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Heat capacity and entropy measurements by PPMS for high-pressure phases in TiO2 and MnSiO3

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Thermodynamic properties of high-pressure minerals are widely used to calculate phase relations at high pressures and high temperatures and to compare with the properties by the first-principles calculations. Standard entropy, S298.15, is determined by integrating Cp/T in the temperature range between 0 and 298.15 K, where Cp is isobaric heat capacity and T is absolute temperature. To measure Cp at the temperature range, adiabatic calorimetry has been widely used with the highest precision. However, Cp of only a few high-pressure minerals have been measured so far, because a sample of more than several gram is required for the adiabatic calorimetry. Recently, low-temperature Cp measurement with thermal relaxation method using the Physical Properties Measurement System (PPMS) has been developed for samples of about ten milligram quantity. In this method, the sample is cooled with liquid helium and Cp is measured at about 2-310 K. By measuring the sample temperature change associated with applied heat pulse, thermal relaxation process is analyzed to obtain Cp. By this method, we measured Cp and determined S298.15 for Mg2SiO4 wadsleyite and ringwoodite, MgSiO3 akimotoite and perovskite, and SiO2 stishovite, in collaboration with Atake-Kawaji laboratory, Tokyo Institute of Technology. Very recently, we have installed the PPMS apparatus in the laboratory in Gakushuin University, and have investigated Cp and S of rutile-type and α-PbO2-type TiO2 and garnet-type MnSiO3.

Using a multianvil apparatus, rutile- and α-PbO2-type TiO2 phases were synthesized at 3 and 8 GPa, respectively, at 600-700 oC, and MnSiO3 garnet was made at 15 GPa and 1000 oC. All the cylindrical samples were polished and fixed with grease on the stage in the PPMS. The Cp measurements in this study were performed at 2-308 K using the polycrystalline samples of 10-21 mg. The Cp measured for α-Al2O3 (NBS SRM-720) by the PPMS apparatus were consistent within experimental errors with those measured by adiabatic calorimetry by Ditmars et al. (1982).

The measured Cp of rutile-type TiO2 were in good agreement with those by previous studies, and the obtained S298.15 was 50.10 J/molK. Our Cp data of α-PbO2-type TiO2 were almost consistent with those with PPMS measurement by Yong et al. (2014), but substantially smaller than those with DSC measurement by Manon (2008). The S298.15 of α-PbO2-type TiO2 was determined as 46.50 J/molK in this study. The Cp data of MnSiO3 garnet indicated an anomaly at 15 K probably due to magnetic transition, and S298.15 of 90.92 J/molK. High-pressure phase relations calculated using the above data are also reported.

Keywords: heat capacity, entropy, high-pressure phase, PPMS apparatus