Redetermination of high-temperature heat capacity of Mg2SiO4 ringwoodite

KOJITANI, Hiroshi1, OOHATA, Madoka1, INOUE, Toru2, AKAOGI, Masaki1

1Dept. of Chemistry, Gakushuin University, 2GRC, Ehime University

It is accepted that (Mg, Fe)2SiO4 ringwoodite is an major constituent mineral in the mantle transition zone. Since Mg2SiO4 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 Mg2SiO4 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 Mg2SiO4 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 Mg2SiO4 forsterite. Therefore, the $C_P$ at temperatures higher than 850 K were calculated using a lattice vibrational model calculation.

A Mg2SiO4 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 Mg2SiO4 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 Mg2SiO4 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 Mg2SiO4 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 Mg2SiO4 ringwoodite is represented as $C_P = 164.30 + 1.0216 \times 10^{-2}T + 7.6665 \times 10^{3}T^{-1} - 1.1595 \times 10^{9}T^{-2} + 1.3807 \times 10^{9}T^{-3}$ (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 Mg2SiO4 than those of previous thermodynamic studies.

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