Experimental and thermodynamic investigations on the stability of Mg$_{14}$Si$_5$O$_{24}$ anhydrous phase B with relevance to Mg$_2$SiO$_4$ forsterite, wadsleyite, and ringwoodite

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ABSTRACT

High-pressure high-temperature phase relation experiments in Mg$_{14}$Si$_5$O$_{24}$ were performed using a 6-8 multi-anvil high-pressure apparatus in the pressure range of 12–22 GPa and temperature range of 1673–2173 K. We first found that Mg$_{14}$Si$_5$O$_{24}$ anhydrous phase B (Anh-B) dissociates to Mg$_2$SiO$_4$ wadsleyite (Wd) and MgO periclase (Per) at about 18 GPa and 1873 K. From the results of the high-pressure experiments, the phase boundaries of 5 Mg$_2$SiO$_4$ forsterite (Fo) + 4 Per = Anh-B and Anh-B = 5 Wd + 4 Per were determined. In addition, the isobaric heat capacity ($C_p$) of Anh-B was measured by differential scanning calorimetry in the temperature range of 300–770 K and the thermal relaxation method using a Physical Property Measurement System (PPMS) in the range of 2–303 K. From the measured low-temperature $C_p$, the standard entropy ($S^{0}_{298.15}$) of Anh-B was determined to be 544.4(2) J/(mol·K). We also performed high-temperature X-ray diffraction measurements in the range 303–773 K to determine the thermal expansivity ($\alpha$) of Anh-B. The obtained $C_p$ and $\alpha$ were theoretically extrapolated to higher temperature region using a lattice vibrational model calculation partly based on Raman spectroscopic data. Thermodynamic calculations by adopting the thermochemical and thermoelastic data for Anh-B obtained in this study and the estimated formation enthalpy for Anh-B of −13 208 kJ/mol gave phase equilibrium boundaries for 5 Fo + 4 Per = Anh-B and Anh-B = 5 Wd + 4 Per that were consistent with those determined by the present high-pressure high-temperature experiments. The results clarified that, in the Mg$_{14}$Si$_5$O$_{24}$ system, Anh-B is stable between 12 and 18 GPa at the expected temperatures of the Earth’s mantle.

Keywords: Anhydrous phase B, phase boundary, heat capacity, entropy, thermal expansivity, Raman spectrum, wadsleyite, ringwoodite

INTRODUCTION

A high-pressure dense magnesium silicate Mg$_{14}$Si$_5$O$_{24}$ anhydrous phase B (Anh-B) was first synthesized by Herzberg and Gasparik (1989) and its crystal structure was determined by Finger et al. (1989, 1991). The crystal structure contains two different stacking layers. One is a forsterite-like layer consisting of MgO$_6$ octahedra and SiO$_6$ tetrahedra, and the other is a layer consisting of MgO$_6$ and SiO$_6$ octahedra. The structure is closely related to that of hydrous Mg$_{12}$Si$_4$O$_{19}$(OH)$_2$ phase B, as the name indicates (Finger et al. 1989, 1991). Due to the SiO$_6$ octahedra, Anh-B has a density higher than that of 5 Mg$_2$SiO$_4$ forsterite (Fo) + 4 MgO periclase (Per). Ganguly and Frost (2006) investigated the phase boundary between 5 Fo + 4 Per = Anh-B and Anh-B = 5 Wd + 4 Per that were consistent with those determined by the present high-pressure high-temperature experiments. The results clarified that, in the Mg$_{14}$Si$_5$O$_{24}$ system, Anh-B is stable between 12 and 18 GPa at the expected temperatures of the Earth’s mantle.

It has been also observed by Presnall and Gasparik (1990) that, in a high-pressure high-temperature run at 16.5 GPa and 2623 K, Anh-B coexists with liquid on the incongruent melting process of Fo. This fact suggests that around 15 GPa Anh-B may be stable at not only low temperature of about 800 K as described above but also high temperature over 2500 K.

Recently, Bindi et al. (2016) reported that Cr-bearing Anh-B appeared as a high-pressure stability phase in the Mg$_2$SiO$_4$–MgCr$_3$O$_4$ system at 12 GPa and 1873 K. The Mg$_2$SiO$_4$–MgCr$_3$O$_4$ system can be a simplified model for podiform chromitites consisting of chromites surrounded by peridotites such as dunite and harzburgite, which are found in ophiolites and are probably formed by reactions between peridotite and melt (Arai 1997; measurement at room temperature and proposed a bulk modulus and its pressure derivative of 151.5 GPa and 5.5, respectively. On the other hand, there have been no other experimentally determined thermoelastic data, such as the temperature derivative of the bulk modulus and thermal expansivity, and no thermochemical data on enthalpy, heat capacity, or entropy. Ottoneo et al. (2010) made a calculation of the phase equilibrium boundary for 5 Fo + 4 Per = Anh-B using the thermodynamic parameters of Anh-B predicted by ab initio calculation and gave a phase boundary very similar to that obtained in Ganguly and Frost (2006).