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 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 \( (\alpha_v = 2.2 \times 10^{-4} \, \text{K}^{-1} \text{ at } T = 1500 \, \text{K and } P = 20 \, \text{GPa}) \) 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

INTRODUCTION

Thermodynamic properties of high-pressure mineral phases in the system MgO-Al2O3-SiO2 are crucial to understand chemico-physical processes in the Earth’s mantle and to constrain the mineralogical constitution of its deeper parts. Among these phases, MgSiO3 majorite garnet and its solid solutions with pyrope \( (\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}) \) are of relevant interest as they are major components of the mantle transition zone, ranging in volume from 40 to 70% according to different petrological models (Bass and Anderson 1984; Ringwood 1991; Vacher et al. 1998; Weidner and Wang 1998; Akaogi et al. 2002). Furthermore, majorite-pyrope garnets undergo phase transitions at high-pressure and high-temperature conditions, which may be at the origin of multiple seismic discontinuities between 520 and 720 km depths (Hirose et al. 2001; Hirose 2002; Deuss et al. 2006; Saikia et al. 2008).

Vibrational spectroscopy, in both its infrared and Raman variants, is an invaluable tool to gather lattice dynamics data that can be used for thermodynamical modeling. Also, Raman barometry techniques are emerging as a tool in the study of mineral inclusions in diamond (e.g., Izraeli et al. 1999), of which majoritic garnets are common examples (cf. Harte 2010). In fact, these methods have been shown to provide reliable estimates of the residual internal pressure exerted by the host diamond on the inclusion, hence of their pressure of formation by the so-called elastic relaxation method (Nestola et al. 2011, 2012; Angel et al. 2014). These reasons make very desirable the availability of accurate spectroscopic characterizations of the majorite-pyrope system, both at ambient- and high-pressure conditions.

Experimental characterization of the vibrational properties of majorite-pyrope garnets is challenging, mainly due to problems affecting their high-pressure synthesis in the laboratory. Pervasive merohedral or pseudomerohedral twinning is always present in the tetragonal end-member of the majorite-pyrope series (\( \text{Mg}_3\text{Si}_4\text{O}_{12} \), or, for simplicity, \( \text{MgSiO}_3 \)), 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 \( (Ia3d \text{ to } I4/\text{a space group}) \) and from possible structural disorder.