First-principles investigation of hydrous post-perovskite

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Abstract

A stable, hydrogen-defect structure of post-perovskite (hy-ppv, $\text{Mg}_{1-x}\text{SiH}_{2x}\text{O}_3$) 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 cm^{-1} per 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.

Keywords: Hydrogen, Post-perovskite, Lower mantle, Elasticity

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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 0.1wt% 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 may be very hydrous, at least locally (Pearson et al., 2014). The H_2O storage capacity of the lower mantle remains highly uncertain due to conflicting estimates of H_2O 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) investigated 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 2x2x2 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, $\text{Mg}_{1-x}\text{SiH}_{2x}\text{O}_3$, 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 Fe^{3+} or Al^{3+} and H^+ for Si^{4+} 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 4x1x1 supercell was replaced with two hydrogen atoms ($\text{Mg}_{0.938}\text{SiH}_{0.125}\text{O}_3$), corresponding to a concentration of approximately 1.14 wt.% H_2O . We also created a second structure in the same scheme as above, but with 2 magnesium vacancies and 4 hydrogen ($\text{Mg}_{0.875}\text{SiH}_{0.250}\text{O}_3$) corresponding to 2.31 wt.% H_2O . In the more hydrous model the magnesium vacancies were created such that the vacancies were far apart ($> 7\text{\AA}$ 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 modes, and hy-ppv2, although stable, has a higher enthalpy than hy-ppv3 at 0 K at all pressures considered in this study (by about 0.10 eV per formula unit).

The stable structure of hy-ppv at 120 GPa is illustrated in Figure 1. At 0 GPa, the O-H bond distance is 0.98 Å, with a hydrogen bond geometry of $d(\text{H}\dots\text{O}) = 2.17$ Å, $d(\text{O}\dots\text{O}) = 2.73$ Å, and hydrogen bond angle 115° . For comparison, the hydrogen-bond geometry in hydrous bridgmanite (Hernandez et al., 2013) is $d(\text{O}-\text{H}) = 1.1$ Å, $d(\text{H}\dots\text{O}) = 1.65$ Å, with a hydrogen-bond angle of about 150° . Thus, the hydrogen bond in hy-ppv is considerably more non-linear than in hy-brg. In hy-ppv, the O-H bond distance increases slightly with pressure as the hydrogen bond distance $d(\text{O}\dots\text{O})$ shortens, consistent with general trends among hydrogen bonds in minerals (Libowitzky, 1999). Lattice parameters, energies, and hydrogen-bond geometry of hy-ppv at 0 and 120 GPa are listed in Table 1. Fractional coordinates of all the atom positions in all structures and all pressures are provided in the supplementary materials.

The effect of hydrogen on the elastic tensor of ppv is shown in Figure 2. Generally C_{44} , C_{55} , C_{66} , and C_{23} are most sensitive to hydration, with the most sensitive component C_{66} , reduced by 20% at 120 GPa for the 2.31 wt.% H_2O hy-ppv structure. We used the Born stability criteria to determine the mechanical stability of hy-ppv compared to ppv (Born and Huang, 1954). In the case of orthorhombic symmetry, these criteria reduce to the following:

$$B_{1,ii} = C_{ii} > 0 \quad (i = 1, 2, 3, \dots, 6) \quad (1)$$

$$B_{2,ij} = \det \begin{vmatrix} C_{ii} & C_{ij} \\ C_{ji} & C_{jj} \end{vmatrix} > 0 \quad (i, j = \{1, 2, 3\}, i \neq j) \quad (2)$$

$$B_3 = \det \begin{vmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{vmatrix} > 0 \quad (3)$$

The Born stability criteria calculated for pure ppv and hy-ppv are shown in Figure 3 and indicate that hydrogen does not destabilize the post-perovskite lattice over lower mantle pressures for a simple Mg-2H substitution.

Bulk elastic properties for ppv and hy-ppv were calculated from the single crystal elastic tensors using the Voigt-Reuss-Hill averaging scheme and are shown in Figure 4 (Hill, 1952). The Hill averaged elastic wave velocities decrease with hydration, as expected, but the bulk sound velocity (V_Φ) is remarkably insensitive to the presence of hydrogen. At 120 GPa V_Φ is reduced by 8 m/s per wt.% H_2O (<0.1% decrease). In contrast to the bulk sound velocity, both the Hill averaged P-wave (V_P) and S-wave (V_S) velocities decrease by approximately 68 m/s per wt.% H_2O (0.5% decrease) and 85 m/s per wt.% H_2O (1.1% decrease), respectively, at 120 GPa. Of particular note is that at 120 GPa the S-wave velocity of hy-ppv is slower than ppv and brg (for the 2.31 wt.% H_2O model), implying that a very hydrous hy-ppv, if present in D'', may be difficult to distinguish from bridgmanite using bulk sound velocity and/or shear-wave profiles alone.

The Hill averages of the bulk and shear moduli of ppv decrease linearly with water content, as shown in Figure 5. At 0 GPa, the bulk modulus of ppv decreases by 9.6 GPa per wt.% H_2O , corresponding to 4.5% reduction per wt.% H_2O relative to the dry ppv $K_0 = 214$ GPa. The effect of water on the bulk modulus is significantly less at 120 GPa, with about 7.4 GPa reduction per wt.% H_2O , corresponding to only about 1% reduction in K per wt.% H_2O relative to the dry $K_{120} = 677$ GPa. In contrast, the shear modulus decreases by 9.3 GPa per wt.% H_2O at 0 GPa, corresponding to a 8.1% reduction per wt.% H_2O relative to the dry $G_0 = 114$ GPa. At 120 GPa, the shear modulus decreases by 10.3 GPa per wt.% H_2O , corresponding to about 3.1% reduction per wt.% H_2O relative to the dry $G_{120} = 336$ GPa. For comparison, the bulk modulus $K_0 = 203$ GPa for Mg hy-ppv containing ~1 wt.% H_2O is 25% lower than the $K_0 = 272$ GPa reported for anhydrous $(Mg_{0.6}Fe_{0.4})$ -ppv (Mao et al., 2006). The reduction in K_0 (4.5%) and G_0 (8.1%) per wt.% H_2O for ppv upon hydration is about half that of ringwoodite, with about 7% reduction in K_0 and 15% reduction in G_0 per wt.% H_2O (Jacobsen et al., 2004). However, one of the most important results of the current calculations is that at pressures of D'', the calculated reduction by 1 wt.% H_2O in ppv is only about 1% in K and only about 3% in G , indicating that the hy-ppv structure is very stiff even in comparison with dry ppv. The combined influence of hydration, Al, and Fe-content in ppv remains to be explored in future work.

At D'' conditions, the effects of hydration on the Hill average of the bulk and shear moduli can be compared with the influence of temperature by applying the temperature derivatives of the moduli for ppv reported by Stackhouse et al. (2005). At 120 GPa, the influence of 1 wt.%

154 H₂O on the bulk modulus is equivalent to raising the temperature by about 300 K, whereas the
 155 effect of 1 wt.% H₂O on the shear modulus is comparable to increasing temperature by about
 156 675 K. There is very little effect of hydration on the V_P/V_S ratio of ppv, which shows about 0.01
 157 increase ($\sim 0.5\%$) both at 0 and 120 GPa for 1 wt.% H₂O (Table 2).

158 The single crystal elastic wave velocities were calculated using the Cristoffel equation:

$$\det |c_{ijkl}n_k n_l - \rho V^2 \delta_{ij}| = 0 \quad (4)$$

159 where c_{ijkl} is the elastic tensor, n is the propagation direction, ρ is the density, V is the velocity
 160 and δ_{ij} is the Kronecker delta (Musgrave, 1970). The effect of H on the single crystal elastic wave
 161 velocities calculated from eqn. 4 at 0 and 120 GPa are shown in Figure 6. The full elastic tensor
 162 and density at 0 and 120 GPa are listed in Table 2. At all pressures the presence of hydrogen
 163 reduces the elastic wave velocities for both P and S phases; however, the S-wave velocities
 164 are more sensitive to hydration. At 120 GPa the single crystal V_P is generally unchanged by
 165 hydration while V_S is reduced by 1.2% per wt.% H₂O.

166 All ppv and hy-ppv structures were fit to 3rd-order Birch-Murnaghan equations of state
 167 (EOS), and EOS parameters are given in Table 3. At 0 GPa the addition of 1.14 wt.% H₂O
 168 increases the molar volume of ppv by 0.5%, and addition of 2.31 wt.% H₂O increases the molar
 169 volume by 0.9%. For comparison, the Mg end-member hydrous ringwoodite containing 2.2 wt.%
 170 H₂O studied by Inoue et al. (1998) had a molar volume 0.27% larger than dry Mg-ringwoodite
 171 (Weidner et al., 1984). Thus, at 0 GPa, the increase in molar volume due to hydration of ppv
 172 is about four times that of ringwoodite. However, due to the increased compressibility of the
 173 hy-ppv phase, at 120 GPa the 1.14 wt.% H₂O hy-ppv structure has a molar volume that is 0.3%
 174 smaller than dry ppv, and the 2.31 wt.% H₂O hy-ppv structure has a molar volume that is 0.7%
 175 smaller than dry ppv.

176 Calculated vibrational density of states and infrared absorption spectra of hy-ppv are shown
 177 in Figure 7. Two O-H stretching bands are observed at 3492 and 3506 cm⁻¹ at ambient pressure
 178 and correlate well with OH vibrational frequencies found in other high-pressure silicates (Li-
 179 bowitzky, 1999). With pressure these bands shift linearly with $dv_{3492}/dP = -2.25 \text{ cm}^{-1}/\text{GPa}$ and
 180 $dv_{3506}/dP = -1.94 \text{ cm}^{-1}/\text{GPa}$. In contrast to phase D we do not see hydrogen bond symmetriza-
 181 tion in hy-ppv even at lower mantle pressures (Tsuchiya et al., 2005). The negative pressure shift
 182 of the OH modes is commonly observed in previous studies and occurs because the hydrogen

183 bonds become more symmetric with increasing pressure which lengthens the O-H bond, thereby
184 reducing the frequency (Libowitzky, 1999). The lower-frequency mode corresponds to in-phase
185 stretching of the two OH groups, and the higher-frequency mode corresponds to 180-degree-
186 out-of-phase stretching between the two OH groups. Measurements of OH in minerals at lower
187 mantle pressures using current techniques is challenging, but experimental observation of OH in
188 ppv may be especially challenging because because ppv is not stable at low pressure (Mao et al.,
189 2006), where many experimental measurements of OH in minerals are carried out.

190 **4. Summary**

191 Recent estimates of the return flux of water to the mantle via subduction suggest that perhaps
192 several hundreds of ppm water may be retained in the slab beyond the depth of magma generation
193 (Parai and Mukhopadhyay, 2012; Garth and Rietbrock, 2014). If slabs carry water through the
194 lower mantle and into D'', then ppv, the major silicate mineral in D'', may be a potential host for
195 water.

196 Primordial components, such as noble gases, in some ridge basalts may imply that magmas
197 deriving from the deep mantle sample unmixed source regions (Craig et al., 1978; Gonnermann
198 and Mukhopadhyay, 2007). The descent of slabs to the core mantle boundary (e.g. Garnero and
199 McNamara, 2008) provides a mechanism of water incorporation into the D'' region, through both
200 nominally anhydrous minerals and potential stability of dense hydrous magnesium silicates such
201 as phase H to lower mantle conditions (Nishi et al., 2014). Though the equilibrium assemblage
202 of hydrous minerals under lower mantle conditions is not well known, and we therefore cannot
203 comment on the most likely host for water in D'', this study has shown for the first time that a
204 stable structure of hy-ppv persists to D'' pressures and displays modified elastic properties which
205 may make it difficult to distinguish from brg from V_S profiles alone.

206 The stability of a hy-ppv structure containing 1-2 wt.% H₂O at D'' pressures implies that
207 post-perovskite can potentially host a significant amount of recycled or primordial hydrogen
208 near the Earth's core-mantle boundary. Future research requires determination of the hydrogen
209 partition coefficient between post-perovskite and other lower mantle phases such as bridgmanite,
210 especially with more realistic compositions that include iron and aluminum. Further constraints
211 on the effects of hydration on the mechanical and elastic properties of post-perovskite, especially
212 at high temperature, will be important for future work that may provide insight into the fate of

213 water in the seismically heterogeneous core-mantle boundary region.

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Figure 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.

Figure 2: Elastic tensor components (using Voigt notation) of ppv (black) and hy-ppv (1.14 wt.% H₂O in blue, 2.31 wt.% H₂O in red). C_{22} , C_{33} , C_{12} , and C_{13} are relatively insensitive to hydration at D'' pressures, while C_{11} , C_{44} , C_{55} , C_{66} , and C_{23} are more sensitive to hydration. At 120 GPa C_{22} and C_{33} are reduced by approximately 0.1% while C_{66} is reduced by approximately 20% with addition of 2.31 wt.% H₂O.

Figure 3: Born stability criteria for ppv (black), and hy-ppv (1.14 wt.% H_2O in blue and 2.31 wt.% H_2O in red). Mechanical stability of the lattice requires each quantity be greater than zero. Addition of hydrogen to the ppv lattice does not destabilize the ppv structure.

Figure 4: Bulk elastic properties of brg (dashed), ppv (black), and hy-ppv (1.14 wt.% H_2O in blue, 2.31 wt.% H_2O in red). Voigt-Reuss-Hill averaged bulk modulus and shear modulus (top), and bulk wave velocities (bottom). Bulk sound velocity is relatively insensitive to hydrogen content, while bulk shear velocity is most sensitive.

Figure 5: Top: Dependence of bulk modulus (top) and shear modulus (bottom), upon water content for ppv at 0 and 120 GPa.

Figure 6: Single crystal elastic wave velocities calculated for dry ppv (black), 1.14 wt.% H₂O (blue), and 2.31 wt.% H₂O (red). The presence of hydrogen has a pronounced effect on S-wave velocities relative to P-wave velocities. The presence of hydrogen does not noticeably change the minimum or maximum velocity directions.

Figure 7: Top: Vibrational density of states for hy-ppv (1.14 wt.% H₂O) at 120 GPa. Bottom: Calculated IR absorption spectra of hy-ppv at mantle pressures. Low-wavenumber peaks are lattice modes, and the two high-wavenumber peaks are characteristic of OH, representing in-phase stretching (low) and out-of-phase stretching (high).

Table 1: Lattice parameters of ppv and hy-ppv at 0 and 120 GPa calculated in the current study. The hydrogen-bond geometry at 0 and 120 GPa is given for structures containing 1.14 and 2.31 wt.% H₂O. Structural information for ppv and hy-ppv at all pressures can be found in the supplementary materials.

Structure	<i>P</i> GPa	<i>a</i> Å	<i>b</i> Å	<i>c</i> Å	<i>V</i> Å ³	<i>E</i> eV/FU	<i>d</i> (O-H) Å	<i>d</i> (O...O) Å	<i>d</i> (H...O) Å	H-bond angle deg.
ppv	0	2.7020	9.1539	6.6966	165.6342	-1470.0485				
	120	2.4694	8.1039	6.1303	122.6800	-1466.8475				
hy-ppv (1.14 wt.%)	0	2.7079	9.1891	6.6867	166.3856	-1470.0176	0.9838	2.734	2.172	114.67
	120	2.4677	8.0965	6.1205	122.2835	-1466.8427	0.9928	2.306	1.707	114.74
hy-ppv (2.31 wt.%)	0	2.7173	9.2101	6.6744	167.0391	-1469.9448	0.9866	2.724	2.160	114.68
	120	2.4677	8.0808	6.1093	121.8254	-1466.6279	0.9977	2.297	1.693	114.78

Table 2: Pressure dependence of elastic properties, density, and Hill averaged bulk wave velocities of ppv and hy-ppv. Elastic tensor, density, and elastic wave velocities at all pressures can be found in supplementary materials.

Structure	P GPa	C_{11} GPa	C_{22} GPa	C_{33} GPa	C_{44} GPa	C_{55} GPa	C_{66} GPa	C_{12} GPa	C_{13} GPa	C_{23} GPa	ρ kg/m ³	V_P km/s	V_S km/s	K GPa	G GPa
ppv	0	600	416	483	68	96	62	40	79	101	4025	9.54	5.33	214	114
	120	1313	971	1295	278	266	416	433	342	495	5435	14.38	7.86	677	336
hy-ppv (1.14 wt.%)	0	570	389	482	64	93	48	34	76	93	3951	9.32	5.16	203	105
	120	1284	968	1291	268	256	386	431	340	476	5375	14.32	7.78	668	326
hy-ppv (2.31 wt.%)	0	544	362	479	55	93	31	27	69	86	3880	9.03	5.16	192	93
	120	1257	968	1292	257	248	334	427	335	461	5320	14.23	7.66	660	312

Table 3: Equation-of-state parameters of post-perovskite with varying hydrogen content. Bulk modulus (K_{T0}) and its pressure derivative (K'_{T0}) were fit using a 3rd-order Birch-Murnaghan equation of state.

Structure	K_{T0} GPa	K'_{T0}	V_{T0} cm ³ /mol
ppv	210	4.27	24.94
hy-ppv (1.14 wt.% H ₂ O)	201	4.28	25.05
hy-ppv (2.31 wt.% H ₂ O)	191	4.32	25.15