

Phase transition and elasticity of enstatite under pressure from experiments and first-principles studies



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ABSTRACT

We have investigated the thermodynamic stability, crystal structure, elastic constants, and sound velocities of MgSiO₃-enstatite using data from X-ray diffraction and ultrasonic measurements up to 16.8 GPa and first-principles calculations up to 30 GPa. The calculated enthalpies provide theoretical support for the phase transition from *Pbca* to *P2₁/c* between 9 and 14 GPa previously observed in natural orthoenstatite and MgSiO₃ enstatite. A density increase of 1.4–1.5% for the *Pbca* → *P2₁/c* transition is obtained from both first-principles and experimental studies. Elastic constants of *Pbca*, *P2₁/c*, *C2/c*, *P2₁ca* and *Pbca-II* are all calculated, and a softening in the shear constant *C*₅₅ is predicted for *Pbca* and *Pbca-II* phases. *C*₅₅ of *Pbca* is found to be closely correlated with the A-site SiO₄ tetrahedra chain angle while *C*₄₄ and *C*₆₆ are correlated with the B-site chain angle. *Pbca*, *P2₁/c* and *C2/c* all exhibit similar volumetric compressibilities at all pressures. The calculated velocities of the *P2₁/c* phase at 12 GPa are equal to those of *Pbca* for *P* and 1.3% higher for *S* waves. The experimentally observed *P* and *S* wave velocity anomalies can be qualitatively described by the transformation from *Pbca* to *P2₁/c*; however, the magnitudes of the velocity decreases between 10 and 14 GPa remain to be verified by future single crystal data or polycrystalline measurements at high pressures. The predicted velocity jumps of 2.8% and 4.5% for *P* and *S* waves, respectively, between *Pbca* and *C2/c* in the pressure range of 5–12 GPa are in excellent agreement with the values of ~3(1)% and ~5(1)% obtained from the directly measured data, thereby making it a plausible candidate for the seismic X-discontinuity at depths of 250–300 km in the Earth's upper mantle.

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1. Introduction

Enstatite is the magnesium end member of the mantle orthopyroxene (Mg_xFe_{1-x})SiO₃ (Ringwood, 1975). At ambient conditions, it crystallizes in orthorhombic structure (space group *Pbca*) consisting of corner-linked SiO₄ tetrahedra chains and edge sharing MgO₆ octahedra. At high pressure and high temperature, it has been consistently shown that orthopyroxene transforms into an unquenchable monoclinic structure with space group *C2/c* at ambient mantle conditions (Pacalo and Gasparik, 1990; Woodland, 1998; Shinmei et al., 1999); however, its crystal structure behavior and physical properties at room temperature as well as low temperatures related to cold subduction zones are still discrepant and under continuous investigation (Chopelas and Boehler, 1992; Lin, 2003; Lin et al., 2005; Kung et al., 2004; Zhang et al., 2011, 2012; Jahn, 2008). The compression mechanism of orthopyroxene has been mainly ascribed to the rotations of the SiO₄ tetrahedral chains in conjunction with compression of the MgO₆ octahedra

(e.g., Hugh-Jones and Angel, 1994). When the configuration and stacking order of the SiO₄ chains are altered under pressure, polymorphic phase transformation will result (Angel et al., 1992; Downs, 2003; Thompson and Downs, 2003; Jackson et al., 2007; Yu and Wentzcovitch, 2009). Single crystal elastic constants from ultrasonic measurements to 3 GPa and impulsive stimulated scattering measurements up to 12.5 GPa reveal nonlinear pressure dependence in some or all elastic constants (Webb and Jackson, 1993; Chai et al., 1997), which are often viewed as indications of mechanical instability under extended pressures. Ultrasonic velocity measurements on polycrystalline MgSiO₃ enstatite up to ~17 GPa suggested that both compressional and shear wave velocities in the pressure range of 10–17 GPa exhibit large anomalies of softening and recovery, providing further support for a pressure-induced instability or phase change in orthopyroxene (Flesch et al., 1998; Kung et al., 2004). Previously, transformation from enstatite to high pressure clinopyroxene (space group *C2/c*) was observed in FeSiO₃ orthoferrosilite at ~4 GPa in single crystal compression study (Hugh-Jones and Angel, 1994); powder X-ray diffraction data collected up to ~17 GPa and Raman spectroscopy up to 60 GPa on MgSiO₃ enstatite, however, do not seem to support

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for a direct transformation from *Pbca* to *C2/c* phase at room temperature (Kung et al., 2004; Lin, 2003; Lin et al., 2005; Serghiou et al., 2000).

In addition to experimental studies, theoretical calculations have also provided important insights into the phase transitions in MgSiO_3 polymorphs (Matsui and Price, 1992; Wentzcovitch et al., 1995; Miyake et al., 2004; Jahn, 2008; Yu and Wentzcovitch, 2009). Recently, density functional theory (DFT) study by Jahn (2008) predicted that enstatite undergoes a transition to a *P2₁/c* phase at 9–10 GPa, followed by a transition to an orthorhombic structure (*Pbca*-II according to Jahn, 2008) at 14 GPa. More recently, it was found that enstatite transforms into a monoclinic *P2₁/c* phase (referred as *P2₁/c* hereafter) at 14.26 GPa in a synchrotron single crystal X-ray diffraction study (Zhang et al., 2012). To date, the elastic behavior for these candidate high pressure structures still have not been explored; as a result, it remains unclear whether the velocity anomalies observed in previous ultrasonic study by Kung et al. (2004) can be reconciled by the newly observed phase transition from *Pbca* to *P2₁/c*. In this study, we examined the X-ray diffraction data of Kung et al. (2004) in the pressure range of 10–17 GPa against these candidate structures to investigate the mineral phase(s) present when *P* and *S* velocities exhibit anomalous softening. We also incorporated first-principles calculations on these candidates structures to evaluate their relative stability, compression behavior, elastic constants and moduli, and sound wave velocities under an extended pressure range, this allows for comparisons among these phases as well as with available experimental data to gain insights into the origin of instabilities and elastic anomalies as well as transformation pathways of under pressure.

2. Methods

The X-ray diffraction data on MgSiO_3 enstatite up to 16.8 GPa were obtained in simultaneous ultrasonic interferometry, X-ray diffraction, and X-ray radiographic imaging measurements. A polycrystalline specimen of enstatite with a bulk density of 3.19(1) g/cm^3 (greater than 99% of the single-crystal X-ray density) was used and the high pressure experiments were conducted in a Kawai type multi-anvil apparatus installed at the 13-ID-D beamline of GSECARS, Advanced Photon Source of the Argonne National Laboratory (Uchida et al., 2002). More detailed experimental procedures as well as results on ultrasonic velocities have been described in a previous report (Kung et al., 2004). In the pressure range of 10–17 GPa where velocity softening was identified, refinement of the X-ray diffraction data was hindered due to the lack of information about the crystal structure at these pressures. In this study, we conducted further analysis of the X-ray diffraction data in the range of 10–17 GPa collected in our previous experiments. The refinements were carried out using a Le Bail method (Le Bail et al., 1988) as implemented in software GSAS/EXPGUI (Toby, 2001).

First-principles calculations were performed using density functional theory within a GGA framework of PBE (Perdew et al., 1996) exchange correlation functional as implemented in the Vienna *ab initio* Simulation Package (VASP) (Kresse and Furthmüller, 1996) and CASTEP (Clark et al., 2005) to obtain equilibrated structures and enthalpies for all candidate phases under pressure. In VASP calculations, the projector-augmented-wave (PAW) potentials (Blöchl, 1994; Kresse and Joubert, 1999) with core cutoff radii (*R_c*) of 2.0, 1.9, and 1.52 a.u. and valence electron configurations of $3s^2$, $3s^23p^2$, and $2s^22p^4$ were used for Mg, Si, and O, respectively; whereas in CASTEP calculations ultrasoft pseudopotentials of Mg (*R_c* = 2.0 a.u., $2p^63s^2$), Si (*R_c* = 1.8 a.u., $3s^23p^2$) and O (*R_c* = 1.0 a.u., $2s^22p^4$) were used. A combination of plane wave cutoff energy

$E_{\text{cut}} = 850$ eV and *k*-point of $3 \times 3 \times 5$ mesh (Monkhorst and Pack, 1976) was used to achieve convergence criteria of 1×10^{-6} eV/atom in energy, 0.01 eV/Å in force and 0.02 GPa in pressure for *Pbca* enstatite, high pressure *P2₁/c*, *P2₁/ca*, and *Pbca*-II (all have similar lattice parameters and 80 atoms in unit cell). For low-pressure clinoenstatite (space group *P2₁/c*, 40 atoms/unit cell, LPCEN hereafter) and high-pressure clinopyroxene (space group *C2/c*, 40 atoms/unit cell), the calculations were performed with $E_{\text{cut}} = 700$ eV and $5 \times 5 \times 5$ *k*-point mesh with the same convergence criteria as specified above. Elastic constants were obtained using a stress–strain approach in which strain amplitudes within $\pm 1\%$ were imposed on equilibrated lattices followed by relaxations of the atomic positions only. It should be noted that, associated with underbinding, zero-point motion and difference in temperature, the current (athermal) GGA (LDA) results overestimate (underestimate) lattice parameters of *Pbca* enstatite by 1.1–1.3% (unit cell volume by 3.8%). A closer comparison with experimental data can be approximated by applying a correction of -3.8 GPa (3.6 GPa) to pressures from GGA (LDA) to account for the Pulay stress at equilibrium volume caused by finite plane-wave basis set (e.g., Karki et al., 1997). Calculations with higher plane wave cutoff energy ($E_{\text{cut}} = 1050$ eV) resulted in changes less than 0.1% in lattice parameters and 0.1–2.3% in the elastic constants.

3. Results and discussion

3.1. Enthalpies of MgSiO_3 phases

The enthalpy of *Pbca* enstatite, LPCEN, high-P clinoenstatite, and recently proposed new high pressure phases (*P2₁/ca*, *Pbca*-II, and *P2₁/c*) from GGA are compared in Fig. 1 as a function of pressure. Low clinoenstatite has lower enthalpies than *Pbca* enstatite at all pressures with a small enthalpy difference of 0.04–0.08 eV per MgSiO_3 formulae unit. At pressures below 7 GPa, *P2₁/ca*, *Pbca*-II, *P2₁/c*, and *C2/c* phases all have higher enthalpies than *Pbca* enstatite. With increasing pressure to 7.5, 13, and 17.5 GPa, *C2/c*, *P2₁/c* and *P2₁/ca*, and *Pbca*-II, respectively, become thermodynamically more stable than *Pbca* driven by lower enthalpy. It should be noted that the results from the current first-principles calculations are in excellent agreement with LDA results from Jahn (2008), except that *P2₁/c* is not included in the latter study; also *P2₁/ca* (e.g., Yang and Prewitt, 2000) was suggested to be the phase observed in experimental studies around 10 GPa.

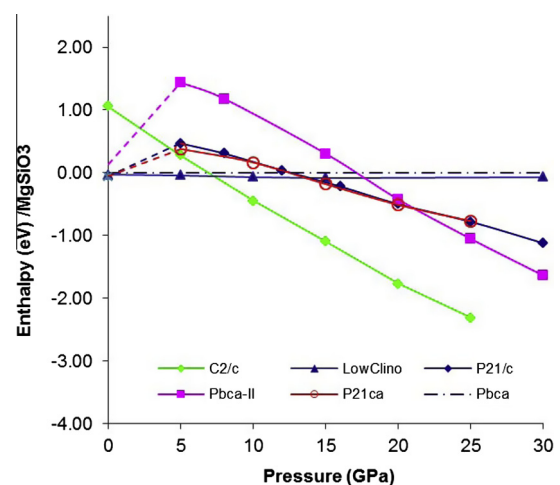


Fig. 1. Comparison of relative enthalpy between *Pbca* and low clinoenstatite (LPCEN), *P2₁/ca*, *P2₁/c*, *Pbca*-II, and *C2/c* phases, respectively.

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