

Raman spectroscopy and heat capacity measurement of MgAl₂O₄ and CaAl₂O₄ calcium ferrites

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Recent high-pressure and high-temperature experiments have reported the presence of Al-rich phases in high-pressure phases of mid-ocean ridge basalt (MORB) at the lower mantle conditions. In particular, a calcium ferrite phase is expected as one of possible candidates for the Al-rich phases. The composition of calcium ferrite observed as a high-pressure phase of MORB shows that major components with divalent cation are MgAl₂O₄ and CaAl₂O₄. To discuss the stability of the calcium ferrite phase at the lower mantle conditions, thermochemical data of them are needed. However no thermochemical data of the calcium ferrites has been reported. In this study, heat capacity (C_p) measurement of CaAl₂O₄ calcium ferrite was performed. Also Raman spectroscopy of MgAl₂O₄ and CaAl₂O₄ calcium ferrites were made. Since the difficulty of high-pressure synthesis of MgAl₂O₄ calcium ferrite does not enable us to direct measurement of its C_p, C_p and lattice vibrational entropy of MgAl₂O₄ calcium ferrite were estimated by using Kieffer model lattice dynamics calculation based on information of lattice vibration from Raman spectra. Calculated C_p of CaAl₂O₄ calcium ferrite by Kieffer model was compared with observed one to examine the validity of an used model for vibrational density of state in the calculation.

MgAl₂O₄ and CaAl₂O₄ calcium ferrites were synthesized by heating MgAl₂O₄ spinel at 27 GPa and 2273 K for 8 minutes and CaAl₂O₄ stuffed tridymite at 15 GPa and 1873 K for 1 hour, respectively, with a Kawai-type multianvil high-pressure apparatus at Gakushuin University. Heat capacity measurement of CaAl₂O₄ calcium ferrite was made by using a differential scanning calorimeter (DSC) at Gakushuin University. Heat capacity data were collected with a heating rate of 6 K/min and 5 K interval in the temperature range of 155-350 K and heating rate of 7 K/min and 10 K interval in the temperature range of 353-733 K. The weight of powdered sample used in the calorimetry was 23.68 mg. corundum was used as a standard. Raman spectroscopy of both MgAl₂O₄ and CaAl₂O₄ calcium ferrites was performed by using micro-Raman spectroscopy system at National Institute of Advanced Industrial Science and Technology with the 514.5 nm line of an argon ion laser. Raman samples were prepared by fixing on a glass slide by epoxy glue and polishing well with very fine corundum (grain size of 1 micrometer). The laser power was approximately 5 mW at the sample surface. The laser beam diameter was 5-10 micrometer. Raman data were collected by repeating exposures of 60 seconds five times. Wave number of Raman shift was calibrated with Ne lamp.

79 C_p data of CaAl₂O₄ calcium ferrite were obtained by DSC measurement in the range of 155-733 K. When the C_p data were fitted to the Berman and Brown's C_p equation, C_p of CaAl₂O₄ calcium ferrite is represented as $C_p(T) = 190.6 - 1.116 \times 10^{-7} T^2 + 1.491 \times 10^{-9} T^3$ above 250 K. In the Raman spectroscopic measurement, 34 Raman peaks were observed for both MgAl₂O₄ and CaAl₂O₄ calcium ferrites. Heat capacities and thermal vibration entropies of MgAl₂O₄ and CaAl₂O₄ calcium ferrites were calculated by the Kieffer model lattice vibrational calculation. In the calculations, phonon density of state for each materials was modeled by using the observed Raman data. The calculated C_p of CaAl₂O₄ calcium ferrite shows good agreement with measured one within errors. The C_p of MgAl₂O₄ calcium ferrite was calculated as $C_p(T) = 223.4 - 1352 T^{-0.5} - 4.181 \times 10^{-6} T^2 + 4.300 \times 10^{-8} T^3$. The lattice vibrational entropies of MgAl₂O₄ and CaAl₂O₄ calcium ferrites at 298 K were obtained to be 97.6 and 114.9 J/mol.K, respectively. The obtained entropy of MgAl₂O₄ calcium ferrite was applied to a phase equilibrium boundary calculation between MgO+Al₂O₃ and MgAl₂O₄ calcium ferrite. A calculated boundary shows about two times steeper negative slope than that determined by high-pressure experiments.