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### **RESEARCH ARTICLE**

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#### **Key Points:**

- Hydrogen dissolution mechanisms in bridgmanite were studied by first-principles calculations and polarized infrared spectroscopy
- Mg and Si vacancies are the dominant hydrogen dissolution mechanisms in bridgmanite
- The dominant Mg and Si vacancy mechanisms can reduce viscosity and enhance electrical conductivity in the lower mantle

#### **Supporting Information:**

Supporting Information may be found in the online version of this article.

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# Hydrogen Dissolution Mechanisms in Bridgmanite by First-Principles Calculations and Infrared Spectroscopy

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**Abstract** Understanding hydrogen dissolution mechanisms in bridgmanite (Bgm), the most abundant mineral in the lower mantle, is essential for understanding water storage and rheological and transport properties in the region. However, interpretations of O-H bands in Fourier transform infrared spectroscopy (FTIR) spectra of Bgm crystals remain uncertain. We conducted density functional theory (DFT) calculations on vibrational characteristics of O-H dipoles and performed polarized FTIR measurements to address this issue. DFT calculations for four substitution models—Mg vacancies, Si vacancies,  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup>, and Al substitution with Mg vacancies-reveal distinct O-H bands with different polarizations. Deconvolution of polarized FTIR spectra on  $Mg_{0.88}Fe^{2+}_{0.035}Fe^{3+}_{0.065}Al_{0.14}Si_{0.90}O_3$  and  $Mg_{0.95}Fe^{2+}_{0.033}Fe^{3+}_{0.027}Al_{0.04}Si_{0.96}O_3$ crystals shows five major O-H bands with distinct polarizations along principal crystallographic axes. These experimental and calculated results attribute O-H bands centered at 3,463-3,480, 2,913-2,924, and 2,452-2,470 cm<sup>-1</sup> to Mg vacancies, Si vacancies, and Al<sup>3+</sup> + H<sup>+</sup> substitution for Si<sup>4+</sup>, respectively. The total absorbance coefficient of bridgmanite was calculated to be 82,702(6,217) L/mol/cm<sup>2</sup>. Mg and Si vacancies account for 43%-74% of the total water content, making them dominant hydrogen dissolution mechanisms in Bgm. The band frequencies for the Mg and Si vacancies in Bgm are drastically different from those in olivine and ringwoodite, corresponding to the significant changes in O-H bond strengths and in the Si and Mg coordination environments from upper-mantle to lower-mantle minerals. These results highlight the need to incorporate hydrogen dissolution mechanisms in Bgm for understanding electrical conductivity and rheology of the lower mantle.

**Plain Language Summary** Bridgmanite, the most abundant mineral in the Earth's lower mantle, plays a key role in storing water deep within the Earth and affects how this region behaves and transports heat. However, we do not fully understand how hydrogen, an essential part of water, gets incorporated into this mineral. This study aims to improve that understanding by combining computer simulations and lab experiments. We used density functional theory (DFT) to model how hydrogen bonds with different elements in bridgmanite and compared these models to measurements from infrared spectroscopy. Our results show that hydrogen can enter bridgmanite in several ways, with the most common involving missing magnesium or silicon atoms. These mechanisms account for most of the water stored in bridgmanite, which has important implications for how the lower mantle conducts electricity and flows under high pressure. These findings enhance our understanding of the deep Earth's water cycle and its influence on geological processes.

#### 1. Introduction

Hydrogen substitution in nominally anhydrous minerals (NAMs) in Earth's mantle can significantly influence rheological properties, melting, and electrical conductivity (Karato, 2006, 2010). Understanding the hydrogen substitution mechanisms in constituent mantle minerals can thus provide invaluable insights into the changes in these physical properties. Olivine, the most abundant mineral in the upper mantle, is the most thoroughly investigated mantle mineral for its water contents and hydration mechanisms associated with mantle dynamics, geophysics, and geochemistry (Blanchard et al., 2017; Karato, 2007, 2015; Kovács et al., 2010; Mei



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Writing – review & editing: Yanyao Zhang, Jun Tsuchiya, ChingChien Li, Takuo Okuchi, Shunichiro Karato, Jennifer Kung, Jung-Fu Lin and Kohlstedt, 2000a, 2000b). Hydrogen can dissolve in several ways including through dissolution at M-site or Si-site vacancies. Creep strength of olivine is weakened by the dissolution of hydrogen both in dislocation creep and diffusion creep (Karato and Jung, 2003; Mei and Kohlstedt, 2000a, 2000b). A possible model to explain this weakening is enhanced diffusion by hydrogen dissolved at Si site. In case of electrical conductivity, a plausible mechanism is high diffusivity of free proton formed by ionization of hydrogen-bearing point defects at M-site (Karato and Wang, 2013). This in turn may lead to lateral or depth variations in rheological properties and electrical conductivity of the upper mantle. Therefore, knowing the dominant hydrogen dissolution mechanism in host minerals is crucial for understanding geophysics and geodynamics of the deep mantle.

In contrast, little is known about the mechanism of hydrogen dissolution in bridgmanite (Bgm), the most abundant mineral of the planet. Knowing its hydrogen substitution mechanism is of paramount importance in deep-mantle geophysics and geodynamics (Figure S1 and Table S1 in Supporting Information S1). Previous FTIR studies on pure-endmember MgSiO<sub>3</sub> Bgm showed O-H bands between 3,420 and 3,490 cm<sup>-1</sup> (Bolfan-Casanova et al., 2000; Litasov et al., 2003; Meade et al., 1994), which are attributed to the presence of Mg vacancies  $((2H)_{ij}^{\mu})$  based on the electron density distribution in the Bgm crystal structure (Ross et al., 2003). When Fe<sup>2+</sup> substitutes at the Mg site (also known as the A site), an additional O-H band at 3,380 cm<sup>-1</sup> appears in FTIR spectra (Bolfan-Casanova et al., 2003; Panero et al., 2015). Trivalent cations like Al<sup>3+</sup> or Fe<sup>3+</sup> typically can substitute at the Si site (B site), creating oxygen vacancies that O-H groups may fill through coupled Al3+ + H+ substitution with Si4+  $((Al^{3+}H^+)_{G_i}^{\lambda})$ , as suggested by hydrogen substitution mechanisms in rare earth perovskites (Kreuer, 2003; Navrotsky, 1999). The influence of such substitution on water concentration in Bgm is debated, primarily because synthesized Al-bearing Bgm crystals often contain hydrous inclusions like superhydrous phase B, brucite, and hydrous melt (Bolfan-Casanova et al., 2003; Litasov et al., 2003; Liu et al., 2021; Murakami et al., 2002). Recently, inclusion-free and chemically homogeneous Fe,Al-bearing Bgm crystals were synthesized, revealing two distinct O-H bands at 3,460 and 3,230 cm<sup>-1</sup>, with the former attributed to coupled  $Al^{3+} + H^{+}$  substitution at the B site and the latter to hydrogen trapped in Mg vacancies, However, such assignment was mainly speculated from O-H band results for olivine's hydrogen substitution mechanisms where site occupancies and bonding strengths can be quite different from that in Bgm (Fu, Yang, Karato, et al., 2019). Further polarized FTIR measurements identified four distinct O-H bands at wavenumbers of 3,480(40), 3,160(20), 2,880(20), and 2,680 (50) cm<sup>-1</sup> (Purevjav et al., 2024), where the peak deconvolutions were not conducted. Time-of-flight neutron diffraction measurements on Bgm crystals with  $(Mg_{0.88}Fe^{2+}_{0.05}Fe^{3+}_{0.05}Al_{0.03})(Si_{0.88}Al_{0.11}H_{0.01})O_3$  suggested coupled  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup> is dominant, corresponding to the peak at 3,160 cm<sup>-1</sup> with O-H dipoles vibrating approximately along the crystallographic b axis (Purevjav et al., 2024).

Besides experiments, ab initio calculations have provided new insights in certain hydrogen dissolution mechanisms and their associated vibrational properties and geometries in mantle minerals (Table S2 in Supporting Information S1) (e.g., Tsuchiya et al., 2008; Tsuchiya and Tsuchiya, 2009). Ouantum molecular dynamics simulations on rare earth perovskite, such as BaCeO<sub>3</sub>, indicate that the dominant mechanism involves coupled trivalent cations + H substitution at the B site, with the proton typically residing outside the  $BO_6$  octahedron, forming a strongly bent hydrogen bond (Münch et al., 2000). Previous ab initio calculations utilizing density functional theory (DFT) focused on the coupled  $Al^{3+} + H^+$  substitution for  $Si^{4+}$  in Bgm (Panero et al., 2015). These calculations have revealed that the lowest energy configuration features hydrogen atoms bonded along the octahedral edge at 0 GPa, with an O-H bond distance of 1.02 Å, an O…H distance of 1.725 Å, and an O-H-O bond angle of 137° (Panero et al., 2015). Recently, a molecular dynamics calculations of hydrogen diffusion in Bgm using machine-learning potentials have been reported, which shows that hydrogen is trapped in Mg defects for the longest time compared to other types of defects (Peng and Deng, 2024). However, these theoretical works did not provide predictions for O-H vibrational frequencies associated with the hydrogen dissolution mechanism, making it challenging to interpret observed O-H bands from FTIR spectra. Instead, density functional perturbation theory (DFPT) can accurately calculate the second-order derivative of the total energy associated with the displacement of atoms, or phonon, by linear response theory (Baroni et al., 2001). It provides a robust method for calculating the vibrational properties of O-H dipoles, including O-H frequencies, polarization, and directions of stretching and bending directions. These calculated properties can then be compared with peak positions and polarizations of O-H bands observed in polarized and unpolarized FTIR spectra, aiding in the better understanding and constraining of hydrogen substitution mechanisms in materials. This approach has been effectively utilized in investigating the hydrogen dissolution mechanism in common silicate minerals, such as olivine, wadsleyite, and stishovite,



Figure 1. Calculated polarized IR spectra and OH stretching vibration directions of Bgm with the  $Mg^{2+} = V_{Mg} + 2H^+$  substitution (Mg vacancy model). (a) Polarized IR spectra calculated along the a, b, and c principal crystallographic axis (//a in black, //b in red, and //c in blue, respectively) show two distinct bands at 3,475.10 and 3,495.29 cm<sup>-1</sup>, whose intensities vary significantly along different axial directions. Optimized crystal structures with OH vibrational directions for 3,475.10 and 3,495.29 cm<sup>-1</sup> bands are shown in (b) and (c), respectively. Orange, blue, black, and red spheres represent Mg, Si, O, and H atoms, respectively. Only O atoms bonded to H atoms are shown for figure clarity. Gray solid and dashed lines represent strong (short) and weak (long) O-H bonds, respectively. Shaded blue areas represent SiO<sub>6</sub> octahedra. Vibrational directions of the O and H atoms are indicated by black and red arrows, respectively. arb. unit, arbitrary unit.

particularly in cases where experimental results are controversial (Palfey et al., 2023; Tsuchiya and Tsuchiya, 2009; Umemoto et al., 2011).

Here we have conducted ab initio calculations and FTIR measurements to explore hydrogen substitution in lowermantle Bgm. Using DFT, we modeled hydrous Bgm at 0 GPa and 0 K, considering dissolution mechanisms including Mg and Si vacancies, coupled  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup>, and combined Al substitution with Mg vacancies. Polarized IR spectra and vibrational directions of O-H dipoles were calculated using DFPT, revealing distinct O-H bands for each substitution model. Polarized FTIR spectra on pre-oriented (Fe,Al)-bearing Bgm single crystals were measured, and the peak deconvolution allowed us to obtain absorption intensities of O-H bands along specific crystallographic axes. Comparison between our experimental and theoretical results shows that Mg and Si vacancies are the most abundant mechanisms to the water content in our (Fe,Al)-bearing Bgm crystals. These results are compared with other major mantle minerals to address O-H bond strength evolution and to discuss the effects of hydration on rheological properties and electrical conductivity of the lower mantle.

#### 2. Computational and Experimental Methods

#### 2.1. Ab Initio Calculations

The structures of H-bearing Bgm are calculated using ab initio calculations based on DFT. The generalized gradient approximation in the Perdew-Burke-Ernzerhof form (GGA-PBE) (Perdew et al., 1996) is used for the exchange-correlation functionals. Norm-conserving pseudopotentials are used for Si, Al, O, and H atoms (Troullier and Martins, 1991). The pseudopotential for Mg is generated by von Barth-Car's method (Karki et al., 2000). These pseudopotentials have been extensively tested in the calculations of hydrous minerals and NAMs (Tsuchiya and Tsuchiya, 2009). The electronic wave function is expanded in plane waves using a kinetic energy cutoff of 80 Ry. The structures used in the calculations are supercells with  $2 \times 2 \times 1$  of the unit cell of MgSiO<sub>3</sub> Bgm, with Mg atoms replaced with two hydrogen atoms (Mg vacancy model; Mg<sub>15</sub>Si<sub>16</sub>O<sub>48</sub>H<sub>2</sub>; Figure 1), Si atoms replaced with four hydrogen atoms (Si vacancy model; Mg<sub>16</sub>Si<sub>15</sub>O<sub>48</sub>H<sub>4</sub>; Figure 2), Si replaced with Al and H (coupled  $Al^{3+} + H^+$  substitution with  $Si^{4+}$ ;  $Mg_{16}Si_{15}AlO_{48}H$ ; Figure 3), as well as Mg and Si replaced with Al and two hydrogen atoms in the Mg vacancy (combined Al substitution and Mg vacancy; Mg<sub>14</sub>AlSi<sub>15</sub>AlO<sub>48</sub>H<sub>2</sub>; Figure 4). Brillouin zone sampling is carried out on  $2 \times 2 \times 4$  Monkhorst-Pack mesh for the supercells (Monkhorst and Pack, 1976). All structural parameters are fully relaxed at static 0 K conditions using damped variable cell shape molecular dynamics (Wentzcovitch, 1991) implemented in the Quantum-espresso code (Giannozzi et al., 2009) until residual forces became less than  $1.0 \times 10^{-5}$  Ry/au. Following relaxation of the structure, the positioning of hydrogen within the structure is obtained. The harmonic vibrational properties such as

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displacements and frequencies of the normal modes at the Brillouin zone center ( $\Gamma$  point) and dielectric properties (Born effective charge tensor and electronic dielectric tensor) are calculated from second-order derivatives of the total energy with respect to atomic displacements and external electric field using linear response theory (Baroni et al., 2001). We computed the vibrational characteristics of the O-H dipoles and polarized IR spectra of hydrous Bgm using this method. Drawings of optimized crystal structures with vibrational directions of O and H atoms are made using the VESTA software (Figures 1–4) (Momma and Izumi, 2011).

#### 2.2. FTIR Measurements

Two batches of Bgm single crystals were synthesized using the 5000-ton Kawai multi-anvil apparatus at the Institute for Planetary Materials, Okayama University (run# 5K2667 and run# 5K2417). These Bgm crystals had



**Figure 3.** Calculated polarized IR spectra and O-H stretching vibration directions of Bgm with the  $Si^{4+} = Al^{3+} + H^+$  substitution (coupled  $Al^{3+} + H^+$  substitution for  $Si^{4+}$  model). (a) Polarized IR spectra *//a*, *//b*, and *//c* are shown in black, red, and blue, respectively. One peak at 2,413.34 cm<sup>-1</sup> can be identified. The optimized structure with OH vibrational direction of this peak is shown in (b). The green spheres represent Al atoms, while other atomic symbols and vibrational arrows are shown the same as Figure 1.



Figure 4. Calculated polarized IR spectra and O-H stretching vibration directions of Al-bearing Bgm with the  $Mg^{2+} + Si^{4+} = 2Al^{3+}$  and  $Mg^{2+} = 2H^+$  substitution (combined Al substitution and Mg vacancies model). (a) Polarized IR spectra *l/a*, *l/b*, and *l/c* are shown in black, red, and blue, respectively. Optimized crystal structures with OH vibrational directions of identified two peaks at 3,495.70 and 3,518.80 cm<sup>-1</sup> are shown in (b) and (c), respectively. Atomic and vibrational symbols are the same as Figure 3.

been used in previous studies where details of the sample synthesis and characterizations can be found (Fu, Yang, Karato, et al., 2019; Okuchi et al., 2015). Briefly, run# 5K2667 and run# 5K2417 used a starting mixture of Mg (OH)<sub>2</sub>, MgSiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and <sup>57</sup>FeO with proportions of 21.6, 58.8, 11.8, 7.8 wt% and 15.7, 74.0, 0.0, 10.3 wt%, respectively. Run# 5K2667 was conducted at 24 GPa and 1800°C for ~20 hr, while run# 5K2417 was conducted at 24 GPa and 1700°C for  $\sim$ 12 hr. The extended heating facilitated the slow growth of large Bgm single crystals with chemical homogeneity and minimized the formation of inclusions, such as super hydrous phase B (Fu, Yang, Karato, et al., 2019; Okuchi et al., 2015). The maximum crystal sizes are approximately 400 and 600 µm in length in run# 5K2667 and run# 5K2417, respectively. Chemical analysis using an electron microprobe (EPMA) and valence state analysis on Fe using a Mössbauer spectroscopy show chemical formula of Mg<sub>0.88</sub>Fe<sup>2+</sup><sub>0.035</sub>Fe<sup>3+</sup><sub>0.065</sub>Al<sub>0.14</sub>Si<sub>0.90</sub>O<sub>3</sub> (denoted as Fe10Al14-Bgm) for run# 5K2667 (Fu, Yang, Karato, et al., 2019) and of  $Mg_{0.95}Fe^{2+}_{0.033}Fe^{3+}_{0.027}Al_{0.04}Si_{0.96}O_3$  (denoted as Fe6Al4-Bgm) for run# 5K2417 (Fu, Yang, Karato, et al., 2019), respectively. X-ray diffraction analysis confirmed the Bgm's single crystal structure and quality, and the density of Fe10Al14-Bgm and Fe6Al4-Bgm are calculated to be 4.221 and 4.195 g/cm<sup>3</sup>, respectively. We should note that the crystals analyzed in this study were synthesized independently from those used in the previous neutron study (Purevjav et al., 2024), particularly with regard to crystal growth conditions which may have led to different H incorporation into bridgmanite reported by Purevjav et al. (2024) than observed in our samples (Table S3 in Supporting Information S1).

Bgm crystals of approximately  $100 \times 200 \ \mu\text{m}^2$  in size from each run were selected under a stereo microscope using their subhedral crystal forms as an initial guide for their crystal orientations. The selected crystals were then mounted on glass fibers to determine their crystallographic orientations using a Bruker D8 venture single crystal X-ray diffractometer at the Core Facility Center, National Cheng Kung University. An indexing process was performed based on the X-ray diffraction data to obtain three principal crystallographic orientations of the crystals. The desired (100), (010), and (001) orientations of the crystals were aligned facing the incident X-ray beam direction by rotating the goniometer with crystals mounted on glass fibers. The pre-oriented crystals were then mounted onto glass sides and double-sided polished with flat surfaces. The principal crystallographic directions of the polished crystals were further confirmed using the diffraction technique. The thickness of polished Bgm platelets was measured using a microscopic imaging system to be 78(1) and 110(1)  $\mu$ m for preoriented (100) and (001) platelets for Fe10A114-Bgm and 102(1), 75(1), and 89(1)  $\mu$ m for pre-oriented (100), (010), and (001) platelets for Fe6Al4-Bgm, respectively.

Polarized and unpolarized FTIR spectra of the pre-oriented Bgm crystals were collected using a Bruker Invernio spectrometer coupled with a Hyperion 1000 microscope with a X15 objective, a condenser, and a mid-infrared beam at the Department of Earth Sciences, National Cheng Kung University.  $N_2$  gas was flushed into the





**Figure 5.** Representative peak deconvolution and substitution mechanisms in Fe6Al4-Bgm and Fe10Al14-Bgm pre-oriented crystal platelets at ambient conditions. The derived peak positions and intensities are plotted as pole figures in Figures 6 and 7. (a) A representative polarized FTIR spectrum along  $60^{\circ}$  away from the *a* axis (*//a* +  $60^{\circ}$ ) and (b) a representative unpolarized FTIR spectrum on the (001) platelet of Fe6Al4-Bgm. (c) A representative polarized FTIR spectrum along the *b* axis direction and (b) a representative unpolarized FTIR spectrum on the (001) platelet of Fe6Al4-Bgm. (c) A representative polarized FTIR spectrum along the *b* axis direction and (b) a representative unpolarized FTIR spectrum on the (001) platelet of Fe10Al14-Bgm. In (a) and (c), raw data, fitted peaks using the Gaussian function, and sum of fitted peaks are shown in black, blue, and red lines, respectively. The peak positions are labeled above each peak. In (b) and (d), five fitted peaks are showed in different colors to highlight their hydrogen substitution mechanisms. I, Mg vacancies; II, Si vacancies and Al<sup>3+</sup> substitution (Purevjav et al., 2024); III, Si vacancies; IV, Fe<sup>3+</sup> substitution; V, coupled Al<sup>3+</sup> + H<sup>+</sup> for Si<sup>4+</sup>. The relative contributions of each substitution can be indicated by the percentages (%) of the total water content shown below each peak.

chamber of the FTIR system to minimize the interference of  $CO_2$  and  $H_2O$  absorption with the sample absorption spectra. Aperture size of  $30 \times 30$  to  $40 \times 40$  µm in length was used to cut down the size of the incident IR beam on the Bgm platelets that were placed on a  $CaF_2$  plate. FTIR spectra were acquired in the range of 2,100–4,000 cm<sup>-1</sup> with a total of 1,000 scans and a spectral resolution of 4 cm<sup>-1</sup>. The polarized spectra were acquired by rotating the polarizer from 0 to 180° with a step size of 10 or 12.8°. FTIR spectra were analyzed using the Origin software (Origin, Version 2022. OriginLab Corporation, Northampton, MA, USA.). The spectral intensity was corrected to 1 cm based on the thickness of each Bgm platelet. The Gaussian function was used to fit the spectra to obtain peak position (in cm<sup>-1</sup>), absorbance (in cm<sup>-1</sup>), and peak area (in cm<sup>-2</sup>) for each O-H band (Figure 5).

### 3. Results

#### 3.1. Mg Vacancies

In this first computation model, we remove one Mg atom from the A site and add two H atoms to its coordinated O atoms in a 2 × 2 × 1 supercell of MgSiO<sub>3</sub> Bgm (Mg<sup>2+</sup> =  $V_{Mg}$  + 2H<sup>+</sup>) (Figure 1; Table 1). The optimized structure has lattice parameters of a = 9.6386 Å, b = 9.9298 Å, c = 6.9390 Å,  $\alpha = 90.000^\circ$ ,  $\beta = 90.003^\circ$ , and  $\gamma = 90.648^\circ$ , with a unit-cell volume of 664.087 Å<sup>3</sup>. The unit-cell volume is approximately 2.3% larger than the experimental value of 649.38 Å<sup>3</sup> (Horiuchi et al., 1987), which is due to the tendency of the GGA method to overestimate volumes (Wentzcovitch et al., 2010). Hydrogen atoms are positioned at H1 (0.52432, 0.53220,



#### Table 1

Calculated and Experimental Peak Positions and Relative Peak Intensities on (100), (010), and (001) Planes

	Relative peak intensity			
Peak position (cm <sup>-1</sup> )	(100) Plane	(010) Plane	(001) Plane	
$Mg_{15}Si_{16}O_{48}H_2$ for Mg vacancies model (Calculation; this study; Figure 1)				
3,475.08	$I_{\prime\prime b} > I_{\prime\prime c}$	$I_{//a} > I_{//c}$	$I_{//a}\approx I_{//b}$	
3,495.29	$I_{\prime\prime b} > I_{\prime\prime c}$	$I_{//a} > I_{//c}$	$I_{\prime\prime a}>I_{\prime\prime b}$	
$Mg_{16}Si_{15}O_{48}H_4$ for Si vacancies model (Calculation; this study; Figure 2)				
2,995.27	$I_{//b} \approx I_{//c}$	$I_{//a} < I_{//c}$	$I_{//a} < I_{//b}$	
3,000.64	$I_{//b} \approx I_{//c}$	$I_{//a} < I_{//c}$	$I_{//a} < I_{//b}$	
3,283.67	$I_{//b} < I_{//c}$	$I_{//a} < I_{//c}$	$I_{\prime\prime a}>I_{\prime\prime b}$	
3,294.79	$I_{//b} < I_{//c}$	$I_{//a} < I_{//c}$	$I_{\prime\prime a}>I_{\prime\prime b}$	
$Mg_{16}Si_{15}AlO_{48}H$ for coupled $Al^{3+} + H^+$ substitution for $Si^{4+}$ (Calculation; this study; Figure 3)				
2,413.34	$I_{//b} > I_{//c}$	$I_{//a} > I_{//c}$	$I_{//a} \approx I_{//b}$	
$(Mg_{14}Al)(Si_{15}Al)O_{48}H_2$ for Al substitution and Mg vacancies (Calculation; this study; Figure 4)				
3,495.70	$I_{//b} > I_{//c}$	$I_{//a} > I_{//c}$	$I_{//a} > I_{//b}$	
3,518.80	$I_{//b} > I_{//c}$	$I_{//a} > I_{//c}$	$I_{//a} > I_{//b}$	
Fe6Al4-Bgm (Experiment; this study; Figure 6)				
3,463	$I_{//b} > I_{//c}$	$I_{//a} > I_{//c}$	$I_{//a} > I_{//b}$	
3,189	$I_{\prime\prime b} > I_{\prime\prime c}$	$I_{//a}\approx I_{//c}$	$I_{//a} < I_{//b}$	
2,924	$I_{//b} \approx I_{//c}$	$I_{//a} < I_{//c}$	$I_{//a} < I_{//b}$	
2,710	$I_{\prime\prime b} > I_{\prime\prime c}$	$I_{//a} > I_{//c}$	$I_{//a} < I_{//b}$	
2,452	$I_{\prime\prime b} > I_{\prime\prime c}$	$I_{//a} > I_{//c}$	$I_{/\!/a}\approx I_{/\!/b}$	
Fe10A114-Bgm (Experiment; this study; Figure 7)				
3,480	$I_{\prime\prime b} > I_{\prime\prime c}$	-	$I_{\prime\prime a}>I_{\prime\prime b}$	
3,156	$I_{\prime\prime b} > I_{\prime\prime c}$	-	$I_{//a} < I_{//b}$	
2,913	$I_{//b} \approx I_{//c}$	-	$I_{//a} < I_{//b}$	
2,690	$I_{\prime\prime b} > I_{\prime\prime c}$	-	$I_{//a} < I_{//b}$	
2,470	$I_{//b} > I_{//c}$	-	$I_{/\!/a}\approx I_{/\!/b}$	
Fe10A111-Bgm (Experiment; Purevjav et al., 2024)				
3,480(40)	$I_{\prime\prime b} > I_{\prime\prime c}$	-	$I_{\prime\prime a}>I_{\prime\prime b}$	
3,160(20)	$I_{\prime\prime b} > I_{\prime\prime c}$	-	$I_{//a} < I_{//b}$	

*Note.* Symbols of  $I_{//a}$ ,  $I_{//b}$ , and  $I_{//c}$  mean the peak intensities (absorbances) along principal crystallographic directions of *a*, *b*, and *c* axes, respectively.  $I_{//a} > I_{//b}$ , for example, means the absorption in the *a* direction is larger than in the *b* direction. The IR beam direction relative to the principal crystallographic axis directions can be referred to Figure 6a.

-0.10931) and H2 (0.52430, 0.53203, 0.60859), with interatomic distances of d(O2-H1...O1) = 0.98273 Å and d(O2-H2...O1) = 0.98280 Å, where O2 is an equatorial oxygen atom shared by two distorted SiO<sub>6</sub> octahedra and O1 is an apical oxygen atom shared by two distorted SiO<sub>6</sub> octahedra (Figure 1). Calculated polarized IR spectra exhibit two bands: one at 3,475 cm<sup>-1</sup> with  $I_{//}$  $_{a} \approx I_{//b} > I_{//c}$ , and the other at 3,495 cm<sup>-1</sup> with  $I_{//a} > I_{//b} > I_{//c}$ , where  $I_{//a}$ ,  $I_{//b}$ , and  $I_{llc}$  represent peak intensities (absorbances) along principal crystallographic directions of a, b, and c, and  $I_{//a} > I_{//b}$ , for example, means the absorption in the a direction is larger than in the b direction (Figure 1a). The former band features an O2-H1 stretching vibration along the [-0.45993, -0.43523, -0.40358] or [0.02903, 0.02723, 0.02477] direction and an O2-H2 vibration along the [0.49452, 0.46900, -0.43303] or [-0.03120, -0.02933, 0.02657] direction (Figure 1b), while the latter band includes an O2-H1 stretching vibration along [-0.49524, -0.46756, -0.43468] or [0.03109, 0.02912, 0.02555] direction and an O2-H2 vibration along [-0.46010, -0.43530, 0.40317] or [0.02887, 0.02711, -0.02366] direction (Figure 1c). These calculations indicate that the O-H dipole in the Mg vacancy model primarily vibrates in the *a-b* plane of Bgm.

#### 3.2. Si Vacancies

In the Si vacancy model, we replace one Si atom with four H atoms in a  $2 \times 2 \times 1$  MgSiO<sub>3</sub> Bgm supercell (Si<sup>4+</sup> = V<sub>Si</sub> + 4H<sup>+</sup>) (Figure 2; Table 1). After optimizing the lattice parameters, we obtain a = 9.6614 Å, b = 10.0008 Å, c = 6.9663 Å,  $\alpha = 90.286^{\circ}$ ,  $\beta = 90.710^{\circ}$ , and  $\gamma = 89.981^{\circ}$ . Hydrogen atoms are positioned at H1 (0.65174, 0.58315, 0.05198), H2 (0.83913, 0.59246, 0.93890), H3 (0.84882, 0.41655, 0.94982), and H4 (0.66139, 0.40717, 1.06261) (Figure 2). These H atoms are bonded to four equatorial O2 atoms with atomic distances of d(O2-H1...O1) = 0.98916 Å, d (O2-H2...O1) = 1.00292 Å, d(O2-H3...O1) = 0.98913 Å, and d(O3-H3...O1) = 0.98913 Å, and d(OH4...O1 = 1.00277 Å. The calculated polarized IR spectra show two pairs of bands. One pair appears at wavenumbers of 2,995 and 3,001 cm<sup>-1</sup> with relative intensities of  $I_{//a} < I_{//b} \approx I_{//c}$ , while the other pair appears at wavenumbers of 3,284 and 3,295 cm<sup>-1</sup> with a relative intensity of  $I_{//b} < I_{//a} < I_{//c}$ (Figure 2a). This indicates that the vibration of the O-H dipole for the first and second pairs of bands is dominant on the *b*-*c* and *a*-*c* plane, respectively. A detailed analysis of the vibration mode of each dipole shows that the diagonally aligned O-H dipoles (i.e., O2-H1 and O2-H3 or O2-H2 and O2-H4) vibrate symmetrically about the center of the equatorial plane of the  $SiO_6$ octahedron for the bands at 2,995 and 3,284 cm<sup>-1</sup>, while they vibrate asymmetrically for the bands at 3,001 and 3,295 cm<sup>-1</sup> (Figures 2b-2e).

#### 3.3. Coupled $Al^{3+} + H^+$ Substitution With $Si^{4+}$

In this model, we consider that an Al atom substitutes a Si atom at the B site. The resulting oxygen vacancy, due to charge balance, is filled by an O-H in a  $2 \times 2 \times 1$  supercell of MgSiO<sub>3</sub> Bgm (Si<sup>4+</sup> = Al<sup>3+</sup> + H<sup>+</sup>) (Figure 3; Table 1). After structure optimization, the lattice parameters are a = 9.6536 Å, b = 9.9536 Å, c = 6.9887 Å,  $a = 90.193^\circ$ ,  $\beta = 90.190^\circ$ , and  $\gamma = 90.350^\circ$ . The H atom is positioned at coordinates

(0.50885, 0.51993, -0.00539) and is bonded to O1 with a distance of d(O1-H···O1) = 1.03833 Å, consistent with previous ab initio calculations on the similar substitution mechanism (Panero et al., 2015). The calculated polarized IR spectra reveal a single band at a wavenumber of 2,413 cm<sup>-1</sup>, with a relative intensity order of  $I_{//a} \approx I_{//}$  $_b > I_{//c}$ . The stretching direction of the O1-H bond is [0.68433, 0.63098, -0.57872], indicating predominant vibration in the *a-b* plane.

#### **3.4.** Combined Al Substitution and Mg Vacancies

In this model, we replace one Mg and one Si atom with two Al atoms based on our initial Mg vacancy model for MgSiO<sub>3</sub> Bgm (i.e., Mg<sup>2+</sup> + Si<sup>4+</sup> = 2Al<sup>3+</sup> and Mg<sup>2+</sup> =  $V_{Mg}$  + 2H<sup>+</sup>). We explore four configurations of Al substitutional positions relative to  $V_{Mg}$ : the first two configurations involve Al atoms positions on both sides of  $V_{Mg}$ , while the remaining two configurations feature Al atoms situated on a single side of  $V_{Mg}$  with respect to the *b*-axis within the *a-b* plane (Figure 4 and Figure S2 in Supporting Information S1; Table 1). Optimization of these four crystal structures yields different enthalpies. Comparing the enthalpies of different structures reveals that the crystal structure with Al on both sides, with coordinates of (0.24706, 0.21983, 0.73013) and (0.75444, 0.49053, -0.00367), exhibits the lowest enthalpy, while the enthalpies of the other three structures are 0.06–0.28 eV higher (Figure S2 in Supporting Information S1). The structure with the lowest enthalpy is the most stable configuration, where two H atoms are situated at H1 (0.51944, 0.53871, -0.11384) and H2 (0.52324, 0.53752, 0.61248), bonded to two O2 atoms with d(O2-H1...O1) = 0.98116 Å and d(O2-H2...O1) = 0.98135 Å (Figure 4). Calculated polarized IR spectra show two bands at wavenumbers of 3,496 and 3,519 cm<sup>-1</sup>, both with relative intensities of  $I_{//a} > I_{//b} > I_{//c}$ , suggesting predominant O-H dipole vibrations in the *a-b* plane. Specifically, for the band at  $3,496 \text{ cm}^{-1}$ , the O2-H1 dipole vibrates along the [-0.44157, -0.41668, -0.40679] or [0.02785, 0.02589, 0.02530] direction, while the O2-H2 dipole vibrates along the [0.49558, 0.48648, -0.45630] or [-0.03125, -0.03040, 0.02809] direction. For the band at 3,519 cm<sup>-1</sup>, the O2-H1 dipole vibrates along the [-0.50370, -0.47441, -0.46539] or [0.03157, 0.02927, 0.02758] direction, while the O2-H2 dipole vibrates along the [-0.43528, -0.42558, 0.40084] or [0.02725, 0.02644, -0.02357] direction. Compared to the Mg vacancy model for pure-endmember MgSiO3 Bgm, the two O-H bands exhibit the same trend of relative intensities, but their wavenumbers are  $\sim 20 \text{ cm}^{-1}$  higher, indicating a slightly stronger O-H bond in the *a-b* plane. This stronger bond results from a ~0.16% reduction in d(O2-H1...O1) and a ~0.15% reduction in d(O2-H2...O1) due to the Al substitution.

#### 3.5. FTIR Results

The deconvolution of the measured polarized and unpolarized FTIR spectra for Fe6Al4-Bgm reveals five distinct O-H bands (Figures 5 and 6; Table 1). Analyses of polarized spectra on the (100), (010), and (001) platelets indicate strong variations of absorbances of these peaks with azimuthal angles. Specifically, the relative intensities of peaks at wavenumbers of 3,463, 3,189, 2,924, 2,710, and 2,452 cm<sup>-1</sup> are  $I_{//b} > I_{//c}$ ,  $I_{//b} > I_{$ 

Positions and polarizations of the identified IR bands, except for the band at 2,470 cm<sup>-1</sup>, are consistent with the previous polarized FTIR study for helping assignment of the primary hydrogen site in the neutron structure analysis conducted by Purevjav et al. (2024). Fu, Yang, Karato, et al. (2019) and Fu, Yang, Tsujino, et al. (2019) utilized Fe10Al14-Bgm crystals with random orientation from the same batch as ours, but they only documented two peaks at ~3,210 and 3,475 cm<sup>-1</sup> (Fu, Yang, Karato, et al., 2019). The use of random orientations prevents the detection of three peaks with wavenumbers below ~3,150 cm<sup>-1</sup>. Furthermore, our FTIR findings differ from earlier studies on Fe,Al-bearing Bgm, which observed a single sharp band at 3,690 cm<sup>-1</sup> and four minor bands at 3,215, 3,448, 3,482, and 3,565 cm<sup>-1</sup> overlaying on the broad band at ~3,400 cm<sup>-1</sup> (Litasov et al., 2003; Murakami et al., 2002). The FTIR data of these studies might have been influenced by hydrous inclusions, such as brucite, and/or coexisting phases, such as magnesiowüstite (Keppler and Bolfan-Casanova, 2006). Our experimental results highlight the significance of employing high-quality crystals with principal orientations and the use of an appropriate background subtraction in FTIR studies.



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**Figure 6.** Representative polarized FTIR spectra and pole figures of Fe6Al4-Bgm pre-oriented crystal platelets at ambient conditions. The spectra were collected from pre-oriented Fe6Al4-Bgm platelets with (a) (100), (b) (010), and (c) (001) orientations. The spectra are off set for clarity. The angle between the polarization of the IR beam and the principal crystallographic axis of the crystal within the platelet is labeled next to each spectrum, where // means parallel to the principal axis labeled. The insert in (a) is an optical image showing a Fe6Al4-Bgm platelet with (100) orientation. The red asterisk shows the IR beam direction perpendicular to the *bc* plane. Five absorption peaks can be identified and used for the FTIR spectral analyses and pole figures (see Figure 7 for details of peak assignments and analysis). Their intensities as a function of azimuthal angles to the principal crystallographic axes in (a), (b), and (c) are shown in pole figures (d), (e), and (f), respectively. Intensities of these five peaks are shown as open circles with different colors for peak positions (in cm<sup>-1</sup>) listed in the figure legend.

#### 4. Discussion

#### 4.1. Hydrogen Dissolution Mechanisms in Bridgmanite

Combined calculated and experimental results of O-H band positions and polarizations can help elucidate the hydrogen substitution mechanisms in Bgm. Our ab initio calculations on the Mg vacancy model reveal O-H bands at approximately 3,475–3,519 cm<sup>-1</sup> with  $I_{//a} > I_{//b} > I_{//c}$  for Al-free and Al-bearing Bgm, consistent with observed FTIR peaks at wavenumbers around 3,463–3,480 cm<sup>-1</sup> with similar polarizations. This band is thus attributed to the Mg vacancies in Bgm. Similarly, the observed O-H band at 2,913–2,924 cm<sup>-1</sup> with  $I_{//a} < I_{//b} \approx I_{//c}$  is linked to





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**Figure 7.** Representative polarized FTIR spectra and pole figures of Fe10Al14-Bgm pre-oriented crystal platelets at ambient conditions. The spectra were collected from pre-oriented Fe10Al14-Bgm platelets with (a) (100) and (b) (001) orientations. The spectra are off set for clarity. Pole figures in (c) and (d) show intensity variations of the five identified peaks with respect to azimuthal angles shown in (a) and (b), respectively (open circles). Peak positions of all the identified peaks (in cm<sup>-1</sup>) are shown in the figure legend. Note that the peak intensities from Purevjav et al. (2024) were not included for comparison due to the use of different background subtraction methods and the absence of peak deconvolution in their spectral analysis.

the Si vacancies. These results show that the peak frequency of absorption is higher for hydrogen at the A site compared to the B site in Bgm, which is the opposite of what is generally believed in olivine and other uppermantle minerals (Kovács et al., 2010). This difference suggests variations in the O-H bond length and strength within the distinct coordination environments of Mg and Si in the upper-mantle and lower-mantle minerals. The higher peak frequencies at the A site in Bgm indicates that the O-H bonds associated with the Mg dodecahedral site are stronger and shorter than those associated with Si octahedral site. This is reflected in our calculations that the average bond length of O-H bonds at the A site is approximately 1.35% shorter than that at the B site (Figures 1

#### Table 2

Substitution Mechanisms, O-H Band Positions, and Polarization of O-H Band Absorbance, and Primary Vibrational Direction of O-H Dipoles for the Lower-Mantle Al, Fe-Bearing Bgm

Substitution mechanisms	O-H band positions (cm <sup>-1</sup> )	Polarization of O-H band absorbance	Primary vibrational plane of O-H dipoles
Mg vacancies	3,463–3,480	$I_{//a} > I_{//b} > I_{//c}$	<i>a-b</i> plane
Si vacancies and Al <sup>3+</sup> substitution <sup>a</sup>	3,156–3,189	$I_{//a} \approx I_{//c} < I_{//b}$	b- $a$ (or $b$ - $c$ ) plane
Si vacancies	2,913–2,924	$I_{//a} < I_{//b} \approx I_{//c}$	<i>b</i> - <i>c</i> plane
Fe <sup>3+</sup> substitution <sup>b</sup>	2,690–2,710	$I_{//b} > I_{//a} > I_{//c}$	<i>a-b</i> plane
Coupled $Al^{3+} + H^+$ for $Si^{4+}$	2,452–2,470	$I_{//a} \approx I_{//b} > I_{//c}$	<i>a-b</i> plane

<sup>a</sup>Suggested by previous neutron experiments (Purevjav et al., 2024). <sup>b</sup>Speculated substitution mechanism. Not predicted in our calculations which do not consider Fe substitutions (please refer to the discussion section (Section 4) for details).

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and 2). Conversely, in olivine, where Si site usually resides in a tetrahedral site, the O-H bonds are stronger at the Si site compared to the Mg site (e.g., O-H bond lengths are 0.98–0.99 Å at the Si site vs. 1.01 Å at the Mg1 site) (Umemoto et al., 2011). These observations highlight how the specific coordination environments of Mg and Si influence the FTIR peak frequencies by affecting the O-H bond characteristics.

The calculated O-H band at 2,413 cm<sup>-1</sup> with the polarization of  $I_{//b} > I_{//a} > I_{//c}$  for the coupled Al<sup>3+</sup> + H<sup>+</sup> substitution model aligns with our observed IR peak at 2,452–2,470 cm<sup>-1</sup> with the same polarization. Therefore, this band, with O-H dipole stretching mainly in the *a-b* plane, is associated with coupled Al<sup>3+</sup> + H<sup>+</sup> substitution in Bgm.

The broad band at 3,156–3,189 cm<sup>-1</sup>, with a full width at half maximum (FWHM) of approximately 300 cm<sup>-1</sup>, likely include the contribution from both Si vacancies and Al<sup>3+</sup> substitution, based on our calculation and the previous neutron study (Purevjav et al., 2024). We should note that our calculations of the Al substitution models do not show a band in this frequency range. There could be two possible explanations on this discrepancy: (a) The structural model is determined at 0 K and does not account for anharmonic effects, while van der Waals forces are essentially unquantifiable; (b) Variables such as iron, vacancies, and defects can also influence the calculations. For example, trace amounts of Fe<sup>3+</sup> substitution at the Si site in stishovite can enhance the peak at 3,112 cm<sup>-1</sup> (sample A-810 in Litasov et al., 2007). Since Bgm has a similar Si coordination environment as stishovite, Fe<sup>3+</sup> substitution may also contribute to absorption in this frequency range. However, our calculations do not consider iron effects.

The O-H band observed at 2,690–2,710 cm<sup>-1</sup> in our FTIR spectra is not predicted by our ab initio calculation. The Fe<sup>3+</sup> substitution can slightly enhance the absorption of the band at ~2,700 cm<sup>-1</sup> in stishovite (sample A-810 in Litasov et al., 2007). The Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio in our Bgm samples increases by approximately 44% from Fe6Al4-Bgm to Fe10Al14-Bgm, which can correlate with an approximately 47% increase in the peak intensities between these two samples (Figures 5b and 5d). Therefore, we speculate this peak to be contributed by the Fe<sup>3+</sup> + H<sup>+</sup> substitution for Si<sup>4+</sup> in Bgm. Future theoretical calculations on the Fe substitution in Bgm are needed.

#### 4.2. Total Absorption Coefficient of Bridgmanite From the FTIR Spectra

Calibrations between absorbance coefficient and wavenumber are essential to determine water contents from FTIR spectra. Paterson calibration (1982) has been frequently used to determine water contents in Bgm and other mantle minerals (Bolfan-Casanova et al., 2000; Fu, Yang, Karato, et al., 2019; Litasov et al., 2003; Liu et al., 2021). However, the suitability to NAMs could be questionable because of the major differences between the calibrants and mantle minerals (Balan et al., 2008; Koch-Müller and Rhede, 2010). Here, we have examined whether Paterson calibration can be applied to Bgm by calculating the total absorbance coefficient of Fe10Al14-Bgm. We have analyzed our polarized FTIR spectra along three principle crystallographic orientations based on its water content obtained by previous Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS) measurements (Fu, Yang, Karato, et al., 2019). According to the Beer-Lambert law (Swinehart, 1962), the absorbance coefficient ( $\epsilon$ , in L/mol/cm<sup>2</sup>) can be calculated using the following equation:

$$r = \frac{A_{total} \times M_{\rm H_2O}}{C_{H_2O} \times \rho_{Bgm}} \times 100$$
(1)

where  $M_{\text{H}_2\text{O}}$  is the molar mass of water (18 g/mol);  $C_{\text{H}_2\text{O}}$  is the water concentration of Fe10Al14-Bgm which is taken from previous NanoSIMS measurements (0.102(7) wt.%);  $\rho_{Bgm}$  is the density of Fe10Al14-Bgm (4,221 g/ L);  $A_{total}$  is the total integrated absorbance of the O-H bands. After the sample thickness correction to 1 cm,  $A_{total}$ can be calculated by summing integrated absorbance along three principle axes from our polarized FTIR data (Figure 7),

$$A_{total} = A_{//a} + A_{//b} + A_{//c}$$
(2)

where  $A_{//a}$ ,  $A_{//b}$ , and  $A_{//c}$  are calculated to be 6,396, 8,816, and 4,569 cm<sup>-2</sup> using the polarized FTIR spectra along *a*, *b*, and *c* axis, respectively. Using Equations 1 and 2, the total absorbance coefficient of Fe10Al14-Bgm is calculated to be 82,702(6,217) L/mol/cm<sup>2</sup>. Furthermore, the mean wavenumber corresponding to the total absorbance coefficient can be calculated using the formula:



$$\overline{\nu} = \frac{\sum_{i=1}^{5} \nu_i A_i}{\sum_{i=1}^{5} A_i} \tag{3}$$

where  $\nu_i$  and  $A_i$  are the peak position and the peak area of the *i*th peak, respectively (Libowitzky and Rossman, 1997). This calculation yields  $\overline{\nu} = 3,033(20) \text{ cm}^{-1}$ .

The total absorption coefficient of Fe10Al14-Bgm is lower than the Paterson calibration line in the absorption coefficient-wavenumber plot (Figure S3 in Supporting Information S1), meaning that the water content would be underestimated if the Paterson calibration was used. Major mantle silicate minerals with the dominant hydrogen substitution of Mg/Si vacancies, such as olivine, ringwoodite, majoritic garnet, and pyroxene, also have lower values than the Paterson calibration line at larger wavenumbers (Bell et al., 1995; Koch-Müller and Rhede, 2010; Koch-Müller et al., 2007; Kovács et al., 2010; Thomas et al., 2009). Other minerals, such as feldspar, quartz, and stishovite, show values in the vicinity of the Paterson calibration line (Johnson and Rossmann, 2003; Mosenfelder et al., 2015; Pawley et al., 1993; Thomas et al., 2009). We should note that the total coefficient reflects an averaged contribution from all peaks, and the linear relationship between the coefficient and mean wavenumber is empirical. To rigorously determine the absorption coefficient as a function of wavenumber, individual site-specific absorption coefficients for each absorption mechanism are necessary (Kovács et al., 2010).

#### 4.3. Water Contents in Bridgmanite

The water concentration of Fe10Al14-Bgm has been previously determined to be 0.102(7) wt.% based on NanoSIMS measurements (Fu, Yang, Karato, et al., 2019). The water content in Fe6Al4-Bgm can be calculated using Equations 1 and 2 with our obtained total absorbance coefficient,  $A_{\text{total}}$  of 6,210.4 cm<sup>-2</sup>, and  $\rho_{Bgm}$  of 4,195 g/L. The calculation yields 0.0322(24) wt.%, where the uncertainty is propagated from that of the total absorbance coefficient.

The water contents in Fe10Al14-Bgm and Fe6Al4-Bgm crystals are significantly lower than 6.7–7 wt.% of the total water content added into the starting mixtures for the sample syntheses. The products from run# 5K2667 showed that Fe10Al14-Bgm crystals are surrounded by the quenched ground matrix, indicating the presence of liquid melt at high-pressure-temperature conditions during the synthesis (Fu, Yang, Karato, et al., 2019). Also, the sample mixtures were likely molten under the synthesis conditions in run# 5K2667 and 5K2417, meaning that Bgm crystals grew from the hydrous water-rich melt (Okuchi et al., 2015; Purevjav et al., 2024). Therefore, the water contents determined here likely present the water content of Bgm in the water-rich regions in the uppermost lower mantle.

#### 4.4. OH Bands Contributions in Bridgmanite

Previous studies on upper-mantle minerals such as olivine showed that hydrogen dissolution mechanism plays a critical role in the rheology of the host mineral (Karato and Jung, 2003; Mei and Kohlstedt, 2000a, 2000b). To correlate the FTIR absorption spectra with the dissolution mechanisms, we have evaluated the percentage of water induced by each IR peak relative to the total water. Based on Equation 1, the water content is proportional to the peak area  $(C_{H,O} \propto A_{total})$ . Here we simply assume  $\varepsilon$  is the same for each peak, and then we can estimate the peak contributions to the total water content based on the individual peak area relative to the total peak area (Figure 5). The analysis shows that the relative contributions for peaks at 3,463, 3,189, 2,924, 2,710, and 2,452 cm<sup>-1</sup> for Fe6Al4-Bgm are approximately 24.7%, 30.0%, 21.6%, 14.2%, and 9.4% while the relative contributions for peaks at 3,480, 3,156, 2,913, 2,690, and 2,470 cm<sup>-1</sup> for Fe10Al14-Bgm are approximately 21.4%, 31.8%, 18.5%, 19.1%, and 9.2%, respectively (Figures 5b and 5d). These analyses indicate that the Mg and Si vacancies, coupled  $Al^{3+} + H^+$  substitution, and Fe<sup>3+</sup> substitution contribute to approximately 43.1%-74.0%, 9.3%-40.2%, and 16.6% of the total water, respectively. The uncertainties in the contribution of Si vacancies and coupled  $Al^{3+} + H^+$ substitutions arise from their uncertain relative contributions for the broad peak at 3,156–3,189 cm<sup>-1</sup>. Therefore, the dominant mechanism for hydrogen substitution in lower-mantle Fe,Al-bearing bridgmanite is the formation of Mg and Si vacancies, followed by the coupling of  $Al^{3+} + H^+$  for Si<sup>4+</sup> and the Fe<sup>3+</sup> substitution. The primary hydrogen substitutions in Bgm are consistent with previous electron density calculations (Ross et al., 2003) and some experimental IR studies (Litasov et al., 2003; Meade et al., 1994). The Al + H substitution mechanism is consistent with previous neutron diffraction measurements (Purevjav et al., 2024).

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**Figure 8.** FTIR peak positions and substitution mechanisms of major mantle silicates and silica minerals. (a) Si vacancies and coupled  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup>; (b) Mg vacancies and Fe<sup>3+</sup> substitution. Minerals include bridgmanite (this study, both calculations and experiments; Purevjav et al., 2024), olivine (Blanchard et al., 2017; Kovács et al., 2010), quartz (Stalder, 2021), orthopyroxene (Rauch and Keppler, 2002), omphacite (Koch-Müller et al., 2004), coesite (Koch-Müller et al., 2003; Yan et al., 2021), garnet (Geiger and Rossman, 2018), wadsleyite (Jacobsen et al., 2005; Smyth et al., 2014), ringwoodite (Mrosko et al., 2013; Thomas, Jacobsen, et al., 2015), majoritic garnet (Thomas et al., 2015b), stishovite (Litasov et al., 2007; Spektor et al., 2011; Zhang et al., 2022), and periclase (Litasov, 2010). Hydrogen dissolution mechanisms and Si and Mg coordination are shown in the figure legend.

## 5. Implications

#### 5.1. O-H Bond Evolution From the Upper-Mantle to Lower-Mantle Minerals

The reversal in OH absorption frequency at the Si and Mg sites between Bgm and olivine highlights a significant shift in O-H bonding strength from upper-mantle to lower-mantle minerals (Figure 8). In the upper mantle and transition zone, silicate minerals like olivine, quartz, orthopyroxene, and others typically have Si in fourfold coordination, where Si vacancies can induce OH absorption at higher frequencies  $(3,459-3,666 \text{ cm}^{-1})$ , indicative of strong O-H bonds (Blanchard et al., 2017; Geiger and Rossman, 2018; Koch-Müller et al., 2003; Kovács et al., 2010; Mrosko et al., 2013; Stalder, 2021; Thomas et al., 2015b; Yan et al., 2021). Conversely, in the lower mantle, minerals like Bgm and stishovite exhibit Si in sixfold coordination, with OH absorption shifting to lower frequencies (2,646–3,383 cm<sup>-1</sup>), reflecting weaker O-H bonds (Litasov et al., 2007; Spektor et al., 2011; Zhang et al., 2022). For Mg, in upper-mantle silicates such as olivine and wadslevite, where Mg is in sixfold coordination, OH absorption bands occur between 3,064 and 3,220 cm<sup>-1</sup> (Blanchard et al., 2017; Jacobsen et al., 2005; Kovács et al., 2010; Mrosko et al., 2013; Rauch and Keppler, 2002; Smyth et al., 2014; Thomas, Jacobsen, et al., 2015). However, in Bgm, with Mg in eightfold/twelvefold coordination, OH absorption frequencies shift higher, around 3,472 cm<sup>-1</sup>. This reversal of OH absorption frequency at Si and Mg sites underscores the evolving O-H bond environment, driven by changes in Si and Mg coordination from fourfold and sixfold to sixfold and eightfold/twelvefold, respectively, and thus revealing the transition in O-H bond strength from upper-mantle to lower-mantle minerals.

The OH absorption frequency associated with coupled  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup> decreases from 3,210 to 3,623 cm<sup>-1</sup> in upper-mantle minerals such as quartz, orthopyroxene, omphacite, and coesite (Koch-Müller et al., 2003; Rauch and Keppler, 2002; Stalder, 2021; Yan et al., 2021), to 2,461–3,130 cm<sup>-1</sup> in lower-mantle minerals like Bgm and stishovite (Litasov et al., 2007; Zhang et al., 2022) (Figure 8). This trend parallels the



decrease in OH frequency due to Si vacancies with increasing depth, likely influenced by changes in site occupancy and coordination environments at the Si site from upper-mantle to lower-mantle minerals.

#### 5.2. Hydrogen Effects on the Lower-Mantle Rheology and Electrical Conductivity

Hydrogen substitution mechanisms in Bgm, particularly through Mg and Si vacancies, have significant implications for the rheological properties and electrical conductivity of the lower mantle. The presence of approximately 100–1,000 ppm of hydrogen in either or both the Mg and Si sites of Bgm would lead to a point defect density of a similar order of magnitude at these sites that is considerably higher than the intrinsic defect density. Plastic deformation in the lower mantle likely occurs via diffusion creep (Karato et al., 1995). Our results suggest that both Mg (Fe) and Si diffusion (by vacancy mechanism) is enhanced by hydrogen dissolution, and therefore hydrogen dissolution will reduce the lower mantle viscosity.

Similarly, hydrogen dissolution will also enhance electrical conductivity because hydrogen dissolved in a mineral such as olivine is known to enhance electrical conductivity (Karato and Wang, 2013). Such enhancement of conductivity by hydrogen dissolution will facilitate the detection of hydrated regions within the mantle through geophysical surveys, providing insights into the water content and distribution deep within the Earth (Karato and Wang, 2013). Future electrical conductivity experiments on dry and wet Bgm at high pressure and high temperature are needed to better understand Earth's deep-water cycle and the global distribution of volatiles.

#### 6. Conclusions

We performed DFT calculations, together with FTIR experiments, to understand hydrogen substitution mechanism in lower-mantle Bgm. The O-H bands centered at 3,463-3,480, 2,913-2,924, and 2,452-2,470 cm<sup>-1</sup> are attributed to Mg vacancies, Si vacancies, and coupled  $Al^{3+} + H^+$  substitution for Si<sup>4+</sup> in the Bgm structure, respectively. The broad band centered at 3,156–3,189 cm<sup>-1</sup> is likely due to a combination of Si vacancies and  $Al^{3+}$  substitution, while the band at 2,690–2,710 cm<sup>-1</sup> is probably due to Fe<sup>3+</sup> substitution. Evaluation of peak contribution shows that the primary hydrogen substitution mechanism is through Mg and Si vacancies, followed by the coupling of  $Al^{3+} + H^+$  for  $Si^{4+}$  and the  $Fe^{3+}$  substitution. The present results have potential implications for how hydrogen might modify physical properties such as electrical conductivity and plastic deformation. The way in which hydrogen affects these properties depends on crystallographic site(s) hydrogen is located. Our study is the first step toward that goal, but we need experimental studies on the role of those properties of Bgm.

#### **Global Research Statement**

Not applicable.

#### **Data Availability Statement**

Data are available at Zhang et al. (2024).

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