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High-pressure Raman spectroscopy of calcium ferrite-type MgAl2O4

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A calcium ferrite phase appears as a high-pressure phase in the basalt under lower mantle conditions. Calcium ferrite-type $MgAl_2O_4$ is one of the major endmembers of the calcium ferrite phase. It is considerably difficult to synthesize a large amount of calcium ferrite-type $MgAl_2O_4$ because it is stable at pressures higher than 25 GPa. This prevents calorimetric measurements for the determination of its enthalpy, entropy and heat capacity, which are needed to discuss the thermodynamic stability. In this study, the thermal Grueneisen parameter used to calculate theoretically the isobaric heat capacity (Cp) was determined by performing high-pressure Raman spectroscopy.

A sample for the Raman spectroscopy was synthesized by keeping a starting sample of $MgAl_2O_4$ spinel at 27 GPa and 2200 C for 1 hour using a Kawai-type multi-anvil high-pressure apparatus. Micro-Raman spectroscopy was done using JASCO NRS-3100 (Nd:YAG laser with 532 nm). Observed Raman shifts were calibrated by those of trichloroethylene. A small chip of the sample was compressed using a diamond anvil cell high-pressure apparatus at ambient temperature. The pressure medium and metal gasket used were a mixture of methanol:ethanol = 4:1 (in volume) and SUS304 with 0.25 mm thickness, respectively. Pressure was determined by the ruby R_1 line.

Frequency changes for eighteen Raman-active lattice vibrational modes with increasing pressure at ambient temperature were observed in the pressure range from 1 atm to 10 GPa, at which the pressure medium is solidified. Mode Grueneisen parameters were calculated using lattice vibrational frequencies at 1 atm, pressure dependences of the frequencies, bulk modulus (K_T) of 241 GPa by Yutani et al. (1997). We obtained mode Grueneisen parameters of 1.07-2.67. The weighted average of them gave the thermal Grueneisen parameter of 1.67(4) by considering the contribution of heat capacity at constant volume (Cv) for each vibrational mode to total one, Cv_i/Cv. The Cv_i was calculated from the Einstein function. The obtained thermal Grueneisen parameter of calcium ferrite-type $MgAl_2O_4$ is slightly larger than that of calcium ferrite-type $CaAl_2O_4$ which was determined as 1.52(2) using the same method. This difference is caused by larger pressure dependencies of vibrational frequencies distributing in the range of 200-300 cm^{-1} for calcium ferrite-type $MgAl_2O_4$ than for calcium ferrite-type $CaAl_2O_4$. The vibrational modes in this region consist mainly of stretching modes of divalent cation (Mg^{2+} or Ca^{2+}). Therefore, it is implied that the lattice vibrations of divalent cations relatively affect the Grueneisen parameters in the calcium ferrite-type crystal structure.

Keywords: calcium ferrite, Raman spectroscopy, High-pressure, lattice vibration, Grueneisen parameter