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High-pressure Raman spectroscopy, vibrational mode calculation, and heat capacity calculation of calcium ferrite-type $MgAl_2O_4$ and $CaAl_2O_4$

Hiroshi Kojitani,[1,*] Daniel M. Többens,[2,†] and Masaki Akaogi[1]

[1]Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
[2]Institution of Mineralogy and Petrography, University of Innsbruck, Innrain 52, Bruno-Sander-Haus, A-6020 Innsbruck, Austria

Abstract

High-pressure micro-Raman spectroscopic measurements of calcium ferrite-type $MgAl_2O_4$ and $CaAl_2O_4$ were made using a diamond-anvil cell high-pressure apparatus. The pressure dependence of frequencies of 18 Raman peaks for calcium ferrite-type $MgAl_2O_4$ and 26 Raman peaks for calcium ferrite-type $CaAl_2O_4$ 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 $MgAl_2O_4$ and 1.31(3) for calcium ferrite-type $CaAl_2O_4$. 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, $MgAl_2O_4$, $CaAl_2O_4$