

Determination of low-temperature heat capacity and standard entropy of $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$ anhydrous phase B

*Hiroshi Kojitani¹, Maki Osawa¹, Saki Terata¹, Masaki Akaogi¹

1.Department of Chemistry, Faculty of Science, Gakushuin University

It is expected that $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$ anhydrous phase B (Anh-B) forms in the Earth's mantle by the reaction $5\text{Mg}_2\text{SiO}_4$ forsterite (Fo) + $4\text{MgO} = \text{Mg}_{14}\text{Si}_5\text{O}_{24}$ Anh-B when SiO_2 component in olivine and pyroxenes dissolves selectively into fluid and the residue is rich in MgO component. Entropy of Anh-B, which is needed to examine its thermodynamical stability, has not been determined experimentally yet. In this study, low-temperature heat capacity (C_p) was measured using PPMS equipment and standard entropy at 298 K was determined from the obtained heat capacity. The measured low-temperature C_p was also applied to modeling of a vibrational density of state used for Kieffer model calculation of the high-temperature C_p .

High-pressure synthesis of Anh-B was performed using a Kawai-type multi-anvil high-pressure apparatus. The starting material of the mixture of Fo and MgO (5:4 in mole ratio) was kept at 15 GPa and 2073-2273 K for 3 hours. After quenching, the sample was decompressed to ambient pressure. Micro-focused X-ray diffractometry and SEM-EDS analysis confirmed that the recovered samples were the single phase of Anh-B. Low-temperature C_p was measured in the temperature range of 2-307 K and with the step of about 2 K using PPMS (Quantum Design) by the thermal relaxation method. The bottom of the cylindrical samples was polished into very flat for better thermal contact with a heating stage. The total weight of the samples used for the PPMS measurement was 10.988 mg.

Low-temperature C_p was measured with the accuracy of about 0.3% at each measurement temperature. The C_p around 300 K obtained in this study is the same as that determined by our DSC measurement. This indicates the validity of the present measurement. By integrating C_p/T from 0 to 298 K using the obtained C_p , the standard entropy at 298 K was determined to be 554.17(1) J/mol.K. This value is smaller than 561.2 J/mol.K obtained by ab initio calculation of Ottonello et al. (2010) and is in good agreement with 547.3 J/mol.K estimated from entropies of the constituent oxides by Ganguly and Frost (2006). In addition, by the Kieffer model calculation using a vibrational density of state model which reproduces the low-temperature C_p measured in this study, the high-temperature C_p was extrapolated above 800 K at which C_p cannot be measured due to the collapse of the crystal structure by heating at 1atm. The C_p was obtained to be $C_p(T) = 6.624 \times 10^2 + 2.123 \times 10^4 T^{-0.5} - 4.827 \times 10^6 T^{-2} + 2.221 \times 10^9 T^{-3} - 1.061 \times 10^{-1} T - 3.643 \times 10^5 T^{-1}$ in the range from 300 to 2000 K.

Keywords: anhydrous phase B, heat capacity, entropy, thermodynamical stability, lattice vibrational model calculation