Redetermination of high-temperature heat capacity of Mg$_2$SiO$_4$ ringwoodite: Measurement and lattice vibrational model calculation

HIROSHI KOJITANI,†* MADOKA OOHATA,‡ TORU INOUE,§ and MASAKI AKAOGI

†Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
‡Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan

ABSTRACT

Isobaric heat capacities ($C_p$) of Mg$_2$SiO$_4$ forsterite and ringwoodite were measured by differential scanning calorimetry in the temperature range of 306–833 K. The measured $C_p$ of Mg$_2$SiO$_4$ forsterite was consistent with those reported by previous studies. On the other hand, the present $C_p$ of Mg$_2$SiO$_4$ ringwoodite was about 3–5% larger than those measured by previous researchers. The calorimetric data of Mg$_2$SiO$_4$ ringwoodite were extrapolated to 2500 K using a lattice vibrational model calculation, which well reproduced the low-temperature $C_p$ data measured by thermal relaxation method. The calculated $C_p$ shows good agreement with the present calorimetric data. The obtained $C_p$ was expressed by the polynomial of temperature: $C_p = 164.30 + 1.0216 \times 10^{-2} T + 7.6665 \times 10^{-7} T^{-1} - 1.1595 \times 10^{-2} T^{-2} + 1.3807 \times 10^{-5} T^{-3} \text{[J/(mol-K)]}$ in the range of 250–2500 K.

Keywords: Mg$_2$SiO$_4$, ringwoodite, heat capacity, DSC, Kieffer model calculation, thermodynamic property, mantle transition zone

INTRODUCTION

It is widely accepted that magnesium-rich (Mg,Fe)$_2$SiO$_4$ olivine, which is the most abundant mineral in the Earth’s upper mantle, transforms to wadsleyite and then ringwoodite in the mantle transition zone and, furthermore, ringwoodite dissociates into magnesium-rich (Mg,Fe)$_2$SiO$_4$ perovskite and ferropericlase at the 660-km boundary between the transition zone and the lower mantle. Therefore, thermodynamic property of Mg$_2$SiO$_4$ ringwoodite, which is the dominant end-member of the ringwoodite phase, is key to understand the Earth’s structure from the mantle transition zone to the uppermost lower mantle.

In a thermodynamic calculation, isobaric heat capacity ($C_p$) is necessary to calculate enthalpy and entropy at high temperatures from those at standard state (298.15 K). Because $C_p$ data of Mg$_2$SiO$_4$ ringwoodite observed at high temperatures have been limited to only those reported by Watanabe (1982) and Ashida et al. (1987) using the differential scanning calorimetry (DSC), many researchers have used the $C_p$ based on them for thermodynamic calculations (e.g., Akaogi et al. 1984; Fei and Saxena 1986; Bina and Wood 1987; Saxena et al. 1993; Jacobs and Oonk 2001; Fabrichnaya et al. 2004). However, results of a lattice dynamics calculation by Price et al. (1987), of a lattice vibrational model calculation based on Raman spectroscopy by Chopelas et al. (1994) and of ab initio calculations by Yu and Wentzcovitch (2006) and Ottonello et al. (2009) indicated larger $C_p$ than those obtained in the two experimental studies beyond the experimental errors. Recently, Akaogi et al. (2007) measured low-temperature $C_p$ of Mg$_2$SiO$_4$ ringwoodite in a temperature range of 2–305 K with thermal relaxation method using the Physical Property Measurement System (PPMS). The $C_p$ by Akaogi et al. (2007) showed about 4% larger value than that of Ashida et al. (1987) in a range of 210–300 K. These discrepancies have required a re-determination of high-temperature $C_p$ of Mg$_2$SiO$_4$ ringwoodite.

There are two methods to obtain $C_p$ from DSC data, namely, “scanning method” and “enthalpy method” (Mraw and Naas 1979). In the scanning method, $C_p$ of a sample is determined using a ratio of heat flow signal intensity from a baseline for the sample to that for a standard (e.g., α-Al$_2$O$_3$) at a certain temperature during a temperature scan. The two previous measurements (Watanabe 1982; Ashida et al. 1987) adopted this method. On the other hand, in the enthalpy method, $C_p$ is determined by dividing heat content by temperature difference during a scan. The heat content is obtained by integrating an area surrounded by a heat flow signal and a baseline over the scan duration. Mraw and Naas (1979) recommended the enthalpy method because of established equilibrium initial and final temperatures before and after energy input, respectively, which eliminate uncertainties from sample temperature lag during the scan. In this study, $C_p$ of Mg$_2$SiO$_4$ forsterite and Mg$_2$SiO$_4$ ringwoodite were measured by the differential scanning calorimetry in a temperature range of 306–833 K using the enthalpy method. Obtained $C_p$ data of Mg$_2$SiO$_4$ ringwoodite were extrapolated to temperatures higher than 830 K using the lattice vibrational model calculation.

EXPERIMENTAL METHODS

Sample preparation

Single crystal of Mg$_2$SiO$_4$ forsterite for a starting material of high-pressure synthesis of Mg$_2$SiO$_4$ ringwoodite was synthesized using the Czochralski method. It was crushed and ground into powder. High-pressure synthesis of Mg$_2$SiO$_4$ ringwoodite was made using a Kawai-type multi-anvil high-pressure apparatus at GRC, Ehime University. A Pt heater-capsule was used. For details of the high-pressure high-temperature technique, see Higo et al. (2006). The starting sample

* E-mail: hiroshi.kojitani@gakushuin.ac.jp