Ab Initio Molecular Dynamic Simulation on the Elasticity of Mg$_3$Al$_2$Si$_3$O$_{12}$ Pyrope

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ABSTRACT: We calculated thermo-elastic properties of pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$) at mantle pressures and temperatures using Ab initio molecular dynamic simulation. A third-order Birch-Murnaghan equation at a reference temperature of 2 000 K fits the calculations with bulk modulus, $K_0=159.5$ GPa, $K_0'=4.3$, $V_0=785.89$ Å$^3$, Grüneisen parameter, $\gamma_0=1.15$, $q=0.80$, Anderson Grüneisen parameter $\delta_T=3.76$ and thermal expansion, $\alpha_0=2.93\times10^{-5}$ K$^{-1}$. Referenced to room temperature, where $V_0=750.80$ Å$^3$, $\gamma_0$ and $\alpha_0$ become 1.11 and 2.47$\times10^{-5}$ K$^{-1}$. The elastic properties of pyrope are found to be nearly isotropic at transition zone conditions.

KEY WORDS: AIMD, thermo-elasticity, pyrope, high pressure.

INTRODUCTION

Silicate garnets are prominent minerals in the earth’s mantle. They are stable over a wide depth range from the silicate garnets (pyrope Mg$_3$Al$_2$Si$_3$O$_{12}$, almandine Fe$_3$Al$_2$Si$_3$O$_{12}$, spessartine Mn$_3$Al$_2$Si$_3$O$_{12}$, grossular Ca$_3$Al$_2$Si$_3$O$_{12}$ and andradite Ca$_3$Fe$_2$Si$_3$O$_{12}$). Pyrope is considered to be the major end-member garnet in the earth’s upper mantle and transition zone. The interpretation of seismic observations for the mantle relies on pressure-volume-temperature relations and both sound velocity values and anisotropies of constituent minerals at relevant pressure and temperature conditions. It is thus of primary importance to know the elasticity and thermal equation of state (EOS) of pyrope at mantle conditions when modelling seismic velocities and densities in the transition zone.

Elastic properties of pyrope have been the focus of extensive experimental and computational studies. Most of the high pressure experimental studies for pyrope were carried out at ambient temperature (Sinogeikin and Bass, 2000; Chen et al., 1999; Zhang and Herzberg, 1994) or high temperature-room pressure conditions (Sinogeikin and Bass, 2002). Most recently, ultrasonic measurement was carried out up to 9 GPa and 1 000 °C (Gwanmesia et al., 2006). Current experimental data do not cover two important parameters: (1) pressure-temperature conditions relevant to the mantle; (2) anisotropies especially shear wave anisotropies which are crucial for interpreting seismic anisotropies (Deuss and Woodhouse, 2001). Computational studies have simulated thermodynamic properties and EOS of...
pyrope, but these studies used semi-empirical interatomic potentials (Mittal et al., 2001; Pavese, 1999). In recent years, Ab initio molecular dynamics (AIMD), which simulates stress-strain relationships at elevated pressure and temperature conditions, has been shown to be a more accurate method than semi-empirical approaches and may be used successfully to predict the structural and elastic properties of mantle silicates (Li et al., 2005; Stackhouse et al., 2004; Oganov et al., 2001a, b). In this article, we use the AIMD method to quantify thermo-elasticity of pyrope at mantle \( P-T \) conditions.

**COMPUTATION METHOD**

\( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \) pyrope has a cubic structure (Ia-3d space group); the tetrahedral (SiO\(_4\)) share corners with the octahedral (AlO\(_6\)). The atoms in the following crystallographic sites: Mg(24c), Al(16a), Si(24d) and O(96h). For a body centred cubic (BCC) structure mineral like pyrope, its primitive cell has half the volume of a unit cell, and contains four formula units (80 atoms) in a parallelepiped unit cell. The primitive cell has three basis vectors of (1 -1 1), (1 1 -1) and (-1 1 1). All calculations were performed using this 80-atom primitive cell.

We used Vienna Ab-initio Simulation Package (VASP) code to perform our AIMD simulations (Kresse and Furthmüller, 1996a, b). We used projector-augmented-wave (PAW) implementation of density functional theory (DFT) (Blöchl, 1994) and the implementation of an efficient extrapolation for the charge density (Alfè, 1999). We used the exchange-correlation functional \( E_{xc} \) in the PW91 form of the generalized gradient approximation (GGA) (Perdew et al., 1992; Wang and Perdew, 1991). \( \Gamma \) point was used for sampling the Brillouin zone. The elastic constants were calculated at three volumes (774.2, 751.0 and 724.0 Å\(^3\), volume term is used here rather than pressure because of the pressure correction term discussed below). At each volume, five temperatures (0, 1500, 2000, 3000 and 3500 K) were considered (0, 1 500, 2 000, 3 000 and 3 500 K). The plane-wave cut-off energy 500 eV is adequate as the effect of using a larger cut-off is found to be insignificant. At elevated temperatures, lattice parameters were fixed and the ionic positions were allowed to relax. The time step used in the dynamic simulation was 1 fs. The core radii were 2.0 a.u. for Mg (core configuration 1s\(^2\)2s\(^2\)2p\(^6\)), 1.9 a.u. for Al (1s\(^2\)2s\(^2\)2p\(^6\)), 1.5 a.u. for Si (1s\(^2\)2s\(^2\)2p\(^6\)) and 1.52 a.u. for O (1s\(^2\)). The equilibrium structure was obtained after at least 2 ps of simulation, when average stresses had converged to within 0.5 GPa. Applying strains (-1%, 1%, 2% and 2.5%) to the equilibrated structure, stresses were calculated over at least 1 ps of simulation. The linearity of stress vs. strain was carefully checked when elastic moduli were derived. The acoustic velocities as a function of crystallographic direction were derived from the calculated single-crystal elastic constants using Christoffel equation (Nye, 1957).

**RESULTS AND DISCUSSION**

**Thermo-elasticity of Pyrope**

The goal of this study is to calculate thermo-elastic properties of pyrope at mantle \( P-T \) conditions. We performed our calculations at five temperatures (0, 1500, 2000, 3000 and 3500 K) and three volumes (774.2, 751.0 and 724.0 Å\(^3\)). At first we define the elastic moduli, bulk modulus, shear modulus, and thermal pressure as a function of volume and temperature. From thermal pressure and bulk modulus, thermal expansion is defined.

Since we wish to define physical parameters along a geotherm, we define the reference state for equation of state as 2000 K and 0 GPa. It is well known that generalized gradient approximation (GGA) model tends to overestimate the pressure when compared with experiment data (Oganov et al., 2001a), we have taken an approach to define, empirically, a pressure offset between the calculated pressure and measured pressure for a given volume (Li et al., 2009, 2006a, b, 2005; Oganov et al., 2001a). With the assumption that the calculations provide the correct physical property as a function of volume and temperature, we correct the pressure by combing our bulk modulus \( (K) \)-volume \( (V) \) relationship with the experimental volume adjusted to 2 000 K using the derived thermal expansion. We take \( \varepsilon(298 K) = 750.76 \text{ Å}^3 \) (Leitner et al., 1980) and define \( V_d(2 000 K) = 785.89 \text{ Å}^3 \). We fitted our \( K(V, T) \) results using a Birch Murnaghan equation of state and deduced \( K_d(2 000 \text{ K}) = 159.5 \text{ GPa}, \left( \partial K/\partial P \right)_T = 4.3, \) and \( \left( \partial K/\partial T \right)_V = 0.003 \text{ 3 GPa/K} \). With this equation of state, we calculated the