High-pressure Raman spectroscopy, vibrational mode calculation, and heat capacity calculation of calcium ferrite-type MgAl$_2$O$_4$ and CaAl$_2$O$_4$

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ABSTRACT

High-pressure micro-Raman spectroscopic measurements of calcium ferrite-type MgAl$_2$O$_4$ and CaAl$_2$O$_4$ were made using a diamond-anvil cell high-pressure apparatus. The pressure dependence of frequencies of 18 Raman peaks for calcium ferrite-type MgAl$_2$O$_4$ and 26 Raman peaks for calcium ferrite-type CaAl$_2$O$_4$ were determined up to 20 GPa at ambient temperature. The mode Grüneisen parameter for each observed Raman mode was obtained from the pressure dependence of frequencies. Vibrational mode calculations by first principles using density functional theory were also performed for assignment of Raman peaks and for estimating frequencies of Raman inactive modes. From the obtained mode Grüneisen parameters and the results of the vibrational mode calculations, thermal Grüneisen parameters were determined to be 1.50(5) for calcium ferrite-type MgAl$_2$O$_4$ and 1.31(3) for calcium ferrite-type CaAl$_2$O$_4$. These thermal Grüneisen parameters were applied to heat capacity and vibrational entropy calculations using Kieffer model.

Keywords: Raman spectroscopy, high pressure, Grüneisen parameter, heat capacity, calcium ferrite, MgAl$_2$O$_4$, CaAl$_2$O$_4$

INTRODUCTION

Calcium ferrite is accepted as one of the high-pressure constituent minerals of mid-ocean ridge basalt at pressures higher than about 25 GPa (Irfune and Ringwood 1993; Kesson et al. 1994; Hirose et al. 1999; Funamori et al. 2000; Ono et al. 2001; Ricolleau et al. 2008). It is expected that the calcium ferrite phase may exist in the Earth’s lower mantle, considering the subducted oceanic crust into the deep mantle. According to Guignot and Andraut (2004), calcium ferrite-type MgAl$_2$O$_4$, which is represented as MgAl$_2$O$_4$ CF hereafter, is the second most common end-member, following NaAlSiO$_4$ CF in the calcium ferrite phase system. It is important to clarify the phase stability of MgAl$_2$O$_4$ CF for better understanding of behaviors of the subducted basaltic crust. Compared to NaAlSiO$_4$, MgAl$_2$O$_4$, and MgFe$_2$O$_4$, CaAl$_2$O$_4$ CF is a less common end-member, (Guignot and Andraut 2004), but it differs from MgAl$_2$O$_4$ CF only in the type of the divalent cations. Moreover, CaAl$_2$O$_4$ CF exhibits a stability pressure that is lower than that of MgAl$_2$O$_4$ CF (Akaogi et al. 1999). Thus the crystal-chemical resemblance between MgAl$_2$O$_4$ CF and CaAl$_2$O$_4$ CF facilitates the comparison of the lattice vibrational features and their effect on the elastic and thermodynamic properties.

To thermodynamically discuss the stability fields of MgAl$_2$O$_4$ CF and CaAl$_2$O$_4$ CF, thermochemical data are needed. However, the available data of enthalpy, entropy, and heat capacity are still limited because of insufficient amounts of high-pressure synthetic samples for calorimetry and their instability at high temperature and ambient pressure. Information of lattice vibration is very useful to estimate entropy and heat capacity of these materials. Kojitani et al. (2003) calculated the heat capacities and the entropies of MgAl$_2$O$_4$ CF and CaAl$_2$O$_4$ CF using the vibrational density of states (VDoS) models based on measured Raman spectra. In that study, only the observed Raman peaks were considered to construct the VDoS models without peak assignments. In addition, their thermal expansivities were assumed to be identical with that of CaFe$_2$O$_4$ in the calculation of the anharmonic effect on the heat capacities. These procedures resulted in large uncertainties of the calculated heat capacities, particularly at high temperature.

An isobaric heat capacity ($C_p$) results from the addition of an anharmonic effect to an isochoric heat capacity ($C_V$) by harmonic vibration. The thermal Grüneisen parameter ($\gamma_{th}$) is an important value, revealing the degree of anharmonicity. If an accurate $\gamma_{th}$ is known, it is possible to evaluate a more reliable anharmonic effect, especially at high temperature. However, $\gamma_{th}$ is generally difficult to measure directly. To constrain the thermal Grüneisen parameter, mode Grüneisen parameters are very useful, which can be defined as

$$\gamma_i = -\frac{\partial \ln \nu_i}{\partial \ln V}$$

where $\nu_i$ and $V$ are the frequency of lattice vibrational mode $i$ and volume, respectively. In this study, high-pressure Raman spectroscopic measurements of MgAl$_2$O$_4$ CF and CaAl$_2$O$_4$ CF were performed to determine the mode Grüneisen parameters from the pressure dependencies of their Raman shifts. Also, lattice vibrational mode calculations from first principles were used for assigning observed Raman peaks and for estimating vibrational frequencies of Raman inactive modes. The obtained mode Grüneisen parameters have been used to determine thermal...