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First-principles investigation of hydrous post-perovskite

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ABSTRACT

A stable, hydrogen-defect structure of post-perovskite (hy-ppv, $\text{Mg}_{1-x}\text{SiH}_2\text{xO}_3$) has been determined by first-principles calculations of the vibrational and elastic properties up to 150 GPa. Among three potential hy-ppv structures analyzed, one was found to be stable at pressures relevant to the lower-mantle D'' region. Hydrogen has a pronounced effect on the elastic properties of post-perovskite due to magnesium defects associated with hydration, including a reduction of the zero-pressure bulk (K_0) and shear (G_0) moduli by 5% and 8%, respectively, for a structure containing ~1 wt.% H_2O . However, with increasing pressure the moduli of hy-ppv increase significantly relative to ppv, resulting in a structure that is only 1% slower in bulk compressional velocity and 2.5% slower in shear-wave velocity than ppv at 120 GPa. In contrast, the reduction of certain anisotropic elastic constants (C_{ij}) in hy-ppv increases with pressure (notably, C_{55} , C_{66} , and C_{23}), indicating that hydration generally increases elastic anisotropy in hy-ppv at D'' pressures. Calculated infrared absorption spectra show two O–H stretching bands at $\sim 3500\text{ cm}^{-1}$ that shift with pressure to lower wavenumber by about $2\text{ cm}^{-1}/\text{GPa}$. At 120 GPa the hydrogen bonds in hy-ppv are still asymmetric. The stability of a hy-ppv structure containing 1–2 wt.% H_2O at D'' pressures implies that post-perovskite may be a host for recycled or primordial hydrogen near the Earth's core-mantle boundary.

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1. Introduction

Seismic investigations of the lowermost several hundred kilometers of the mantle (called the D'' region) have revealed a heterogeneous region with large-scale structures including large low-shear-velocity provinces (LLSVPs) and ultralow-velocity zones (ULVZs) overlying the core (Garnero and McNamara, 2008). The bridgmanite (brg) to post-perovskite (ppv) phase transition of MgSiO_3 has been invoked to explain some of the features within the D'' region (Murakami et al., 2004; Tsuchiya et al., 2004; Oganov and Ono, 2004; Wookey et al., 2005; Nowacki et al., 2010). The composition and mineralogy of D'' remains unresolved due to uncertainties in core-mantle boundary (CMB) temperature (Nomura et al., 2014), spatial heterogeneity of D'' material (e.g. slab graveyards) (Garnero and McNamara, 2008), and the effect of major element substitution on physical properties of the brg/ppv phase boundary for candidate lower mantle compositions (Grocholski et al., 2012).

Previous studies have investigated the effect of major-element substitution on the bridgmanite to post-perovskite phase

transition and on physical properties of post-perovskite (Murakami and Hirose, 2005; Mao et al., 2006; Grocholski et al., 2012). In Al-free systems, increasing Fe^{2+} decreases the pressure of the phase boundary, whereas increasing Fe^{3+} and Al-content suppresses the phase boundary to higher pressures (greater depths) (Grocholski et al., 2012). The brg to ppv transition should occur above the CMB in harzburgite and MORB but potentially below the CMB conditions in pyrolite (Grocholski et al., 2012). However, the influence of hydrogen on ppv structure and physical properties has not been determined.

The bulk H_2O content of the mantle is among the least well constrained compositional parameters of the Earth, with estimates varying by orders of magnitude due to uncertainty in the bulk mantle and core hydrogen content (e.g. Williams and Hemley, 2001). The water storage capacity of the uppermost mantle varies with depth, but in the peridotite system olivine and pyroxene can contain about 0.1 wt.% H_2O at 400 km depth (Tenner et al., 2012; Ferot and Bolfan-Casanova, 2012). The transition zone water storage capacity is likely much higher because wadsleyite and ringwoodite can incorporate 1–2 wt.% H_2O into their structures (Bolfan-Casanova et al., 2000; Inoue et al., 2010; Kohlstedt et al., 1996). The recent discovery of a hydrous ringwoodite inclusion in diamond containing ~1.5 wt.% H_2O suggests the transition zone

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may be very hydrous, at least locally (Pearson et al., 2014). The H₂O storage capacity of the lower mantle remains highly uncertain due to conflicting estimates of H₂O storage capacity of bridgmanite, which range from about 0.001 wt.% (Bolfan-Casanova et al., 2003) to 0.4 wt.% (Murakami et al., 2002) and values in between (Litasov et al., 2003). A recent computational investigation by Hernandez et al., 2013 calculated the hydrogen partition coefficient between ringwoodite, ferropericlase, and bridgmanite and estimated that bridgmanite may contain up to 1000 ppm (0.1 wt.%) water. Contrast in the H₂O storage capacity between ringwoodite and bridgmanite may lead to dehydration melting below the 660 km discontinuity and provide evidence for regional scale hydration of the transition zone (Schmandt et al., 2014).

In contrast to bridgmanite, the post-perovskite structure is potentially more accommodating of hydrogen because both oxygen sites of the structure are slightly under-bonded. Magnesium is coordinated to eight oxygens with interatomic distances less than 2 Å and to two oxygens with distances slightly longer than 2 Å (Zhang et al., 2013). If the two longer oxygens are excluded from the Pauling bond strength sum, both O1 and O2 have the potential to protonate with charge balance achieved by an Mg-site vacancy. To test the idea that ppv may store seismically detectable amounts of hydrogen at D'' pressures, we have investigated several potential hydrous post-perovskite structures using density functional theory (DFT). We describe the most favorable hy-ppv structure and calculate its elastic and vibrational properties under static conditions in order to determine its mechanical stability, single-crystal and bulk-elastic wave velocities, and infrared absorption spectra.

2. Methods

Post-perovskite is orthorhombic with space group *Cmcm* (Murakami et al., 2004; Tsuchiya et al., 2004; Oganov and Ono, 2004). The structure contains alternating layers of corner-sharing SiO₆ octahedra and Mg polyhedra in eight coordination to oxygen (Murakami et al., 2004; Zhang et al., 2013). DFT calculations were carried out using the PWSCF code, part of the Quantum ESPRESSO package using the Perdew–Ernzerhof–Burke generalized gradient approximation (Hohenberg, 1964; Kohn and Sham, 1965; Perdew et al., 1996; Giannozzi et al., 2009). Wavefunctions were expanded with plane waves using an energy cutoff of 100 Ry. Norm-conserving pseudopotentials were used to describe H, O, and Si (Troullier and Martins, 1991). The Mg pseudopotential was generated by the method of U. von Barth and R. Car and has been used in previous investigations of hydrogen in silicates (Karki and Wentzcovitch, 2000; Tsuchiya et al., 2004; Tsuchiya and Tsuchiya, 2009). A supercell consisting of 4x1x1 ppv unit cells (80–82 atoms) was used for all calculations. The irreducible

Brillouin zone was sampled on a 2 × 2 × 2 Monkhorst–Pack mesh (Monkhorst and Pack, 1976). Both plane-wave cutoff energy and mesh size were tested for adequate total energy convergence. Unit-cell parameters and atomic coordinates were simultaneously relaxed at 0 K with a force convergence criterion of 10^{−5} Ry/Bohr.

Because there are no experimental data available for hydrous ppv, H defects were created by introducing Mg-site vacancies, Mg_{1−x}SiH_{2x}O₃, as similar vacancy structures have been reported in other high-pressure silicates such as wadsleyite and ringwoodite (Tsuchiya and Tsuchiya, 2009; Kudoh and Inoue, 1999; Li et al., 2009; Ganskow et al., 2010; Verma and Karki, 2009). Coupled substitutions of Fe³⁺ or Al³⁺ and H⁺ for Si⁴⁺ may also be important in the ppv phase, but in this study we first consider only charge-balanced vacancy substitutions in which one magnesium atom from the ppv 4 × 1 × 1 supercell is replaced with two hydrogen atoms (Mg_{0.938}SiH_{0.125}O₃), corresponding to a concentration of approximately 1.14 wt.% H₂O. We also created a second structure in the same scheme as above, but with 2 magnesium vacancies and 4 hydrogens (Mg_{0.875}SiH_{0.250}O₃) corresponding to 2.31 wt.% H₂O. In the more hydrous model the magnesium vacancies were created such that the vacancies were far apart (>7 Å at 0 GPa) to minimize interactions between vacancies. The 9 single-crystal elastic components were obtained from calculations of total energy and stress for incrementally strained orthorhombic super-cells (Karki et al., 2001). The largest strain was 0.01 and was checked to ensure a linear response. The infrared spectrum of hy-ppv was calculated for several pressures at the Γ -point under 0 K conditions via density functional perturbation theory under the linear-response theory of Baroni et al., 2001, in which the dynamical matrix along with dielectric quantities such as the Born effective charge tensor are evaluated at the Γ -point. The scheme outlined above is similar to previous ab initio calculations of IR spectra for hydrous silicates (Karki and Wentzcovitch, 2000; Blanchard et al., 2009; Verma and Karki, 2009; Brodholt and Refson, 2000; Umemoto et al., 2011).

3. Results and discussion

Three potential OH-defect structures of post-perovskite were studied by positioning hydrogen in a magnesium vacancy of the ppv supercell using the electron localization function (Gibbs et al., 2003) to identify initial H positions. The first model (hy-ppv1) features one O1–H group and one O2–H group, the second (hy-ppv2) features two approximately symmetric O2–H groups, and the third model (hy-ppv3) features two asymmetric O2–H groups. After calculation of phonons and enthalpy under static conditions for all structures, the stable H-defect structure is hy-ppv3 (hereafter hy-ppv), which features two distinct asymmetric hydrogen bonds as O2–H groups oriented in a plane normal to the *a*-axis. The hy-ppv1 structure was rejected due to unstable phonon

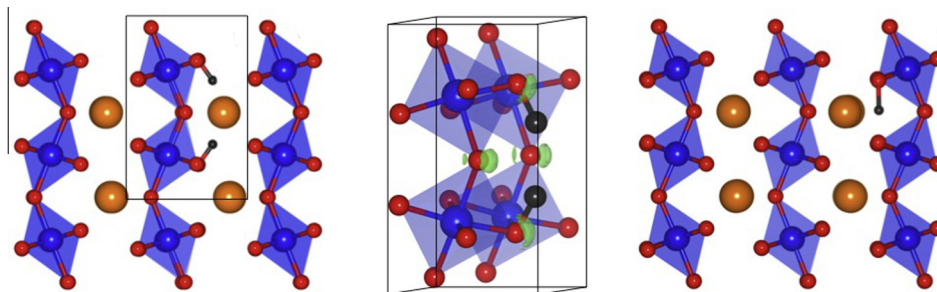


Fig. 1. Predicted stable hydrogen defect structure of hy-ppv at 120 GPa. Left: view of hy-ppv down the *a*-axis. Right: electron localization function 93-percentile iso-surface (green) of a Mg vacancy site in hy-ppv with super-imposed hydrogen groups. Atom positions are shown as oxygen (red), silicon (blue), magnesium (orange), and hydrogen (black). Lattice parameters and hydrogen-bond distances of the structure at 0 and 120 GPa are listed in Table 1. Fractional coordinates of atom positions for all structures are provided in the Supplementary materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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