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

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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 Gr"uneisen 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 Gr"uneisen parameters, thermal expansivity, ab initio quantum mechanical calculations, CRYSTAL code

INTRODUCTION

Thermodynamic properties of high-pressure mineral phases in the system MgO-Al$_2$O$_3$-SiO$_2$ are crucial to understand chemophysical processes in the Earth’s mantle and to constrain the mineralogical constitution of its deeper parts. Among these phases, MgSiO$_3$ majorite garnet and its solid solutions with pyrope (Mg$_3$Al$_2$Si$_3$O$_12$ or, for simplicity, MgSiO$_3$), as revealed by TEM studies (Angel et al. 1989; Hatch and Ghose 1989; Wang et al. 1993). The finding of single crystals for structural refinement is thus hindered, and IR and Raman spectra currently available for this phase could be obtained exclusively on polycrystalline samples (Kato and Kumazawa 1985; McMillan et al. 1989; Rauch et al. 1996; Manghnani et al. 1998; Chopelas 1999). Additional complications in the interpretation of the vibrational spectra arise from lowering of symmetry with respect to cubic garnets (Ia3d to I4/m space group) and from possible structural disorder.

Ab initio simulation has proved to be an excellent method to provide accurate descriptions of the vibrational properties of silicate minerals, especially when exploiting hybrid density functionals (Zicovich-Wilson et al. 2004, 2008; Prencipe et al. 2004, 2014; Pascale et al. 2005a, 2005b; Orlando et al. 2006; Valenzano et al. 2009, 2010; Ferrari et al. 2009; Dovesi et al. 2009, 2011; De La Pierre et al. 2011; Demichelis et al. 2012; Noël et al. 2012; Ulian et al. 2013; Maschio et al. 2013a, 2014; Belmonte et al. 2014; Erba et al. 2015). Contrary to the experiments, it permits one to easily investigate “ideal” systems, free...