American Mineralogist, Volume 101, pages 162–174, 2016

Ab initio investigation of majorite and pyrope garnets: Lattice dynamics and vibrational spectra

Marco De La Pierre[1,*] and Donato Belmonte[2]

[1]Nanochemistry Research Institute, Curtin Institute for Computation, Department of Chemistry, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia
[2]DISTAV, Università di Genova, Corso Europa 26, 16132 Genova, Italy

Abstract

A detailed ab initio quantum-mechanical characterization is presented of the vibrational properties of pyrope and majorite garnets, using the hybrid B3LYP functional and large all electron Gaussian type basis sets. Discussed quantities include infrared (both TO and LO) and Raman frequencies, normal mode coordinates, spectroscopic intensities, mode Grüneisen parameters, isotopic substitution, and infrared and Raman spectra. Comparison with data available in the literature demonstrates the accuracy of the adopted method. Main spectral features of the two garnets are interpreted in terms of either symmetry analysis or structural contributions to the vibrational modes. Missing peaks in the experiments are discussed in light of the simulated spectra. The present high-quality vibrational data can be used to compute thermal expansivities at high-pressure and high-temperature conditions. Calculated values for majorite at the bottom of the mantle transition zone ($\alpha_V = 2.2 \times 10^{-5}$ K^{-1} at $T = 1500$ K and $P = 20$ GPa) turn out to be sensibly greater (up to three times) than those currently adopted in geophysical thermodynamic databases, thus calling for a careful revision of the numerical models for thermo-chemical convection of the Earth's mantle.

Keywords: Infrared spectrum, Raman spectrum, vibrational frequencies, mode Grüneisen parameters, thermal expansivity, ab initio quantum mechanical calculations, CRYSTAL code