



## RESEARCH ARTICLE

10.1029/2019JB018447

# Stability and Solubility of the FeAlO<sub>3</sub> Component in Bridgmanite at Uppermost Lower Mantle Conditions

**Key Points:**

- We studied phase relations in the system MgSiO<sub>3</sub>-FeAlO<sub>3</sub> at 27 GPa and 2000 K
- We determined the stability, solubility, and thermoelastic properties of the FeAlO<sub>3</sub> component in bridgmanite
- We applied this knowledge of the FeAlO<sub>3</sub> component to obtain new insight into the mineralogy of the lower mantle

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**Citation:**

Liu, Z., McCammon, C., Wang, B., Dubrovinsky, L., Ishii, T., Bondar, D., et al. (2020). Stability and solubility of the FeAlO<sub>3</sub> component in bridgmanite at uppermost lower mantle conditions. *Journal of Geophysical Research: Solid Earth*, 125, e2019JB018447. <https://doi.org/10.1029/2019JB018447>

Received 30 JUL 2019

Accepted 5 FEB 2020

Accepted article online 7 FEB 2020

**Abstract** We report the stability and solubility of the FeAlO<sub>3</sub> component in bridgmanite based on phase relations in the system MgSiO<sub>3</sub>-FeAlO<sub>3</sub> at 27 GPa and 2000 K using a multi-anvil apparatus combined with in situ synchrotron X-ray diffraction measurements. The results demonstrate that the FeAlO<sub>3</sub> component dominates Fe<sup>3+</sup> and Al<sup>3+</sup> substitution in bridgmanite, although trace amounts of oxygen- and Mg-site vacancy components are also present. Bridgmanite with more than 40 mol% FeAlO<sub>3</sub> transforms into the LiNbO<sub>3</sub>-type phase upon decompression. The FeAlO<sub>3</sub> end-member decomposes into corundum and hematite and does not form single-phase bridgmanite. We determined the maximum solubility of the FeAlO<sub>3</sub> component in bridgmanite at 27 GPa and 2000 K to be 67 mol%, which is significantly higher than previously reported values (25–36 mol%). We determined the partial molar volume (27.9 mol/cm<sup>3</sup>) and bulk modulus (197 GPa) of hypothetical FeAlO<sub>3</sub> bridgmanite, which are significantly higher and lower than those of AlAlO<sub>3</sub> and FeSiO<sub>3</sub> bridgmanite, respectively. The non-ideality of MgSiO<sub>3</sub>-FeAlO<sub>3</sub> solid solution ( $W = 13$  kJ/mol, where  $W$  is the interaction parameter) is significantly larger than that for MgSiO<sub>3</sub>-AlAlO<sub>3</sub> (5 kJ/mol) and MgSiO<sub>3</sub>-FeSiO<sub>3</sub> (3 kJ/mol) solid solutions. The rapid decrease in abundance of the MgAlO<sub>2.5</sub> component in bridgmanite with increasing pressure is enhanced by the presence of the FeAlO<sub>3</sub> component. The FeAlO<sub>3</sub> content in pyrolite and mid-ocean ridge basalt is far below its solubility limit in bridgmanite and provides new insight into the mineralogy of the lower mantle.

## 1. Introduction

Bridgmanite is not a pure MgSiO<sub>3</sub> phase in Earth's lower mantle but contains a significant amount of other elements such as aluminum (Al) and iron (Fe) (Irifune, 1994; McCammon, 1997). Although the oxidation state in the lower mantle is considered very reduced, Fe preferably forms the charge-coupled Fe<sup>3+</sup>AlO<sub>3</sub> component in bridgmanite in addition to the Fe<sup>2+</sup>SiO<sub>3</sub> component in the presence of Al (Frost et al., 2004; Frost & Langenhorst, 2002; McCammon, 1997). The FeAlO<sub>3</sub> component is one of the dominant trivalent components in bridgmanite (Frost & Langenhorst, 2002; Richmond & Brodholt, 1998). The incorporation of FeAlO<sub>3</sub> can significantly affect physical and chemical properties of bridgmanite such as elasticity (e.g., Andrault et al., 2007; Boffa Ballaran et al., 2012), electrical conductivity (e.g., Xu et al., 1998; Yoshino et al., 2016), spin-transition pressure of Fe (e.g., Badro et al., 2004; Fujino et al., 2012), and Mg-Fe partitioning (Frost & Langenhorst, 2002). The component can thus influence seismic wave velocities (Glazyrin et al., 2014) and viscosity (Shim et al., 2017) in the lower mantle. In particular, Kurnosov et al. (2017) reported that FeAlO<sub>3</sub>-dominated bridgmanite shows lower bulk and shear moduli than the MgSiO<sub>3</sub> component. Therefore, studies of the chemical and physical behavior of the FeAlO<sub>3</sub> component in bridgmanite are important for understanding the structure and dynamics of Earth's lower mantle.

In spite of its significance, our knowledge of the chemical-physical behavior of the FeAlO<sub>3</sub> component in bridgmanite is limited. Ab initio simulations by Richmond and Brodholt (1998) suggested that the charge-coupled FeAlO<sub>3</sub> component is energetically favored for Fe<sup>3+</sup> and Al<sup>3+</sup> substitution in bridgmanite throughout the lower mantle. Petrological experiments showed that the FeAlO<sub>3</sub> content in bridgmanite increases with increasing trivalent cation content (Frost & Langenhorst, 2002; Lauterbach et al., 2000) and pressure

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(Andrault et al., 2018). Furthermore, the end-member  $\text{FeAlO}_3$  was found to possess a  $\text{Rh}_2\text{O}_3(\text{II})$  structure rather than the perovskite structure at lower mantle conditions (Nagai et al., 2005); hence, there is a solubility limit for  $\text{FeAlO}_3$  in bridgmanite as a function of pressure and temperature. Indeed, Nishio-Hamane et al. (2005) reported that the abundance of the  $\text{FeAlO}_3$  component in bridgmanite was slightly lower and higher than 25 mol% at 24 and 51 GPa, respectively, at 2100 K based on laser-heated diamond anvil cell experiments. Their study was only qualitative, however, and could not provide quantitative data regarding  $\text{FeAlO}_3$  component solubility because Fe oxidation state was not measured. Subsequently, Boffa Ballaran et al. (2012) reported that bridgmanite can contain up to 36 mol%  $\text{FeAlO}_3$  component based on synthesis from a hydrous oxide mixture at 25 GPa and 1600 K using a multi-anvil press but did not investigate the maximum solubility limit. The question of the stability and solubility of the  $\text{FeAlO}_3$  component in bridgmanite thus still remains open. We further emphasize that determination of the maximum solubility of the  $\text{FeAlO}_3$  component requires synthesis of bridgmanite coexisting with excess  $\text{FeAlO}_3$ ,  $\text{FeO}_{1.5}$ , or  $\text{AlO}_{1.5}$ -rich phase, which has not been achieved in previous experiments.

Here, we investigate the stability and solubility of the  $\text{FeAlO}_3$  component in bridgmanite by studying phase relations in the system  $\text{MgSiO}_3$ - $\text{FeAlO}_3$  at 27 GPa and 2000 K using a multi-anvil apparatus. We determine the phase stability of bridgmanite and  $\text{LiNbO}_3$ -type phase as a function of  $\text{FeAlO}_3$  content and the maximum solubility of the  $\text{FeAlO}_3$  component in bridgmanite. Finally, we discuss the chemistry and thermoelastic properties of bridgmanite and implications for the mineralogy and dynamics of the lower mantle.

## 2. Materials and Methods

### 2.1. Starting Material Preparation

The main starting materials were glass powders with  $\text{FeAlO}_3$  contents of  $\text{En}_x\text{FA}_{100-x}$ , where  $x = 90, 75$ , and 60 ( $x$  means mol%; En:  $\text{MgSiO}_3$ , FA:  $\text{Fe}^{3+}\text{AlO}_3$ ), and fine-grained oxide mixtures with  $\text{FeAlO}_3$  contents of  $\text{En}_{50}\text{FA}_{50}$  and  $\text{En}_{25}\text{FA}_{75}$  ( $^{57}\text{Fe}_2\text{O}_3$  was used in some samples to facilitate determination of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of run products). A mixture of 90 mol%  $\text{En}_{25}\text{FA}_{75}$  fine-grained oxide mixtures and 10 mol%  $^{57}\text{Fe}_2\text{O}_3$  hematite was prepared to ensure excess  $\text{Fe}^{3+}$ . In addition to these mixtures with the  $\text{MgSiO}_3$  component, we also prepared an  $\text{FeAlO}_3$  ( $\text{FA}_{100}$ ) compound with the  $\text{FeGaO}_3$ -type structure.

Glasses were prepared from mixtures of reagent-grade chemicals of  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  that were fused at 2000 K for 30 min and quenched into water. This process was repeated three times to ensure homogeneity of the glasses. Fine-grained oxide mixtures were prepared by mechanically mixing reagent-grade oxide chemicals (grain sizes below 1  $\mu\text{m}$ , which were sufficient to ensure reaction at 27 GPa and 2000 K) with ethanol for 3 hr.  $\text{FeGaO}_3$ -structured  $\text{FeAlO}_3$  was synthesized by heating a fine-grained mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  with molar ratio 1:1 at 1670 K in air for 15 hr.

### 2.2. High-Pressure and High-Temperature Experiments

Starting materials were loaded into platinum capsules and heated to 800 K for 1 hr before placing into high-pressure cell assemblies to avoid reduction of  $\text{Fe}_2\text{O}_3$  and minimize adsorbed water. We used  $\text{Cr}_2\text{O}_3$ -doped  $\text{MgO}$  octahedra with 7-mm edge length and  $\text{LaCrO}_3$  sleeves for heating (Liu et al., 2019) in combination with tungsten carbide cubes with 3-mm truncated edge length. Experiments were performed in a Kawai-type multi-anvil apparatus (IRIS-15) with a maximum press load of 15 MN at the Bayerisches Geoinstitut, University of Bayreuth (Ishii et al., 2016). Experiments were quenched after heating at 27 GPa and 2000 K for 6 to 24 hr (Table 1).

### 2.3. Analytical Methods

Phases in recovered samples were identified using a micro-focus X-ray diffractometer with a Co anode operated at 40 kV and 500 mA.  $\text{MgSiO}_3$  bridgmanite was used as an external standard to calibrate the Bragg angle ( $2\theta$ ) of the diffractometer. X-ray diffraction (XRD) profiles were collected for 3 hr for each sample. Backscattered electron (BSE) images of  $\text{En}_{90}\text{FA}_{10}$  and  $\text{En}_{75}\text{FA}_{25}$  samples were obtained using a LEO1530 scanning electron microscope operating at an acceleration voltage of 15 kV. Phase compositions and BSE images of other samples were determined by a JEOL JXA-8200 electron probe microanalyzer operating at an acceleration voltage of 15 kV and a beam current of 5–10 nA with standards of enstatite for Mg and Si, corundum for Al, and iron metal for Fe.

**Table 1**  
*Details of Experimental Runs at 27 GPa and 2000 K*

Run No.	Starting composition	Heating time (hr)	Phases
IRIS483	En <sub>90</sub> FA <sub>10</sub>	6	Brg
IRIS428	En <sub>75</sub> FA <sub>25</sub>	20	Brg
IRIS517	En <sub>60</sub> FA <sub>40</sub>	20	Brg/LN
IRIS427 <sup>a</sup>	En <sub>50</sub> FA <sub>50</sub>	24	LN
IRIS461	En <sub>25</sub> FA <sub>75</sub>	26	LN + Cor + trace Hem
	FA <sub>100</sub>		Cor + Hem + trace Ox
IRIS493	En <sub>25</sub> FA <sub>75</sub> + <sup>57</sup> Fe <sub>2</sub> O <sub>3</sub>	24	LN + Cor + Hem

Abbreviations: Brg = bridgmanite; Cor = corundum; Hem = hematite; LN = LiNbO<sub>3</sub>-type phase; Ox = iron oxide (Fe<sub>4</sub>O<sub>5</sub>).

<sup>a</sup>Reported in Liu, Dubrovinsky, et al. (2019).

We selected crystals of dominant phases (bridgmanite and LiNbO<sub>3</sub>-type phase) in run products for determination of Fe<sup>3+</sup>/ΣFe ratios using Mössbauer spectroscopy, which was conducted in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370-MBq <sup>57</sup>Co point source in a 12-μm Rh matrix. The velocity scale was calibrated relative to α-Fe. The dimensionless Mössbauer thickness of each sample varied from 4 to 50, and spectra were collected for between 10 hr and 5 days each. Spectra were fit with MossA software using doublets with pseudo-Voigt lineshapes and the full transmission integral (Prescher et al., 2012). Fe<sup>3+</sup>/ΣFe ratios were determined from relative areas. Further information about the Mössbauer setup can be found in McCammon (1994).

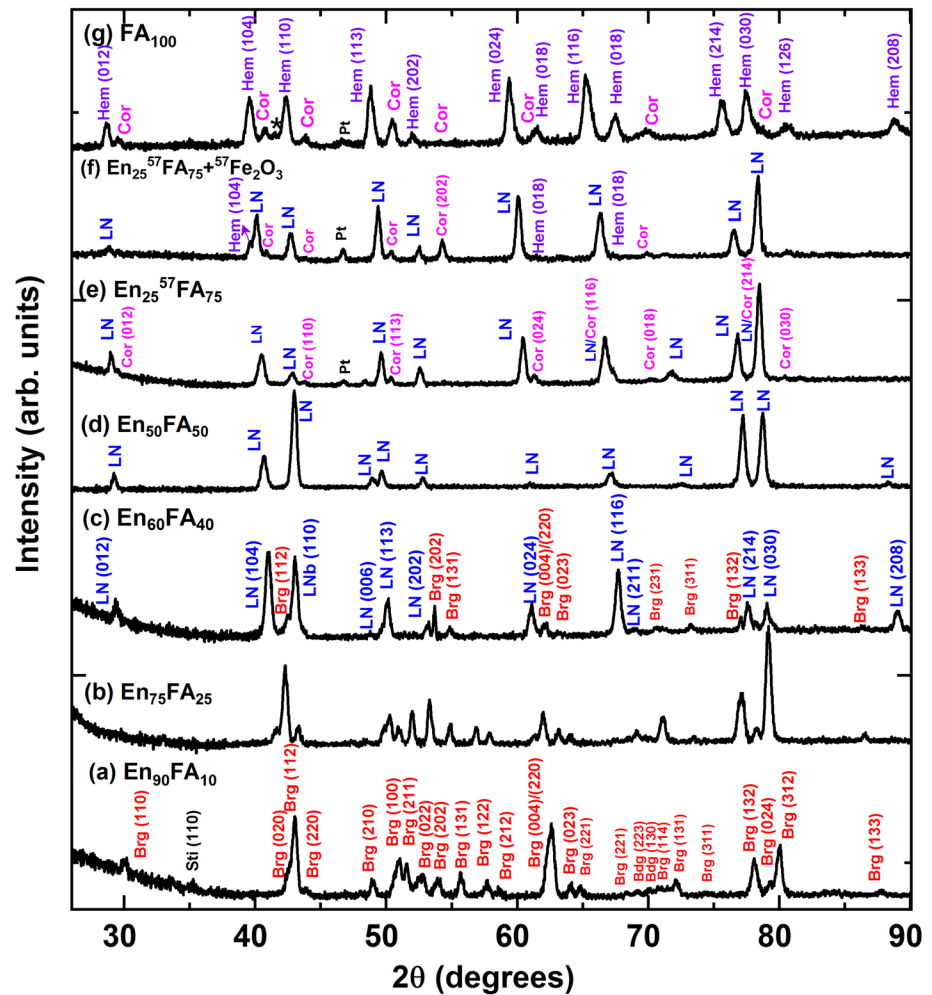
#### 2.4. In Situ X-ray Diffraction Experiments

A run product from the En<sub>50</sub>Cor<sub>50</sub> starting material was found to have the LiNbO<sub>3</sub>-type structure instead of the perovskite structure; so in order to investigate its stability, in situ XRD experiments were performed at 28 GPa and 2000 K using tungsten carbide anvils with truncated edge length of 3 mm as second-stage anvils in a DIA-type multi-anvil apparatus at the synchrotron radiation facility, SPring-8 (SPEED-Mk. II). The experimental facility for in situ XRD measurements was described by Katsura et al. (2004), and the in situ high-pressure cell assembly was almost identical to that of the synthesis experiment except that the former has two open circles as X-ray windows in the middle position of the LaCrO<sub>3</sub> heater. Au powder was placed between the sample, and MgO powder was placed on top of the hot junction of the thermocouple. Pressures were determined based on the *P-V-T* equation of state of Au proposed by Tsuchiya (2003). Uncertainties in pressure determination in these in situ experiments are approximately ±0.2 GPa. Sample temperatures were measured with a W<sub>97</sub>Re<sub>3</sub>-W<sub>75</sub>Re<sub>25</sub> thermocouple, whose hot junction was placed in the middle position of the LaCrO<sub>3</sub> heater. The sample was compressed to the target pressure and then heated at the target temperature for 1 hr. In situ XRD patterns were collected for 1 hr at the target pressure and temperature. Then, the run was quenched by turning off the electric power, and the pressure was released slowly over several hours.

### 3. Results

#### 3.1. Phase Identification by XRD Patterns and BSE Images of Quench Experiments

Table 1 lists the starting materials, experimental conditions, and run products. Figures 1 and 2, respectively, show all XRD patterns and BSE images of recovered samples. All XRD peaks of the recovered samples for the En<sub>90</sub>FA<sub>10</sub> and En<sub>75</sub>FA<sub>25</sub> samples can be assigned to bridgmanite. BSE images further confirm that there is only a single phase of bridgmanite with grain size of 2–10 μm. In contrast, sample En<sub>60</sub>FA<sub>40</sub> shows several strong diffraction peaks that can be assigned to the LiNbO<sub>3</sub> (LN)-type phase (Megaw, 1968) in addition to peaks of bridgmanite (Figure 1c). The BSE image shows no distinguishable BSE signal intensities between bridgmanite and the LN-type phase, indicating nearly identical compositions of these two phases. The BSE image (Figure 2c) demonstrates that the grain size of this sample is relatively large, approximately 100 μm. The XRD pattern of sample En<sub>50</sub>FA<sub>50</sub> (Figure 1d) shows only the LN-type phase. Its BSE image (Figure 2d) shows a uniform phase composition and a large grain size of 200–300 μm, which is even larger than the grain size of sample En<sub>60</sub>FA<sub>40</sub> (Figure 2c).

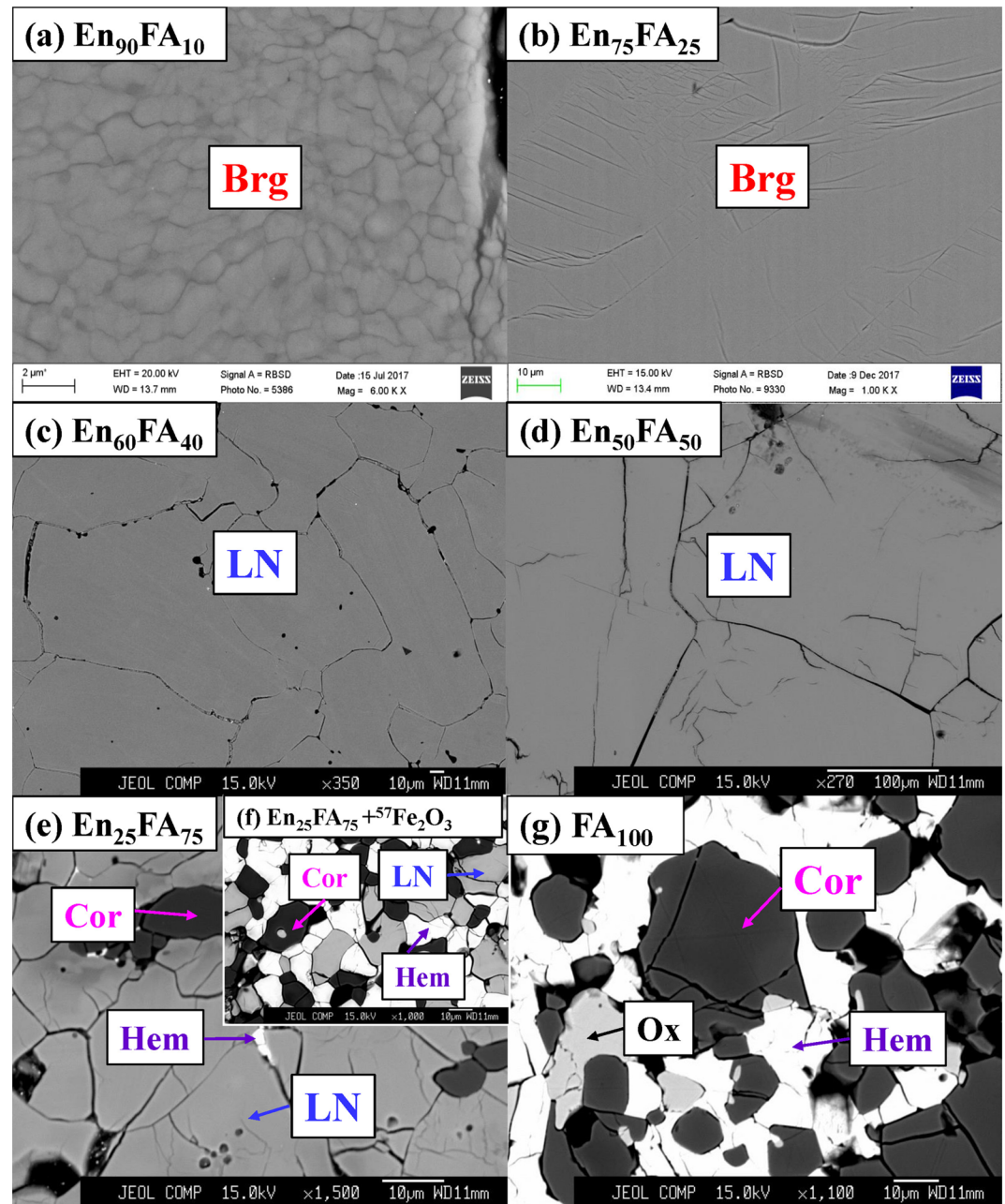


**Figure 1.** XRD profiles of  $En_xFA_{100-x}$  ( $x = 90, 75, 60, 50, 25,$  and  $0$  mol%) in the system  $MgSiO_3$  (En)- $FeAlO_3$  (FA). Asterisks represent peaks from the iron oxide phase ( $Fe_4O_5$ ). Brg = bridgmanite; Cor = corundum; Hem = hematite; LN =  $LiNbO_3$ -type phase; Sti = stishovite.

XRD patterns of the  $En_{25}FA_{75}$  composition without additional  $^{57}Fe_2O_3$  show the LN-type phase plus corundum (Figure 1e). The BSE image shows a trace amount of an  $Fe_2O_3$  phase (hematite) in this sample (Figure 2e). The XRD pattern of  $En_{25}FA_{75}$  with excess  $^{57}Fe_2O_3$  shows strong peaks of hematite as expected (Figure 1f) in addition to the LN-type phase and corundum, which appears in the sample without additional  $^{57}Fe_2O_3$  (Figure 1e). The BSE image of this sample (Figure 2f) combined with the XRD pattern suggests the coexistence of the LN-type phase, hematite, and corundum. The XRD pattern (Figure 1g) and BSE image (Figure 2g) of the  $FeAlO_3$  sample show the coexistence of corundum, hematite, and trace amounts of an iron oxide phase. The XRD pattern suggests that the iron oxide phase may be  $Fe_4O_5$ . Neither bridgmanite nor the LN-type phase was observed in this sample.

### 3.2. $Fe^{3+}/\sum Fe$ Ratios by Mössbauer Spectroscopy

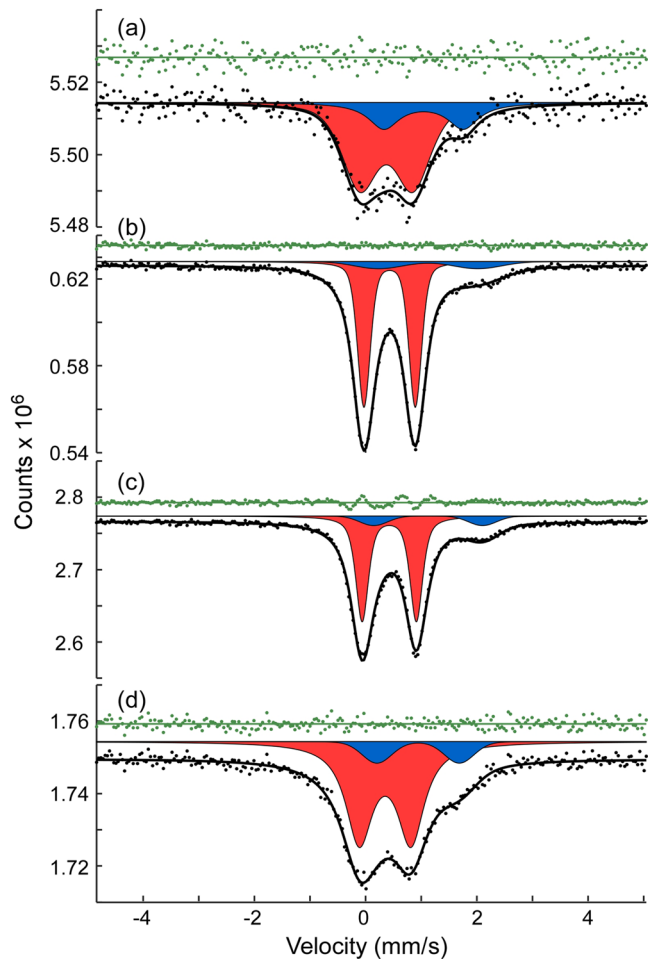
Figure 3 shows Mössbauer spectra of bridgmanite and LN-type phase from four samples. Hyperfine parameters (Table 2) are consistent with those reported by McCammon et al. (2004) for bridgmanite. In other words, hyperfine parameters are highly similar for bridgmanite and the LN-type phase. The  $Fe^{3+}/\sum Fe$  ratios were found to be 85–90 mol% within analytical uncertainty except for the  $En_{90}FA_{10}$  sample, which may be smaller (76%), although its analytical error is large (15%). The  $Fe^{3+}/\sum Fe$  ratio of the  $En_{50}FA_{50}$  sample is close to 100% within uncertainty according to our recent study (Liu, Dubrovinsky, et al., 2019).



**Figure 2.** BSE images of run products of the  $En_xFA_{100-x}$  sample ( $x = 90, 75, 60, 50, 25,$  and  $0$  mol%). Brg = bridgmanite; Cor = corundum; Hem = hematite; LN =  $LiNbO_3$ -type phase;  $O_x$  = iron oxide phase.

### 3.3. Phase Transition Observed by In Situ XRD

We conducted in situ XRD on one pre-synthesized LN-type ( $Mg_{0.5}Fe^{3+}_{0.5}(Si_{0.5}Al^{3+}_{0.5})O_3$ ) phase up to 28 GPa and 2000 K. As shown in Figure 4a, the peaks can be assigned to those of LN-type phase with some MgO peaks from surrounding cell parts at ambient conditions. The sample was compressed to 13 MN (33 GPa), which is the same press load used for in-house synthesis experiments; at this pressure, the material already transformed into bridgmanite according to XRD observations (Figure 4a). We increased temperature to 2000 K, then reduced pressure to 28 GPa, and the sample remained in the perovskite structure with lattice parameters of  $a = 4.697$  (2) Å,  $b = 4.883$  (1) Å,  $c = 6.813$  (2) Å, and  $V = 156.3$  (2) Å<sup>3</sup>. After decompression, we collected a micro-XRD pattern of the recovered sample and found that it had reverted to the LN-type



**Figure 3.** Room temperature Mössbauer spectra of bridgmanite and the *LN*-type phase: (a)  $\text{En}_{90}\text{FA}_{10}$ , (b)  $\text{En}_{75}\text{FA}_{25}$ , (c)  $\text{En}_{60}\text{FA}_{40}$ , and (d)  $\text{En}_{25}\text{FA}_{75}$ . Absorption assigned to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  is shaded blue and red, respectively, and the fit residual is shown in green above each spectrum.

40 mol%  $\text{FeAlO}_3$ . Ishii et al. (2017) argued that the transition from bridgmanite to the *LN*-type phase occurs because the ionic radii of cations in the A site are too small to preserve the perovskite structure during decompression. The ionic radii of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  in sixfold coordination (ionic radii in 12-fold coordination are unavailable) are 0.72 and 0.535 Å, respectively (Shannon, 1976). On the other hand, the ionic radius of high-spin  $\text{Fe}^{3+}$  in sixfold coordination is 0.645 Å (Shannon, 1976), which is between those of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ . This can explain why the  $\text{FeAlO}_3$  component requires a higher abundance for the bridgmanite to the *LN*-type phase transition compared to the  $\text{Al}_2\text{O}_3$  component. In addition, the closer similarity of ionic radii between  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  compared to  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  allows less pressure for accommodation of the  $\text{FeAlO}_3$  component than for  $\text{Al}_2\text{O}_3$ , which can explain the lower pressure required for the transition from bridgmanite to the *LN*-type phase.

#### 4.2. Fraction of Trivalent and Divalent Components in Bridgmanite

Bridgmanite/*LN*-type phase contains more components than  $\text{MgSiO}_3$  and  $\text{FeAlO}_3$ , since some  $\text{Fe}^{3+}$  was reduced to  $\text{Fe}^{2+}$  and the amount of Al was not equal to that of Fe. However, the species and their proportions in bridgmanite/*LN*-type phase cannot be uniquely determined because of these potential additional components. Therefore, we calculated fractions of trivalent and divalent components according to the following assumptions. Firstly, the divalent cations  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  will be accommodated in the A site, whereas the tetravalent cation  $\text{Si}^{4+}$  will be accommodated in the B site. Secondly, the majority of  $\text{Fe}^{3+}$  cations will be accommodated in the A ( $\text{Mg}^{2+}$ ) site, while the majority of  $\text{Al}^{3+}$  cations will be accommodated in the B

phase again (Figure 4b). In situ XRD observations clearly demonstrate that the  $\text{FeAlO}_3$ -rich *LN*-type phase is formed by back-transformation from bridgmanite upon decompression.

## 4. Discussion

### 4.1. Phase Transition of Bridgmanite to the *LN*-Type Phase Upon Decompression

Bridgmanite was observed in XRD and BSE data of run products for starting compositions with relatively low  $\text{FeAlO}_3$  contents ( $\text{En}_{90}\text{FA}_{10}$ ,  $\text{En}_{75}\text{FA}_{25}$ , and  $\text{En}_{60}\text{FA}_{40}$ ), whereas the *LN*-type phase was observed in those with higher  $\text{FeAlO}_3$  contents ( $\text{En}_{60}\text{FA}_{40}$ ,  $\text{En}_{50}\text{FA}_{50}$ , and  $\text{En}_{25}\text{FA}_{75}$ ). These two phases coexisted in the same  $\text{En}_{60}\text{FA}_{40}$  sample. One possible explanation for the presence of these two phases is that they are both stable at different bulk compositions. If this is the case, these phases form a binary phase loop, in which a compositional gap should exist between the two phases. Nevertheless, the compositions of coexisting bridgmanite and *LN*-type phase are highly similar as mentioned previously. Hence, we infer that one of these phases must be metastable.

Previous studies demonstrated that  $\text{Al}_2\text{O}_3$ -rich bridgmanite transforms to the *LN*-type phase upon decompression at ambient temperature (Funamori et al., 1997; Ishii et al., 2017; Liu et al., 2016; Liu, Ishii, & Katsura, 2017; Liu, Dubrovinsky, et al., 2019; Miyajima et al., 1999). In situ XRD observations (Figure 4) demonstrate that the same phase transition occurs in the  $\text{En}_{50}\text{FA}_{50}$  sample. The crystal structure of  $\text{En}_{50}\text{FA}_{50}$  *LN*-type phase has been described by Liu, Dubrovinsky, et al. (2019). The coexistence of bridgmanite and *LN*-type phase in the sample  $\text{En}_{60}\text{FA}_{40}$  can thus be explained by an incomplete phase transition from bridgmanite to the *LN*-type phase upon decompression.

Early studies found that bridgmanite with pyrope composition, namely, 25 mol% of  $\text{Al}_2\text{O}_3$  component, transformed into the *LN*-type phase upon quenching from 45 GPa at 2000 K (Ishii et al., 2017; Liu et al., 2016; Liu, Nishi, et al., 2017). The present study demonstrates that this transition occurs at a lower pressure of 27 GPa but with a secondary component of

**Table 2**  
Compositions, Cation Components, and Hyperfine Parameters of Bridgmanite/LiNbO<sub>3</sub>-Type Phase

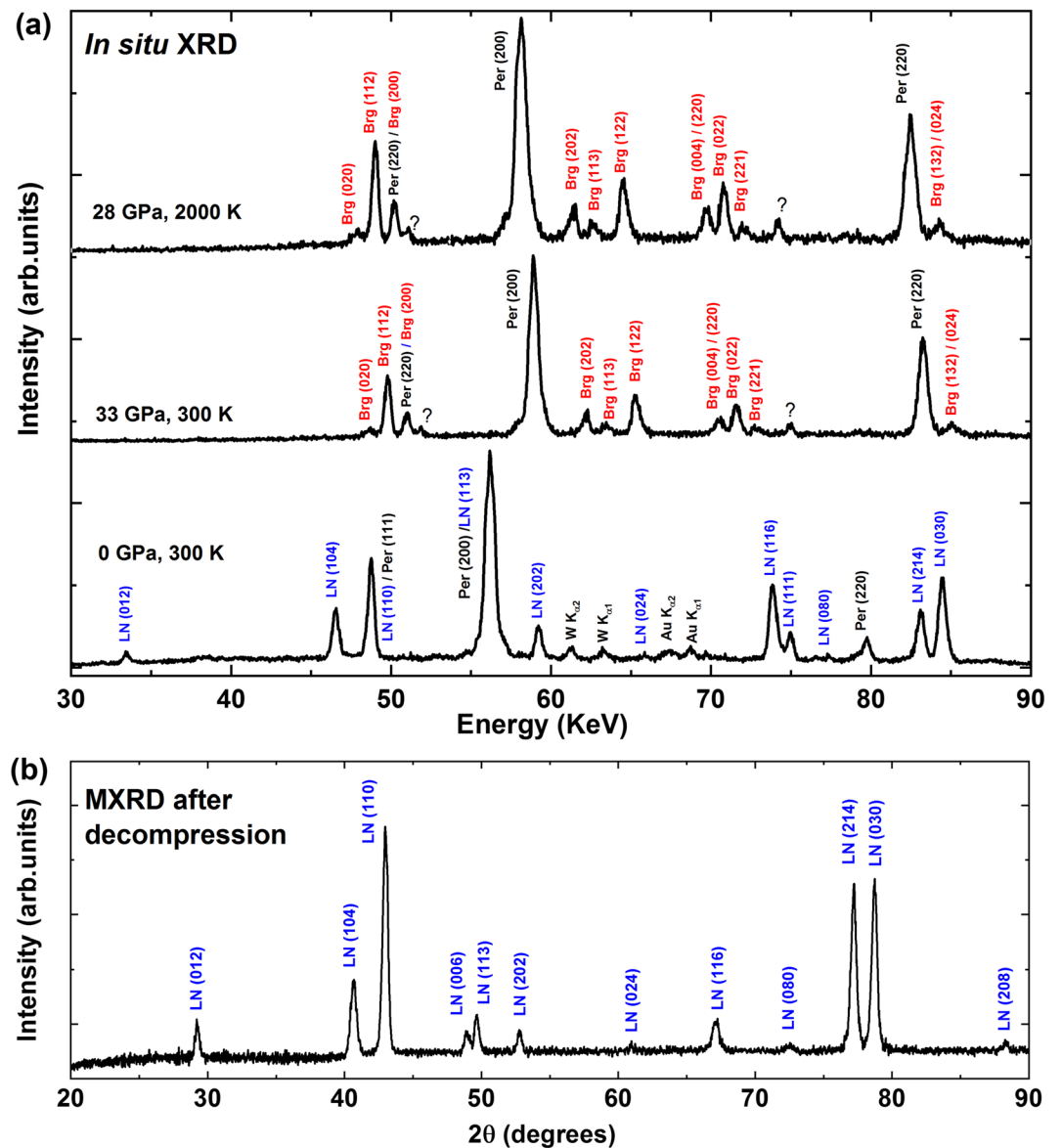
	Run. No.					
	IRIS483	IRIS428	IRIS517	IRIS427 <sup>a</sup>	IRIS461	IRIS493
	Composition					
	En <sub>90</sub> FA <sub>10</sub>	En <sub>75</sub> FA <sub>25</sub>	En <sub>60</sub> FA <sub>40</sub>	En <sub>50</sub> FA <sub>50</sub>	En <sub>25</sub> FA <sub>75</sub>	En <sub>25</sub> FA <sub>75</sub> + <sup>57</sup> Fe <sub>2</sub> O <sub>3</sub>
	Brg ( <i>n</i> = 10)	Brg ( <i>n</i> = 30)	Brg/LN ( <i>n</i> = 10)	LN ( <i>n</i> = 15)	LN ( <i>n</i> = 25)	LN ( <i>n</i> = 35)
MgO	34.74 (36)	29.11 (46)	20.63 (36)	16.95 (57)	7.79 (47)	7.61 (47)
Al <sub>2</sub> O <sub>3</sub>	5.35 (42)	12.02 (35)	19.14 (23)	22.90 (28)	28.96 (46)	25.74 (78)
FeO	5.25 (25)	11.38 (63)	23.81 (32)	30.73 (50)	45.55 (76)	47.58 (92)
SiO <sub>2</sub>	54.06 (44)	46.06 (39)	34.24 (54)	25.97 (61)	13.15 (68)	15.41 (82)
Total	99.40 (48)	98.55 (81)	97.82 (58)	96.54 (88)	95.75 (74)	96.34 (60)
Fe <sup>3+</sup> ΣFe	76 (15)	87 (4)	87 (4)	100	89 (5)	85 (8)
Mg	0.881 (13)	0.768 (9)	0.574 (10)	0.487 (11)	0.244 (14)	0.236 (14)
Al	0.107 (8)	0.251 (7)	0.421 (6)	0.517 (10)	0.718 (13)	0.630 (20)
Fe <sup>3+</sup>	0.056 (9)	0.144 (9)	0.320 (12)	0.493 (9)	0.671 (10)	0.692 (16)
Fe <sup>2+</sup>	0.037 (20)	0.022 (6)	0.046 (11)		0.118 (10)	0.123 (13)
Si	0.919 (12)	0.815 (8)	0.639 (8)	0.502 (9)	0.277 (12)	0.320 (16)
O	3.001 (12)	3.013 (7)	3.010 (9)	3.008 (5)	2.029 (5)	2.981 (6)
Component (mol%)						
MgSiO <sub>3</sub>	88 (1)	77 (1)	57 (1)	49 (1)	20 (1)	20 (2)
FeSiO <sub>3</sub>	4 (2)	2 (1)	5 (1)	0	9 (3)	12 (0)
FeAlO <sub>3</sub>	6 (1)	11 (1)	29 (2)	49 (1)	65 (4)	63 (2)
AlAlO <sub>3</sub>	2 (2)	7 (1)	7 (1)	1 (1)	N	N
FeFeO <sub>3</sub>	N	N	N	N	0	1 (1)
MgAlO <sub>2.5</sub>	N	N	N	N	6 (3)	N
MgFeO <sub>2.5</sub>	N	N	N	N	N	4 (1)
Al <sub>2/3</sub> SiO <sub>3</sub>	N	N	N	1 (1)	N	N
Fe <sub>2/3</sub> SiO <sub>3</sub>	N	3 (2)	2 (2)	N	N	N
Total	100	100	100	100	100	100
Hyperfine parameters						
CS Fe <sup>2+</sup>	1.04 (9)	1.13 (4)	1.12 (3)	N	1.01 (fixed)	0.94 (6)
QS Fe <sup>2+</sup>	1.43 (13)	1.78 (6)	1.96 (7)	N	1.55 (fixed)	1.48 (9)
FWHM Fe <sup>2+</sup>	0.67 (32)	1.01 (13)	0.59 (12)	N	1.10 (fixed)	0.63 (20)
CS Fe <sup>3+</sup>	0.37 (3)	0.43 (1)	0.43 (1)	0.34 (1)	0.35 (1) <sup>b</sup>	0.35 (2)
QS Fe <sup>3+</sup>	0.94 (6)	0.92 (1)	0.98 (1)	0.91 (1)	0.88 (1)	0.93 (3)
FWHM Fe <sup>3+</sup>	0.77 (7)	0.27 (1)	0.27 (1)	0.18 (2)	0.53 (2)	0.59 (6)

Abbreviations: Bdg = bridgmanite; CS = center shift relative to α-Fe (mm/s); FWHM = full width at half maximum (mm/s); LN = LiNbO<sub>3</sub>-type phase; *n* = number of analysis points; N = not present; QS = quadrupole splitting (mm/s).

<sup>a</sup>Reported in Liu, Dubrovinsky, et al. (2019). <sup>b</sup>Broad magnetic Fe<sup>3+</sup> component also present with CS = 0.25 mm/s, BHF (magnetic hyperfine field) = 8.3 (28) T, and FWHM = 3.5 (3) mm/s.

(Si<sup>4+</sup>) site based on the similar effective ionic radii of Fe<sup>3+</sup> (0.645 Å) and Mg<sup>2+</sup> (0.72 Å) and those of Al<sup>3+</sup> (0.535 Å) and Si<sup>4+</sup> (0.40 Å; Shannon, 1976). This assumption is valid at least in the uppermost part of the lower mantle (Fujino et al., 2012). If the number of Fe<sup>3+</sup> or Al<sup>3+</sup> cations is too large for the A or B site, the rest of Fe<sup>3+</sup> or Al<sup>3+</sup> will be accommodated in the B or A site, respectively. Thirdly, oxygen- and A-site cation vacancies will form if the cation/anion ratio is larger or smaller, respectively, than two thirds (Ismailova et al., 2016). Namely, if the cation number difference *d* = (Si-Mg-Fe<sup>2+</sup>) is positive, an A-site vacancy will form as a Fe<sub>2/3</sub>SiO<sub>3</sub> component. If the value of *d* is negative, the oxygen vacancy component MgAlO<sub>2.5</sub> will form. Fourthly, the remaining Fe<sup>3+</sup> and Al<sup>3+</sup> will firstly form FeAlO<sub>3</sub>, and then either FeFeO<sub>3</sub> or AlAlO<sub>3</sub> components if the amount of the remaining Fe<sup>3+</sup> or Al<sup>3+</sup> is not equal.

The results of our calculations are shown in Table 2. The trivalent and divalent components considered are MgSiO<sub>3</sub>, FeSiO<sub>3</sub>, FeAlO<sub>3</sub>, MgAlO<sub>2.5</sub>, MgFeO<sub>2.5</sub>, AlAlO<sub>3</sub>, FeFeO<sub>3</sub>, and Fe<sub>2/3</sub>SiO<sub>3</sub>. The most important conclusion is that the maximum FeAlO<sub>3</sub> content reaches 65 mol% at our experimental conditions of 27 GPa and 2000 K. Bridgmanite thus accommodates a large amount of the FeAlO<sub>3</sub> component. Other important features are as follows: (1) At very low FeAlO<sub>3</sub> contents (En<sub>90</sub>FA<sub>10</sub>), bridgmanite is nearly stoichiometric; (2) at slightly higher FeAlO<sub>3</sub> contents (En<sub>75</sub>FA<sub>25</sub> and En<sub>60</sub>FA<sub>40</sub>), the A-site vacancy component Al<sub>2/3</sub>SiO<sub>3</sub>



**Figure 4.** (a) In situ energy-dispersive XRD patterns of synthetic  $En_{50}FA_{50}$  LN-type phase at different conditions. (b) MXRD of the recovered sample shown in (a). Brg = bridgmanite; LN =  $LiNbO_3$ -type phase; Per = periclase from surrounding MgO sleeves.

appears; (3) at even higher  $FeAlO_3$  contents ( $En_{50}FA_{50}$  and  $En_{25}FA_{75}$ ), no A-site vacancy but rather oxygen vacancy components appear; (4) at the highest  $Fe_2O_3$  composition,  $Fe^{3+}$  enters the B site to form the oxygen vacancy component  $MgFeO_{2.5}$  and the charge-coupled  $FeFeO_3$  component. If we consider that all Fe is  $Fe^{3+}$  as in the case of the  $En_{50}FA_{50}$  sample, the maximum  $FeAlO_3$  content in bridgmanite would be even higher than the present result because of the charge-coupled substitution of  $Fe^{3+}$  and  $Al^{3+}$  in oxidized environments.

### 4.3. Solubility of the $FeAlO_3$ Component in Bridgmanite

As shown in Table 2, the  $FeAlO_3$  component in bridgmanite/LN-type phase monotonically increases from 6 to 49 mol% with increasing  $FeAlO_3$  component in the bulk starting composition from  $En_{90}FA_{10}$  to  $En_{50}FA_{50}$ . The maximum  $FeAlO_3$  content of 65 mol% was obtained from the starting material of  $En_{25}FA_{75}$ , where bridgmanite/LN-type phase coexists with corundum and hematite (see compositions in Table 3). This content is much higher than the maximum  $Al_2O_3$  content in bridgmanite so far achieved, namely, 30 mol% at



**Table 3**  
Composition of Other Phases Coexisting With Bridgmanite and LiNbO<sub>3</sub>-Type Phase

Let.	Phases	MgO	Al <sub>2</sub> O <sub>3</sub>	FeO	SiO <sub>2</sub>	Total	Mg	Al	Fe <sup>3+</sup>	Si	O
IRIS461											
En <sub>25</sub> FA <sub>75</sub>	Cor ( <i>n</i> = 10)	2.27 (11)	82.58 (40)	10.90 (62)	3.19 (13)	98.94 (91)	0.060 (3)	1.725 (9)	0.159 (8)	0.056 (2)	2.998 (1)
	Hem ( <i>n</i> = 3)	6.25 (20)	7.12 (13)	80.14 (64)	0.35 (6)	88.93 (71)	0.219 (7)	0.197 (4)	1.575 (8)	0.008 (1)	2.895 (3)
FA <sub>100</sub>	Cor ( <i>n</i> = 10)		83.63 (81)	14.57 (69)		97.93 (92)		1.604 (15)	0.396 (15)		3.000 (0)
	Hem ( <i>n</i> = 11)		4.83 (41)	84.64 (84)		89.47 (71)		0.077 (7)	1.923 (7)		3.000 (0)
	Ox ( <i>n</i> = 8)		26.82 (53)	63.15 (70)		89.96 (72)					
FA <sub>100</sub>	Cor ( <i>n</i> = 10)		83.63 (81)	14.57 (69)		97.93 (92)		1.604 (15)	0.396 (15)		3.000 (0)
	Hem ( <i>n</i> = 11)		4.83 (41)	84.64 (84)		89.47 (71)		0.077 (7)	1.923 (7)		3.000 (0)
	Ox ( <i>n</i> = 8)		26.82 (53)	63.15 (70)		89.96 (72)					
IRIS493											
En <sub>25</sub> FA <sub>75</sub> + <sup>57</sup> Fe <sub>2</sub> O <sub>3</sub>	Cor ( <i>n</i> = 10)	1.75 (11)	77.02 (78)	16.70 (24)	2.32 (20)	97.80 (91)	0.048 (3)	1.659 (5)	0.251 (5)	0.039 (3)	2.990 (1)
	Hem ( <i>n</i> = 12)	6.27 (18)	7.20 (17)	79.61 (81)	0.36 (5)	93.43 (71)	0.223 (6)	0.203 (5)	1.565 (9)	0.006 (1)	2.887 (3)

Note. The total cation number of corundum and hematite is normalized to 2 assuming that all iron is ferric iron. Abbreviations: Cor = Corundum; Hem = hematite; *n* = number of analysis points; Ox = iron oxide; Lett=Letter.

52 GPa and 2000 K (Liu et al., 2016; Liu, Nishi, et al., 2017). Furthermore, the present high FeAlO<sub>3</sub> content was obtained at 27 GPa, which is much lower than 52 GPa. The easier accommodation of the FeAlO<sub>3</sub> component compared to the Al<sub>2</sub>O<sub>3</sub> component can be explained by the more similar ionic radii between Mg and Fe<sup>3+</sup> compared to Mg and Al<sup>3+</sup> as discussed above.

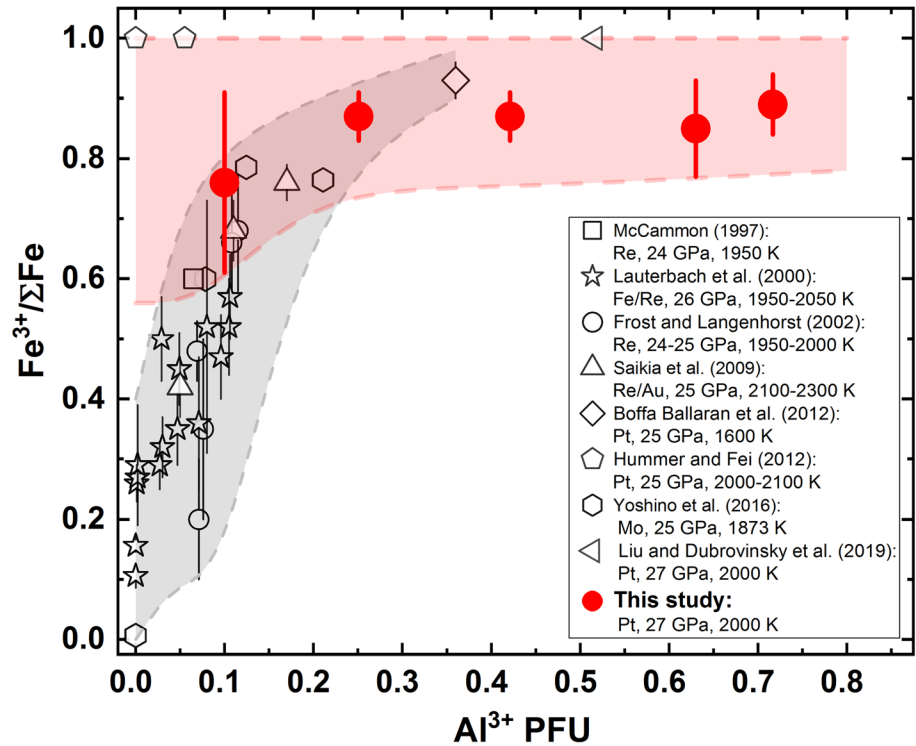
Nishio-Hamane et al. (2005) reported that the amount of the FeAlO<sub>3</sub> component in bridgmanite at pressures of 24 and 51 GPa was slightly lower and higher, respectively, than 25 mol% at 2100 K based on the laser-heated diamond anvil cell experiments. However, the present study demonstrates that the maximum solubility of the FeAlO<sub>3</sub> component in bridgmanite is much higher (65 mol%). This difference may be attributed to the challenge for LH-DAC experiments to achieve chemical equilibrium and also that FeAlO<sub>3</sub>-rich starting compositions were not used. Furthermore, Mössbauer spectroscopy demonstrates that some fraction of Fe<sup>3+</sup> in starting materials are reduced under high-pressure and high-temperature conditions; hence, the assumption that Fe maintains its valence state throughout is not valid. We suggest that experiments using high-pressure multi-anvil technology provide more reliable information regarding equilibrium compositions compared to LH-DAC experiments.

#### 4.4. Relations Between Fe<sup>3+</sup>/ΣFe and Al<sup>3+</sup> in Bridgmanite

Previous data suggest that the Fe<sup>3+</sup>/ΣFe ratio in bridgmanite increases with increasing Al<sup>3+</sup> content in bridgmanite at oxygen fugacities imposed by Fe and Re capsules at 24–26 GPa and 1900–2300 K (grey shaded region in Figure 5; McCammon, 1997; Lauterbach et al., 2000; Frost & Langenhorst, 2002; Saikia et al., 2009). In contrast, Hummer and Fei (2012) reported 100% Fe<sup>3+</sup>/ΣFe in Al-free bridgmanite synthesized in the Pt capsule material at 25 GPa and 2000–2100 K, and Boffa Ballaran et al. (2012) obtained 93% Fe<sup>3+</sup>/ΣFe-bearing bridgmanite with Al content of 0.36 PFU at 25 GPa and 1600 K under a hydrous environment. Our results at 27 GPa and 2000 K show that Al content has a limited effect on Fe<sup>3+</sup>/ΣFe in bridgmanite (red-shaded region in Figure 5) when oxygen fugacity is high when Pt capsules are used for synthesis experiments. We note that the correlation between Fe<sup>3+</sup> and Al<sup>3+</sup> also depends on synthesis pressure and temperature, which will be discussed below. As mentioned above, however, the similar ionic radii of Al<sup>3+</sup> and Si<sup>4+</sup> promote substitution of Al<sup>3+</sup> in the B site, which stabilizes Fe<sup>3+</sup> in the A site even under reducing conditions to maintain charge balance. On other hand, oxidizing conditions stabilize Fe<sup>3+</sup>, so that the Fe<sup>3+</sup> content is independent of Al<sup>3+</sup> content. Although it is possible that part of Fe<sup>3+</sup> might be reduced to Fe<sup>2+</sup> by charge-coupled substitution with Si<sup>4+</sup>, there is no evidence for this possibility.

#### 4.5. Partial Molar Volume of Bridgmanite

The molar volume of FeAlO<sub>3</sub>-, AlAlO<sub>3</sub>-, and FeSiO<sub>3</sub>-bearing bridgmanite is shown in Figure 6a, and lattice parameters are given in Table 4. Our data for FeAlO<sub>3</sub>-bearing bridgmanite agree with earlier data reported by Saikia et al. (2009) and Boffa Ballaran et al. (2012). To compare the effect of FeAlO<sub>3</sub>, AlAlO<sub>3</sub>, and FeSiO<sub>3</sub>



**Figure 5.**  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of bridgmanite/*LN*-type phase as a function of its  $\text{Al}^{3+}$  content (PFU = atoms per formula unit with total cation number of two). Grey- and red-shaded regions represent estimated uncertainties of previous and present data, respectively.

components on the molar volume of bridgmanite, we fitted the current reported data using a linear function with molar volume of  $\text{MgSiO}_3$  bridgmanite fixed to  $24.44 \text{ cm}^3/\text{mol}$  (Horiuchi et al., 1987):

$$V(X) = 24.44 + (dV/dX) \times X_{\text{FeAlO}_3/\text{AlAlO}_3/\text{FeSiO}_3}, \quad (1)$$

where  $V$  is the molar volume in  $\text{cm}^3/\text{mol}$  and  $X_{\text{FeAlO}_3/\text{AlAlO}_3/\text{FeSiO}_3}$  is the  $\text{FeAlO}_3$  or  $\text{AlAlO}_3$  or  $\text{FeSiO}_3$  content in mol% in bridgmanite. Because the fractions of the  $\text{MgAlO}_{2.5}$ ,  $\text{MgFeO}_{2.5}$ , and  $\text{Fe}_{2/3}\text{SiO}_3$  components are limited in the present samples, we only consider the molar volumes of the  $\text{FeAlO}_3$ ,  $\text{AlAlO}_3$ , and  $\text{FeSiO}_3$  components in our calculation. Literature data (Mao et al., 1991; Andrault et al., 2001; Lundin et al., 2008; Tange et al., 2009; Dorfman et al., 2013; Wolf et al., 2015; Irifune et al., 1996; Zhang & Weidner, 1999; Daniel et al., 2004; Yagi et al., 2004; Walter et al., 2004, 2006; Liu et al., 2016; Liu, Nishi, et al., 2017) suggest that  $dV/dX$  for the  $\text{FeSiO}_3$  and  $\text{AlAlO}_3$  components are  $0.0094 \pm 0.0003$  and  $0.0140 \pm 0.0003 \text{ cm}^3/\text{mol}^2$ , respectively, leading to partial molar volumes of  $25.38 \pm 0.03$  and  $25.84 \pm 0.03 \text{ cm}^3/\text{mol}$ . We have subtracted the effects of the  $\text{FeSiO}_3$  and  $\text{AlAlO}_3$  components from the present volume data to derive the partial molar volume of the pure  $\text{FeAlO}_3$  component. Following this process, we obtained the molar volume of  $\text{MgSiO}_3$ - $\text{FeAlO}_3$  bridgmanite as:

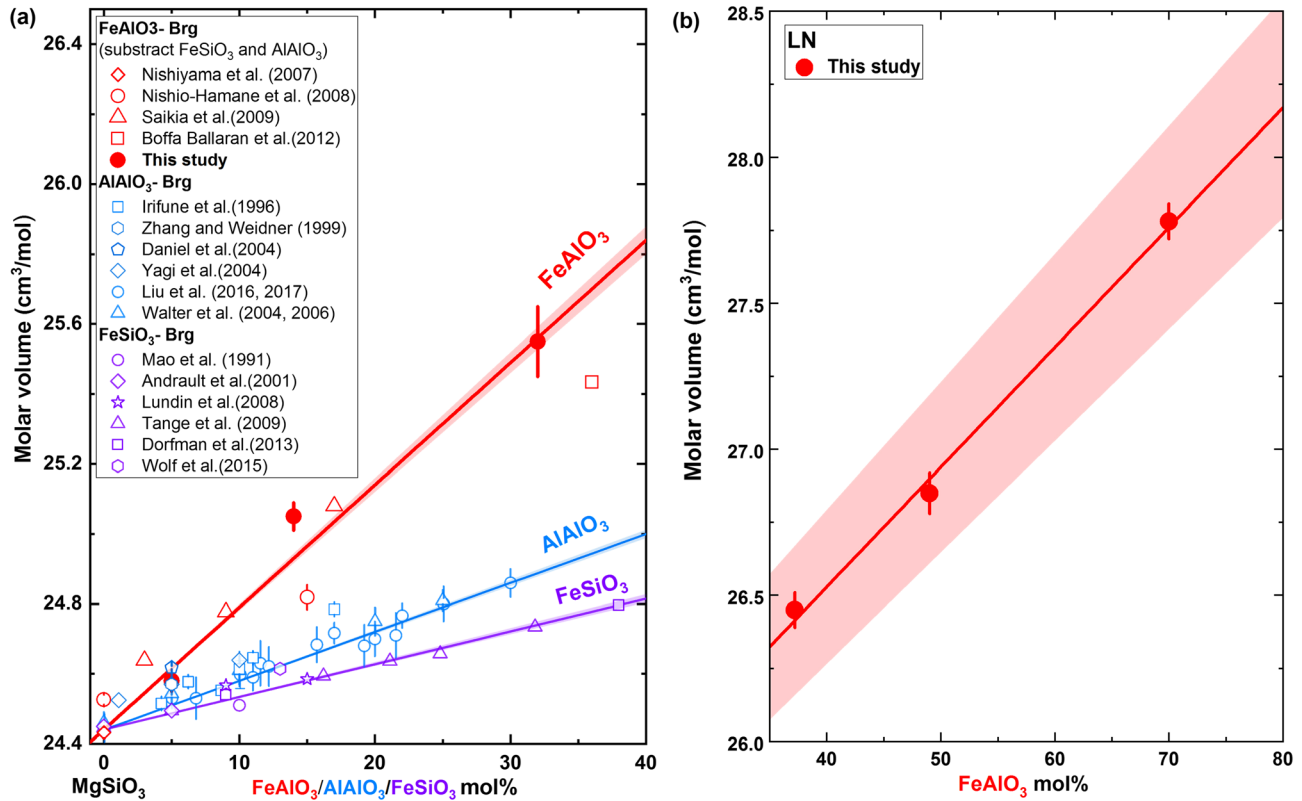
$$V(X) = 24.44 + 0.035(1) \times X_{\text{FeAlO}_3} (0 < X_{\text{FeAlO}_3} \leq 36), \quad (2)$$

where the number in parentheses is the standard deviation of the last digit. We derived the partial molar volume of the  $\text{FeAlO}_3$  component to be  $27.9 \pm 0.1 \text{ cm}^3/\text{mol}$ , which is much larger than the value for the other three components.

Figure 6b shows the molar volume of the *LN*-type phase as a function of the  $\text{FeAlO}_3$  component fitted to the following equation:

$$V(X) = 24.89(15) + 0.041(3) \times X_{\text{FeAlO}_3} (36 < X_{\text{FeAlO}_3} < 70). \quad (3)$$

Comparison of equations (2) and (3) indicates that the volume of *LN*-type phase is larger than that of bridgmanite, which is expected since the *LN*-type phase forms on decompression to ambient pressure. The larger



**Figure 6.** Molar volume of (a) FeAlO<sub>3</sub>-, AlAlO<sub>3</sub>-, and FeSiO<sub>3</sub>-bearing bridgmanite and (b) LN-type phase in present and previous studies. The solid line shows the linear fitting results, while the shaded region indicates uncertainties of linear fitting. Brg = bridgmanite; LN = LiNbO<sub>3</sub>-type phase.

$dV/dX$  value for the LN-type phase compared to bridgmanite suggests that the transition of bridgmanite to the LN-type phase has a larger driving force at higher FeAlO<sub>3</sub> content, in agreement with our experimental observations.

Davies and Navrotsky (1983) and Navrotsky (1987) suggested that non-ideality of solid solutions is due to a mismatch of component volumes. Based on this idea, they expressed the Margules parameter of regular solutions ( $W_G$  in kJ/mol) by the following formula:

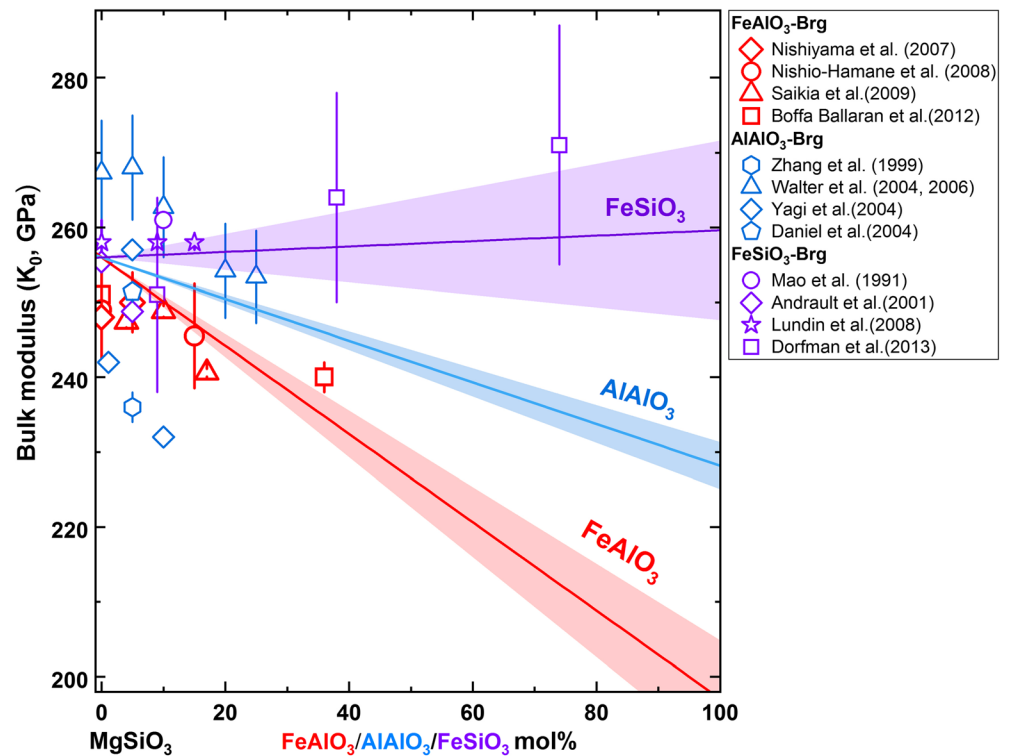
$$W_G = 100.8 \cdot \Delta V - 0.4 \frac{\text{kJ}}{\text{mol}}, \quad (4)$$

$$\Delta V = \frac{V_A - V_B}{(V_A + V_B)/2}, \quad (5)$$

**Table 4**  
Lattice Parameters of Bridgmanite and LiNbO<sub>3</sub>-Type Phase

Run No.	Starting composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Molar $V$ (cm <sup>3</sup> /mol)
Brg						
IRIS483	En <sub>90</sub> FA <sub>10</sub>	4.792 (3)	4.950 (5)	6.934 (5)	164.55 (31)	24.77 (6)
IRIS428	En <sub>75</sub> FA <sub>25</sub>	4.800 (2)	4.975 (4)	6.992 (5)	166.95 (37)	25.12 (4)
IRIS517	En <sub>60</sub> FA <sub>40</sub>	4.799 (8)	5.022 (8)	7.072 (4)	170.45 (51)	25.65 (6)
LN						
IRIS517	En <sub>60</sub> FA <sub>40</sub>	4.867 (3)	—	12.848 (13)	263.55 (63)	26.45 (6)
IRIS427	En <sub>50</sub> FA <sub>50</sub>	4.886 (3)	—	12.936 (13)	267.51 (62)	26.84 (6)
IRIS461	En <sub>25</sub> FA <sub>75</sub>	4.934 (3)	—	13.136 (9)	276.96 (45)	27.80 (5)

Abbreviations: Brg = bridgmanite; LN = LiNbO<sub>3</sub>-type phase;  $V$  = volume.



**Figure 7.** Bulk modulus of  $\text{FeAlO}_3$ -,  $\text{AlAlO}_3$ -, and  $\text{FeSiO}_3$ -bearing bridgmanite. Solid lines show linear fits, while shaded regions indicate uncertainties of linear fitting. The blue line and its uncertainty are derived from the theoretical study by Panero et al. (2006). Brg = bridgmanite.

where  $V_A$  and  $V_B$  are the molar volumes of the larger and smaller components, respectively. In the present case, the molar volumes of  $\text{MgSiO}_3$ ,  $\text{FeAlO}_3$ ,  $\text{AlAlO}_3$ , and  $\text{FeSiO}_3$  components are  $24.44$ ,  $27.94 \pm 0.10$ ,  $25.84 \pm 0.03$  and  $25.38 \pm 0.03$   $\text{cm}^3/\text{mol}$ , respectively. These values give Margules interaction parameters of  $\text{MgSiO}_3$ - $\text{FeAlO}_3$ ,  $\text{MgSiO}_3$ - $\text{Al}_2\text{O}_3$  (i.e.,  $\text{AlAlO}_3$ ), and  $\text{MgSiO}_3$ - $\text{FeSiO}_3$  solid solutions as  $13.1 \pm 0.3$ ,  $5.2 \pm 0.1$ , and  $3.4 \pm 0.1$   $\text{kJ/mol}$ , respectively. Thus, non-ideality of the  $\text{FeAlO}_3$  component is much larger than for the  $\text{AlAlO}_3$  and  $\text{FeSiO}_3$  components. The maximum  $\text{Al}_2\text{O}_3$  and  $\text{FeSiO}_3$  contents reported so far are small, only 30 mol% (Liu et al., 2016; Liu, Nishi, et al., 2017) and 32 mol% (Tange et al., 2009), respectively. One may consider that solid solutions in  $\text{MgSiO}_3$ - $\text{Al}_2\text{O}_3$  and  $\text{MgSiO}_3$ - $\text{FeSiO}_3$  bridgmanite are limited due to non-ideality. However, our results suggest that the non-ideality of these solid solutions is much smaller than that of  $\text{MgSiO}_3$ - $\text{FeAlO}_3$  bridgmanite, and its compositional range extends to at least 67 mol%  $\text{FeAlO}_3$ . We suggest that  $\text{Al}_2\text{O}_3$  and  $\text{FeSiO}_3$  component amounts higher than 70 mol% should be possible in bridgmanite at higher pressures and temperatures.

#### 4.6. Elasticity of Bridgmanite

Figure 7 shows the bulk modulus ( $K_0$ , GPa) as a function of  $\text{FeAlO}_3$ ,  $\text{AlAlO}_3$ , and  $\text{FeSiO}_3$  components. We selected the value  $K_0 = 256$  GPa for end-member  $\text{MgSiO}_3$  bridgmanite determined at mid-lower mantle conditions by recent studies (Boffa Ballaran et al., 2012; Katsura et al., 2009; Tange et al., 2012). We then used a linear fit to evaluate the compositional effect on  $K_0$ :

$$K_0(X) = 256 + (dK_0/dX) \times X_{\text{FeAlO}_3/\text{AlAlO}_3/\text{FeSiO}_3}, \quad (6)$$

where  $X_{\text{FeAlO}_3/\text{AlAlO}_3/\text{FeSiO}_3}$  is the  $\text{FeAlO}_3$  or  $\text{AlAlO}_3$  or  $\text{FeSiO}_3$  content in mol% in bridgmanite. The value of  $dK_0/dX$  for  $\text{FeAlO}_3$ -bearing bridgmanite is derived to be  $-0.59 \pm 0.08$  GPa/mol using current data (Nishiyama et al., 2007; Nisho-Hamane et al., 2008; Saikia et al., 2009; Boffa Ballaran et al., 2012). Based on the large uncertainties of  $K_0$  for  $\text{FeSiO}_3$ -bridgmanite reported by Dorfman et al. (2013), the derived  $dK_0/dX$  for the  $\text{FeSiO}_3$  component is close to zero ( $dK_0/dX = 0.03 \pm 0.12$  GPa/mol). Although there are many

studies on  $K_0$  of AlAlO<sub>3</sub>-bridgmanite (e.g., Zhang et al., 1999; Daniel et al., 2004; Yagi, et al., 2004; Walter et al., 2004, 2006), the reported data are highly scattered due to the strong variation of AlAlO<sub>3</sub> and MgAlO<sub>2.5</sub> components with pressure (Brodholt, 2000; Liu, Ishii, & Katsura, 2017), temperature (Brodholt, 2000; Liu, Akaogi, & Katsura, 2019), and Mg/Si ratio of the bulk composition (Andrault et al., 2001; Liu, Boffa Ballaran, et al., 2019) in the lower mantle. We therefore used  $dK_0/dX = -0.010 \pm 0.003$  GPa/mol for the AlAlO<sub>3</sub> component based on a theoretical study by Panero et al. (2006). The derived bulk modulus of hypothetical FeAlO<sub>3</sub> bridgmanite is  $197 \pm 8$  GPa, which is significantly lower than that of FeSiO<sub>3</sub> ( $259 \pm 12$  GPa) and AlAlO<sub>3</sub> (255 GPa). The lower value suggests that a lower mantle dominated by FeAlO<sub>3</sub>-bridgmanite would be more compressible than if it were dominated by FeSiO<sub>3</sub> or AlAlO<sub>3</sub>-bridgmanite.

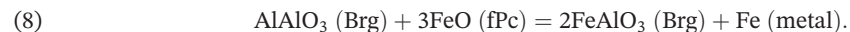
We derived the bulk sound velocity ( $V_\phi$ ) at ambient conditions based on estimated densities ( $\rho$ ) and bulk moduli ( $K_0$ ) of the three components for bridgmanite using the following equation:

$$V_\phi = \sqrt{\phi} = \sqrt{K_0/\rho}. \quad (7)$$

The derived values of  $V_\phi$  for FeAlO<sub>3</sub>, AlAlO<sub>3</sub>, and FeSiO<sub>3</sub> bridgmanite are  $7.9 \pm 0.3$ ,  $9.8 \pm 0.1$ , and  $8.6 \pm 0.4$  km/s, respectively. The FeAlO<sub>3</sub> component thus gives lower velocities than the AlAlO<sub>3</sub> and FeSiO<sub>3</sub> components, hence has a large effect on the elasticity of bridgmanite.

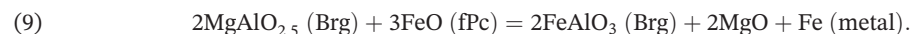
#### 4.7. Expected Pressure Dependence of FeAlO<sub>3</sub> Solubility in Bridgmanite

Frost et al. (2004) proposed that bridgmanite coexists with ferropericlase and metallic iron in the lower mantle, so the incorporation of the FeAlO<sub>3</sub> component can be considered to occur by consumption of the AlAlO<sub>3</sub> component according to the following reaction:



Based on ambient conditions molar volumes of AlAlO<sub>3</sub>, FeO, FeAlO<sub>3</sub>, and Fe of 25.84, 12.06, 27.94, and 7.09 cm<sup>3</sup>/mol, respectively, the molar volume change for reaction (8) is found to be 0.95 cm<sup>3</sup>/mol. Therefore, we expect the maximum solubility of the FeAlO<sub>3</sub> component in bridgmanite to decrease with increasing pressure, which is consistent with the recent LH-DAC study by synchrotron Mössbauer spectroscopy (Shim et al., 2017) but inconsistent with discussion in Frost and McCammon (2008). Further studies of iron oxidation state in Fe- and Al-bearing bridgmanite at deep lower mantle conditions are required.

Significant amounts of the oxygen vacancy component MgAlO<sub>2.5</sub> have been proposed for bridgmanite in the uppermost part of the lower mantle (Brodholt, 2000; Grüninger et al., 2019; Liu, Akaogi, & Katsura, 2019; Liu, Boffa Ballaran, et al., 2019; Liu, Ishii, & Katsura, 2017). Therefore, we also consider the incorporation of FeAlO<sub>3</sub> by consumption of MgAlO<sub>2.5</sub> as follows:



The molar volumes of MgO and the MgAlO<sub>2.5</sub> component in bridgmanite are 11.24 and 26.64 cm<sup>3</sup>/mol, respectively (Liu, Akaogi, & Katsura, 2019), so the molar volume change for reaction (9) is  $-4.0$  cm<sup>3</sup>/mol. Therefore, we expect the amount of the MgAlO<sub>2.5</sub> component to decrease with increasing pressure in order to form the FeAlO<sub>3</sub> component, whose amount is expected to increase with increasing pressure. The rapid decrease in the amount of the MgAlO<sub>2.5</sub> component observed with increasing pressure in the MgSiO<sub>3</sub>-MgAlO<sub>2.5</sub> system (Liu, Akaogi, & Katsura, 2019) is thus strengthened by the presence of the FeAlO<sub>3</sub> component.

#### 4.8. Implications for the Mineralogy of the Lower Mantle

We consider the amount of the FeAlO<sub>3</sub> component in uppermost lower mantle bridgmanite, namely, at conditions of 27 GPa and 2000 K. In a pyrolite composition (Sun, 1982), the Si:Al:Fe:Mg ratio is 0.50:0.06:0.04:0.40. If bridgmanite is composed of MgSiO<sub>3</sub>, FeSiO<sub>3</sub>, and FeAlO<sub>3</sub> components and all excess MgO forms periclase, the ratio MgSiO<sub>3</sub>:FeSiO<sub>3</sub>:FeAlO<sub>3</sub> will be 0.85:0.06:0.09. Thus, the abundance of the FeAlO<sub>3</sub> component in bridgmanite in bulk pyrolitic mantle is far below its solubility limit. In a MORB composition (Green et al., 1979), the Si:Al:Fe:Mg ratio is 0.55:0.21:0.07:0.17. If bridgmanite is composed of

MgSiO<sub>3</sub>, FeAlO<sub>3</sub>, and AlAlO<sub>3</sub> components and excess SiO<sub>2</sub> forms stishovite, their proportions will be 0.548:0.226:0.226. However, the solubility of the AlAlO<sub>3</sub> component in bridgmanite is only 12 mol% at 27 GPa and 2000 K, so the ratio of MgSiO<sub>3</sub>, FeAlO<sub>3</sub>, and AlAlO<sub>3</sub> components would change to 0.62:0.26:0.12. The amount of the FeAlO<sub>3</sub> component is still far below its maximum solubility in bridgmanite in the present study but outside the solubility limit reported by Nishio-Hamane et al. (2005; 24 mol%). Nevertheless, bridgmanite is the main phase for the FeAlO<sub>3</sub> component in the lower mantle.

Chemical heterogeneity is considered one possibility to explain seismically observed lateral velocity heterogeneities and slab stagnation in the middle lower mantle (e.g., Fukao & Obayashi, 2013; Karato & Karki, 2001; Kennett et al., 1998). Since bridgmanite is the most abundant phase in this region, knowledge of its chemistry is crucial for understanding seismically observed anomalies. The content of FeAlO<sub>3</sub> in bridgmanite changes from 9 to 22 mol% in going from bulk pyrolitic mantle to basaltic slabs. Furthermore, a decrease in ΣFe<sup>3+</sup>/Fe ratio and oxygen vacancy component in bridgmanite has been proposed to explain slab stagnation in the mid-lower mantle (Liu, Ishii, & Katsura, 2017; Shim et al., 2017). Although the presence of the FeAlO<sub>3</sub> component may decrease with increasing depth based on the molar volume change for reaction (8), it should also suppress the oxygen vacancy component in bridgmanite. Furthermore, the dominant FeAlO<sub>3</sub> component may stabilize a dry bridgmanite because the charge-coupled component cannot provide cation sites to stabilize water in the crystal structure (e.g., Bolfan-Casanova et al., 2003; Litasov et al., 2003; Liu, Ishii, & Katsura, 2017; Navrotsky, 1999). These considerations suggest that subducted basaltic slabs dominated by bridgmanite may become stiffer than the bulk lower mantle. The variation of the FeAlO<sub>3</sub> component in bridgmanite may thus provide insight into seismically observed slab stagnation in the mid-lower mantle.

#### Acknowledgments

The authors thank E. Posner, H. Fei, D. Krauße, R. Huang, R. Njul, H. Fischer, and S. Übelhack for assistance with sample and high-pressure assembly preparation. The manuscript was greatly improved by the constructive comments of two anonymous reviewers and the handling editor Stephen Parman. The synchrotron XRD measurements were carried out at beam line BL04B1 at Spring-8 (Proposal No. 2017B1078). All data used to produce the figures in this paper are available on Zenodo (<http://doi.org/10.5281/zenodo.3378342>). Z. L. was financially supported by the Bayerisches Geoinstitut Visitor's Programme, the National Natural Science Foundation of China (41902034), and the Fundamental Research Funds for the Central Universities of Ministry of Education of China (Grant 45119031C037). This project received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Horizon 2020 Framework Programme; Proposal No. 787 527). It was also supported by research grants to T. K. (Bundesministerium für Bildung und Forschung [BMBF]: 05K13WC2 and 05K16WC2; Deutsche Forschungsgemeinschaft [DFG]: KA3434/3-1, KA3434/7-1, KA3434/8-1, and KA3434/9-1), L. D. (DU393/9-2 and DU393/13-1), and C. M. (MC3/20-2). All authors confirm no conflicts of interest and participated in discussion of results and preparation of the manuscript.

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