Heat capacity measurement, and Raman and infrared spectroscopy of calcium ferrite-type NaAlSiO4

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High-pressure high-temperature experiments of mid-oceanic ridge basalt considering subduction of oceanic plate into deep Earth's mantle show that a phase with calcium ferrite-type crystal structure appears at pressures higher than about 20 GPa. The calcium ferrite phase accommodates Na^+ and K^+ because it includes large cation sites in the structure. It can be treated as solid solutions in the $NaAlSiO_4$-$MgAl_2O_4$-Mg_2SiO_4 system. The $NaAlSiO_4$ endmember accounts for more than half. In this study, we measured heat capacity at constant pressure (Cp) of the calcium ferrite-type $NaAlSiO_4$ and determined its entropy at 298 K, which are needed to discuss the stability of the calcium ferrite phase by thermodynamic approach. The Cp in a high temperature range were estimated using the Kieffer model calculation based on Raman and infrared (IR) data due to collapse of the crystal structure above 600 K at ambient pressure.

Samples for the Cp measurement and Raman and IR spectroscopy were synthesized by keeping a starting material of $NaAlSiO_4$ carnegieite at 23-27 GPa and 1673 K for 15 min using a Kawai-type multi-anvil high-pressure apparatus. Cp data were obtained using a differential scanning calorimeter in the temperature range of 125-400 K with a step of 5 K. Enthalpy calibration was made using corundum. Raman data were measured using a micro-Raman spectrometer at Gakushuin University. Excitation laser with the wavelength of 532 nm was irradiated on the well-polished surface of a polycrystalline sample. IR spectra were collected using a FT-IR spectrometer at Tokyo University. Polycrystalline sample was ground into powder in an agate mortar. The KBr pellet method in the mid-infrared region and the nujol method with polyethylene film in the far-infrared region were adopted.

Obtained Raman and IR spectra show considerable broadening. These facts support the random distribution of Al^{3+} and Si^{4+} in (Al, Si)O_6 octahedral sites. Observed Cp data are about 5% smaller than those of calcium ferrite-type $CaAl_2O_4$ over the measurement temperature range. This result is consistent with the relative peak shifts in the Raman profile of calcium ferrite-type $NaAlSiO_4$ to higher wavenumber from those of calcium ferrite-type $CaAl_2O_4$. The lattice vibrational entropy was determined as 86.7 J/mol.K. By assuming perfect random distribution of Al^{3+} and Si^{4+} in the (Al, Si)O_6 sites, configurational entropy was calculated to be 11.5 J/mol.K. From the summation of these values, entropy at 298 K was obtained as ${S^0}_{298}$ = 98.2 J/mol.K. Cp above 400 K were estimated to be Cp = 246.79 -1.9624x$10^3 * T^{-0.5}$ -2.3007x$10^6 * T^{-2}$ + 1.8426x$10^8 * T^{-3}$ by the Keffer model calculation.