the thermodynamically calculated post-spinel phase boundary in Mg_2SiO_4 than those of previous thermodynamic studies.

Keywords: ringwoodite, Mg2SiO4, heat capacity, high temperature, DSC, lattice vibrational model calculation