



Elasticity and phase stability of pyrope garnet from ab initio computation



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ABSTRACT

We study the high-pressure stability and elastic properties of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ pyrope garnet using the density functional first principles computation method. Pyrope garnet is found to dissociate into an assemblage of MgSiO_3 Mg-perovskite (Pv) and Al_2O_3 corundum (Cor) solid solutions at ~ 19.7 GPa at static conditions. Then, this assemblage undergoes a phase transition to pyropic (Al-bearing) Pv at ~ 65 GPa. The enthalpy of an assemblage of MgAl_2O_4 calcium ferrite (CF), MgPv, and stishovite (St) is less stable than that of MgPv plus Cor. A continuous reaction in the MgSiO_3 – Al_2O_3 system suggested by this study is consistent with previous experimental and computational studies but not with a recently modeled phase diagram. This implies that the formation of pyropic Pv could not cause any seismic scatterers in the mid-lower mantle. The investigated anisotropy of elastic velocities further indicates that pyrope garnet is a very isotropic mineral. Our results suggest that seismological anisotropy inferred in the upper mantle could not be due to garnet.

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1. Introduction

Pyrope garnet ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is considered to be one of the major end-member garnets (majorite, pyrope, almandine, and grossular) and a typical indicator for high-pressure metamorphic rocks such as eclogite. In order to understand the fate of subducted materials and how the high-pressure rocks are exhumed, it is important to clarify the high-pressure stability and elastic properties of pyrope garnet. Silicate garnets are considered to comprise ~ 40 and ~ 90 vol% of pyrope and basaltic compositions in the upper mantle and mantle transition zone, respectively (e.g., Irifune and Tsuchiya, 2007). Typical upper mantle compositions such as pyrope were reported not to be accountable for global seismological models such as PREM (Dziewonski and Anderson, 1981), suggesting possible chemical variations in the mantle transition zone (Irifune et al., 2008; Cobden et al., 2008). To better understand dynamics in these regions, these elastic properties are essential.

MgPv is found to be the major host of aluminum in a pyrope composition with ~ 5 mol% of Al_2O_3 in the lower mantle (Irifune,

1994; Tsuchiya and Tsuchiya, 2008). Phase relations in the MgSiO_3 – Al_2O_3 system have been studied so far. Irifune et al. (1996) showed that majorite garnet with less than ~ 15 mol% of Al_2O_3 transforms to the Pv structure via a mixture of these two phases. Pyrope (i.e., 25 mol% of Al_2O_3) was, on the other hand, shown to form almost pure Pv at 38 GPa using multi-anvil apparatus (Ito et al., 1998; Kubo and Akaogi, 2000; Hirose et al., 2001). In contrast with these experimental studies, there are few theoretical studies on the phase stability of pyrope. Due to the slow kinetics of garnet decomposition, it is important to study the energetics of pyrope garnet theoretically.

Elastic properties of pyrope garnet in the upper mantle have been experimentally studied as a function of pressure up to 20 GPa (Sinogeikin and Bass, 2002; Conrad et al., 1999; Leitner et al., 1980; Chen et al., 1999; Gwanmesia et al., 2006; Zou et al., 2012a,b). Some theoretical studies investigated the zero-pressure thermodynamic and elastic properties of pyrope using semi-empirical interatomic potentials (Mittal et al., 2001; Pavese, 1999). Few theoretical studies have investigated the high-pressure stability and elastic properties of pyrope. In addition, a previous first principles computation that examined the thermo-elastic behavior of pyrope shows a significant deviation of the bulk modulus from experimental values and does not report on its stability (Li et al., 2011). Therefore, in this study we investigate the

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high-pressure stability and elasticity of pyrope garnet by means of ab initio density functional computation methods.

2. Computation details

Our first principles calculations are based on density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) with the local density approximation (LDA) (Ceperley and Alder, 1980; Perdew and Zunger, 1981) for elasticity and with the generalized gradient approximation (GGA) (Perdew et al., 1996) for stability. While the transition pressure calculated by LDA tends to be low (Hamann, 1996), the elasticity calculated by LDA is more plausible than that by GGA. One electron wavefunction satisfying the Kohn–Sham equation describes a stationary electron state, which was expanded in a plane wave basis. Ionic core potentials were described based on the pseudopotential method. Pseudopotentials were generated using von Barth and Car’s methods for Mg, Vanderbilt’s (1990) method for O, and Troullier and Martins’ (1991) methods for Al and Si. The electron configurations included in these pseudopotentials are $3s^2 3p^0$, $3s^1 3p^1$, $3s^1 3p^{0.5} 3d^{0.5}$, $3s^1 3p^{0.5}$, and $3s^1 3d^1$ with decreasing weights 1.5, 0.6, 0.3, 0.3, and 0.2 respectively for Mg, $3s^2 3p^1$ for Al, $3s^2 3p^2 3d^0$ for Si, and $2s^2 2p^4$ for O. Most of these have been well tested in our previous studies (Tsuchiya et al., 2004a,b, 2005; Kawai and Tsuchiya, 2010). The plane wave energy cutoff was set to 70 Ry, and the irreducible part of the Brillouin zone was sampled by a $2 \times 2 \times 2$ mesh for the primitive cell of pyrope (80 atoms) and perovskite with a pyrope composition (20 atoms) using the Monkhorst–Pack method (Monkhorst and Pack, 1976). The effects of using larger cutoff and k-points on the calculated properties were found to produce insignificant variations in results. For example, variations in pressure when applying a 100 Ry cutoff and a $4 \times 4 \times 4$ sampling are 0.03 GPa only. Using the above conditions, total energies converged within 0.01 eV/atom. The full elastic constant tensors of the cubic structure with three independent components for pyrope garnet were calculated using stress–strain relations (Karki et al., 2001). The magnitude of all applied strains was 0.01. We confirmed that a linear relation was sufficient for this strain range (Tsuchiya and Kawai, 2013). All structural parameters were fully relaxed to a static (0 K) configuration by the damped variable cell shape constant pressure molecular dynamics technique (Wentzcovitch, 1991) using the PWSCF code (Giannozzi et al., 2009) until residual forces became less than 1.0×10^{-5} Ry/a.u.

3. Results and discussion

Pyrope garnet has a cubic crystal structure with the space group $la\bar{3}d$, which contains 48 point-symmetry operations (Fig. 1). The primitive cell in our calculations includes 80 atoms ($Z = 4$). Pyrope garnet is composed of MgO_8 triangular dodecahedra, AlO_6 octahedra, and SiO_4 tetrahedra (Novak and Gibbs, 1971). Pressure–volume relations of pyrope garnet calculated within the LDA and GGA are shown in Fig. 2. As the LDA is well known to sometimes underestimate volumes even when effects of the finite temperature are taken into account due to its general overbinding tendency (e.g., Hamman, 1996), the volumes computed within LDA in this study are found to be smaller than experimental values (Fig. 2). On the other hand, as GGA tends to sometimes overestimate volumes, the volumes computed within GGA in this study is larger than experimental results. The equation of state parameters (zero-pressure bulk modulus, B_0 , and its pressure derivative, B'_0) are determined by least-squares fitting the LDA data to the third-order Birch–Murnaghan equation (Table 1). The parameters obtained are $B_0 = 179.1$ GPa and $B'_0 = 4.4$, which are in

Pyrope

$la\bar{3}d$ (No. 230)

$Z=8$

$a=11.383$ Å

(0 GPa, 0 K)

$x_{Mg} = 0$; $y_{Mg} = 1/4$; $z_{Mg} = 1/8$
 $x_{Al} = 0$; $y_{Al} = 0$; $z_{Al} = 0$
 $x_{Si} = 3/8$; $y_{Si} = 0$; $z_{Si} = 1/4$
 $x_O = .0325$; $y_O = .0514$; $z_O = .6523$

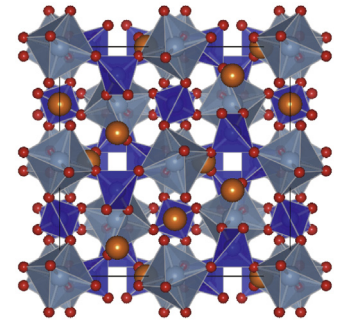


Fig. 1. The crystal structure of $Mg_3Al_2Si_3O_{12}$ pyrope garnet projected onto the {100}. Orange and red spheres are Mg and O atoms, respectively. Lattice constants and fractional coordinates of atoms are also shown. The garnet framework is formed by corner sharing AlO_6 octahedra (light blue) and SiO_4 tetrahedral (dark blue). Mg^{2+} ions are located in empty spaces of this framework, and form eightfold coordinated dodecahedra. Pyrope is the Mg and Al end-member of silicate garnet. The chemical formula of oxide garnets can be generally written as $X_3Y_2Z_3O_{12}$, where X is a divalent cation such as Ca^{2+} , Fe^{2+} , and Mg^{2+} ; Y is a trivalent cation such as Al^{3+} and Fe^{3+} ; and Z is Si^{4+} for the silicate garnets. Since Ca^{2+} , Mg^{2+} , and Fe^{2+} tend to be dissolved into X cation sites and Al^{3+} and Fe^{3+} tend to be dissolved into Y cation sites, the solid solution of pyrope garnet is formed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

good agreement with experimental data (Zou et al., 2012a,b; Zhang et al., 1998; Leger et al., 1990; Gwanmesia et al., 2006).

We investigated the high-pressure stability limit of pyrope garnet. According to the experimental reports (e.g., Kubo and Akaogi, 2000), pyrope dissociates into Pv and Cor solid solutions. Therefore, we examined the enthalpy balance calculated within GGA (1) between pyrope and an assemblage of MgPv and Cor solid solutions, (2) between pyrope and an assemblage of CF ($MgAl_2O_4$), MgPv, and stishovite (SiO_2), and (3) between pyrope and pyropic perovskite (perovskite with a pyrope composition, $Mg_3Al_2Si_3O_{12}$). For the case (1), compositions of the solid solution phases are taken from an experimental phase diagram at 1900 K (Kubo and Akaogi, 2000). According to their study, pyrope dissociates approximately into $(Mg_{0.9}Al_{0.1})(Si_{0.9}Al_{0.1})O_3$ Pv and $(Al_{0.75}Mg_{0.25})(Al_{0.75}Si_{0.25})O_{12}$ Cor. In this study, to calculate energies of these solid solutions we consider supercells containing 80 atoms for both Pv and Cor. For the Cor solid solution an $(Al_{12}Mg_4)(Al_{12}Si_4)O_{48}$ supercell is taken. For the Pv solid solution, we interpolate energies between $(Mg_{15}Al)(Si_{15}Al)O_{48}$ and $(Mg_{14}Al_2)(Si_{14}Al_2)O_{48}$ supercells since the above composition cannot fit to the 80 atom supercell. As transition pressures generally tend to be underestimated based on the LDA (Hamman, 1996), we calculated enthalpies within the GGA. The obtained enthalpy of pyrope becomes higher at 19.7 GPa than the sum of the enthalpies of the MgPv and Cor solid solutions, indicating that pyrope’s dissociation occurs here. Although the reported Clapeyron slope is nearly 0 MPa/K at pressures from 24 to 27 GPa in the temperature range between 1000 and 2300 K, it is controversial regarding whether it is positive (Kubo and Akaogi, 2000) or negative (Hirose et al., 2001). The phase boundary pressure obtained in this study is ~ 3 –6 GPa lower than results obtained experimentally. This may be due to the temperature difference between ~ 1900 K in the experiments and static condition in our computations. Then, we estimate the Gibbs free energy change including the mixing entropy contribution, which is approximated to be the ideal form $\Delta S = -nR\sum_i x_i$, where n , R are the total number of moles, the gas constant, and the mole fraction of component i , respectively. This ideal approximation was reported to be appropriate for the aluminous MgPv solid solutions at the lower mantle temperatures (Tsuchiya and Tsuchiya, 2008). With a temperature of 1900 K as a test, the enthalpy of the assemblage of CF, MgPv, and stishovite is found to be distinctly larger

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