



RESEARCH ARTICLE

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Stability and Solubility of the FeAlO₃ Component in Bridgmanite at Uppermost Lower Mantle Conditions

Key Points:

- We studied phase relations in the system MgSiO₃-FeAlO₃ at 27 GPa and 2000 K
- We determined the stability, solubility, and thermoelastic properties of the FeAlO₃ component in bridgmanite
- We applied this knowledge of the FeAlO₃ component to obtain new insight into the mineralogy of the lower mantle

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Abstract We report the stability and solubility of the FeAlO₃ component in bridgmanite based on phase relations in the system MgSiO₃-FeAlO₃ 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 FeAlO₃ component dominates Fe³⁺ and Al³⁺ substitution in bridgmanite, although trace amounts of oxygen- and Mg-site vacancy components are also present. Bridgmanite with more than 40 mol% FeAlO₃ transforms into the LiNbO₃-type phase upon decompression. The FeAlO₃ end-member decomposes into corundum and hematite and does not form single-phase bridgmanite. We determined the maximum solubility of the FeAlO₃ 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/cm³) and bulk modulus (197 GPa) of hypothetical FeAlO₃ bridgmanite, which are significantly higher and lower than those of AlAlO₃ and FeSiO₃ bridgmanite, respectively. The non-ideality of MgSiO₃-FeAlO₃ solid solution ($W = 13$ kJ/mol, where W is the interaction parameter) is significantly larger than that for MgSiO₃-AlAlO₃ (5 kJ/mol) and MgSiO₃-FeSiO₃ (3 kJ/mol) solid solutions. The rapid decrease in abundance of the MgAlO_{2.5} component in bridgmanite with increasing pressure is enhanced by the presence of the FeAlO₃ component. The FeAlO₃ 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 MgSiO₃ 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 Fe³⁺AlO₃ component in bridgmanite in addition to the Fe²⁺SiO₃ component in the presence of Al (Frost et al., 2004; Frost & Langenhorst, 2002; McCammon, 1997). The FeAlO₃ component is one of the dominant trivalent components in bridgmanite (Frost & Langenhorst, 2002; Richmond & Brodholt, 1998). The incorporation of FeAlO₃ 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 FeAlO₃-dominated bridgmanite shows lower bulk and shear moduli than the MgSiO₃ component. Therefore, studies of the chemical and physical behavior of the FeAlO₃ 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 FeAlO₃ component in bridgmanite is limited. Ab initio simulations by Richmond and Brodholt (1998) suggested that the charge-coupled FeAlO₃ component is energetically favored for Fe³⁺ and Al³⁺ substitution in bridgmanite throughout the lower mantle. Petrological experiments showed that the FeAlO₃ 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 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 FeAlO_3 in bridgmanite as a function of pressure and temperature. Indeed, Nishio-Hamane et al. (2005) reported that the abundance of the 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 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% 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 FeAlO_3 component in bridgmanite thus still remains open. We further emphasize that determination of the maximum solubility of the FeAlO_3 component requires synthesis of bridgmanite coexisting with excess 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 FeAlO_3 component in bridgmanite by studying phase relations in the system MgSiO_3 - FeAlO_3 at 27 GPa and 2000 K using a multi-anvil apparatus. We determine the phase stability of bridgmanite and LiNbO_3 -type phase as a function of FeAlO_3 content and the maximum solubility of the 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 FeAlO_3 contents of $\text{En}_x\text{FA}_{100-x}$, where $x = 90, 75$, and 60 (x means mol%; En: MgSiO_3 , FA: $\text{Fe}^{3+}\text{AlO}_3$), and fine-grained oxide mixtures with 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 Fe^{3+} . In addition to these mixtures with the MgSiO_3 component, we also prepared an FeAlO_3 (FA_{100}) compound with the FeGaO_3 -type structure.

Glasses were prepared from mixtures of reagent-grade chemicals of MgO , SiO_2 , Fe_2O_3 , and Al_2O_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 μm , which were sufficient to ensure reaction at 27 GPa and 2000 K) with ethanol for 3 hr. FeGaO_3 -structured FeAlO_3 was synthesized by heating a fine-grained mixture of Fe_2O_3 and Al_2O_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 Fe_2O_3 and minimize adsorbed water. We used Cr_2O_3 -doped MgO octahedra with 7-mm edge length and 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. MgSiO_3 bridgmanite was used as an external standard to calibrate the Bragg angle (2θ) 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 ₉₀ FA ₁₀	6	Brg
IRIS428	En ₇₅ FA ₂₅	20	Brg
IRIS517	En ₆₀ FA ₄₀	20	Brg/LN
IRIS427 ^a	En ₅₀ FA ₅₀	24	LN
IRIS461	En ₂₅ FA ₇₅	26	LN + Cor + trace Hem
	FA ₁₀₀		Cor + Hem + trace Ox
IRIS493	En ₂₅ FA ₇₅ + ⁵⁷ Fe ₂ O ₃	24	LN + Cor + Hem

Abbreviations: Brg = bridgmanite; Cor = corundum; Hem = hematite; LN = LiNbO₃-type phase; Ox = iron oxide (Fe₄O₅).

^aReported in Liu, Dubrovinsky, et al. (2019).

We selected crystals of dominant phases (bridgmanite and LiNbO₃-type phase) in run products for determination of Fe³⁺/ΣFe ratios using Mössbauer spectroscopy, which was conducted in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370-MBq ⁵⁷Co 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). Fe³⁺/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 En₅₀Cor₅₀ starting material was found to have the LiNbO₃-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 LaCrO₃ 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 W₉₇Re₃-W₇₅Re₂₅ thermocouple, whose hot junction was placed in the middle position of the LaCrO₃ 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 En₉₀FA₁₀ and En₇₅FA₂₅ 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 En₆₀FA₄₀ shows several strong diffraction peaks that can be assigned to the LiNbO₃ (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 En₅₀FA₅₀ (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 En₆₀FA₄₀ (Figure 2c).

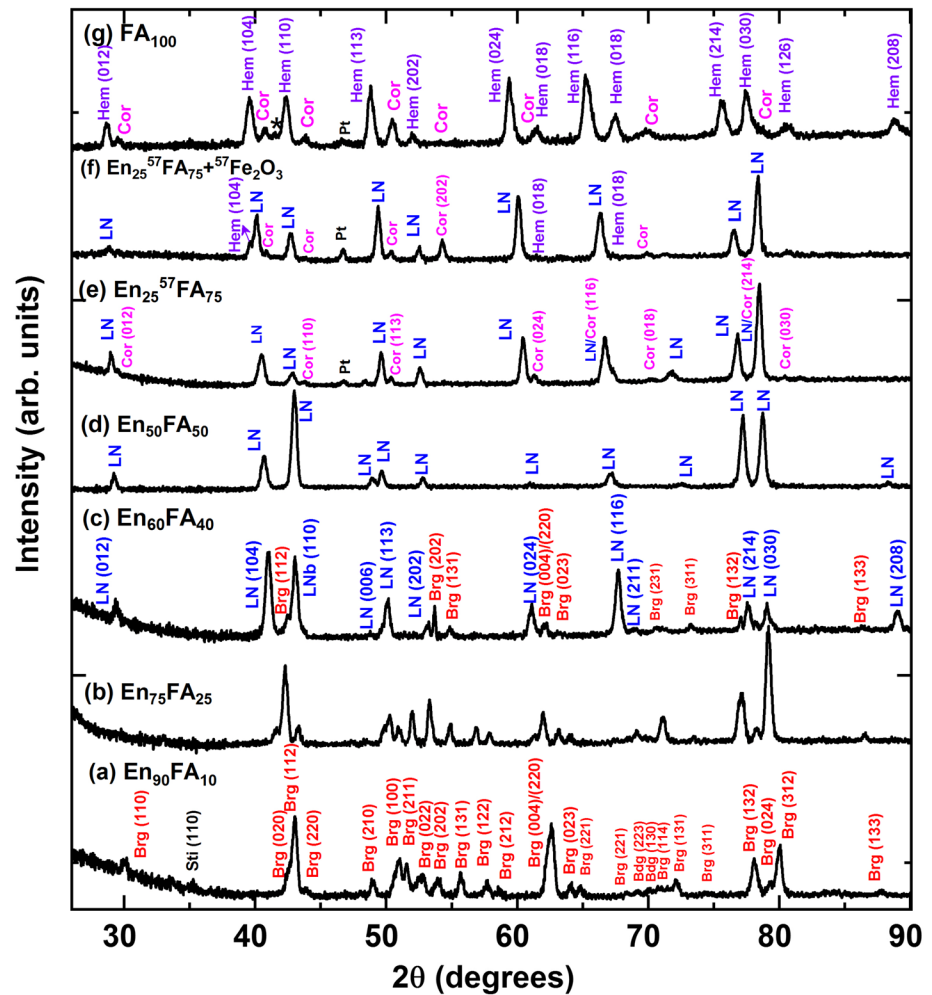


Figure 1. XRD profiles of En_xFA_{100-x} ($x = 90, 75, 60, 50, 25,$ and 0 mol%) in the system $MgSiO_3$ (En)- $FeAlO_3$ (FA). Asterisks represent peaks from the iron oxide phase (Fe_4O_5). Brg = bridgmanite; Cor = corundum; Hem = hematite; LN = $LiNbO_3$ -type phase; Sti = stishovite.

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. $Fe^{3+}/\Sigma Fe$ 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 $Fe^{3+}/\Sigma Fe$ 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 $Fe^{3+}/\Sigma Fe$ ratio of the $En_{50}FA_{50}$ sample is close to 100% within uncertainty according to our recent study (Liu, Dubrovinsky, et al., 2019).

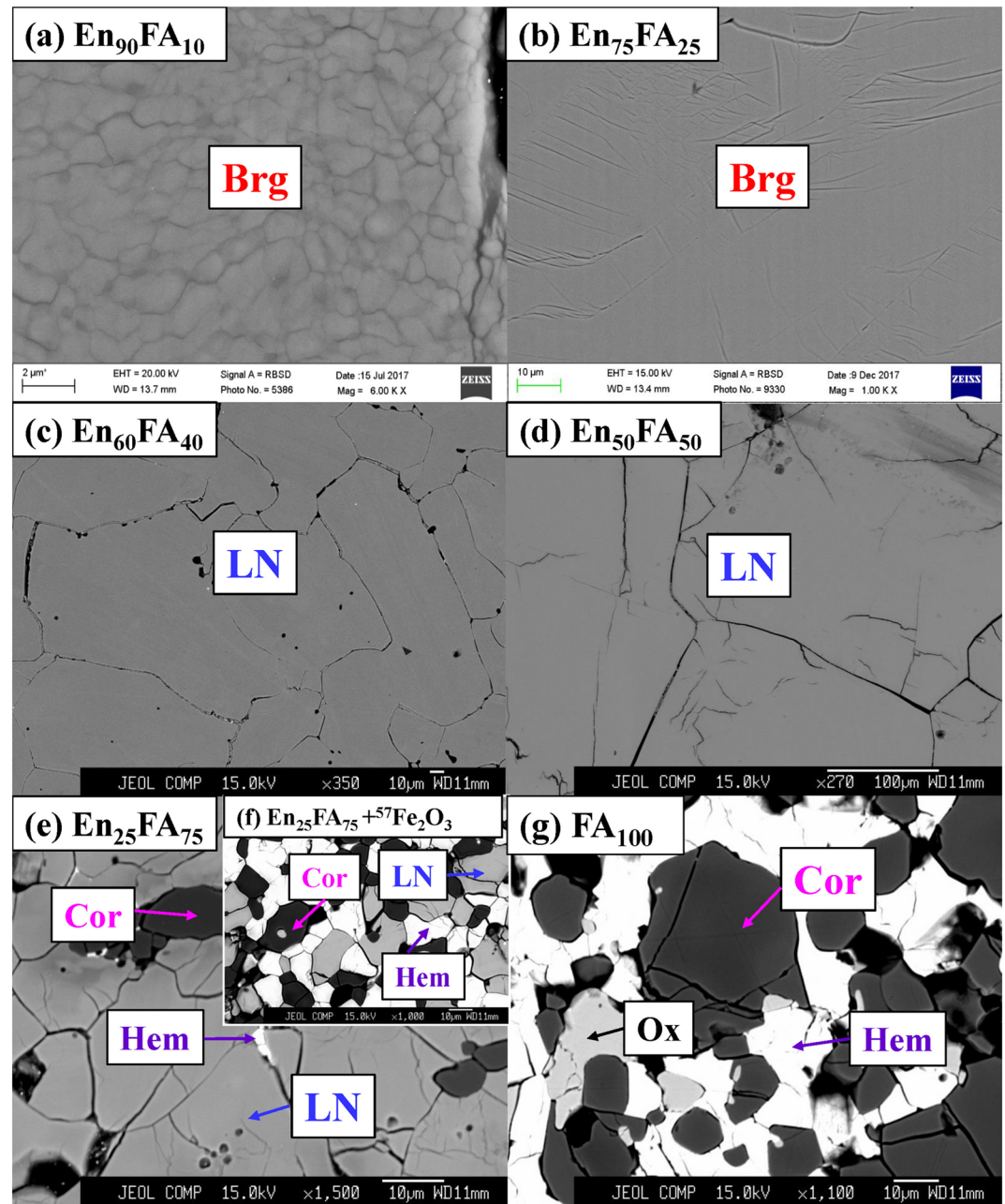


Figure 2. BSE images of run products of the En_xFA_{100-x} sample ($x = 90, 75, 60, 50, 25,$ and 0 mol%). Brg = bridgmanite; Cor = corundum; Hem = hematite; LN = $LiNbO_3$ -type phase; O_x = iron oxide phase.

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) Å³. After decompression, we collected a micro-XRD pattern of the recovered sample and found that it had reverted to the LN-type

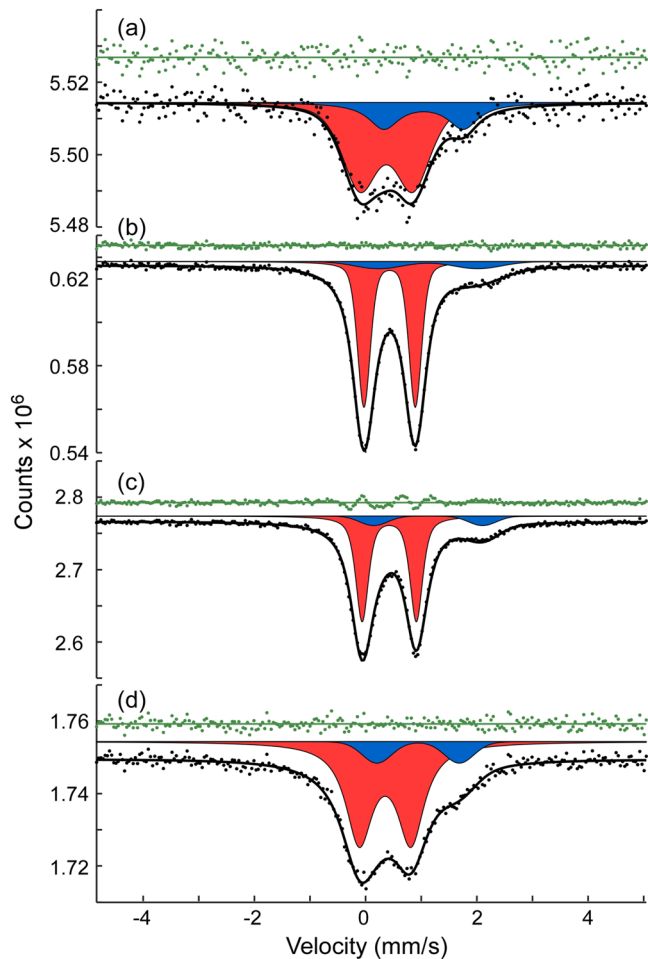


Figure 3. Room temperature Mössbauer spectra of bridgmanite and the *LN*-type phase: (a) $\text{En}_{90}\text{FA}_{10}$, (b) $\text{En}_{75}\text{FA}_{25}$, (c) $\text{En}_{60}\text{FA}_{40}$, and (d) $\text{En}_{25}\text{FA}_{75}$. Absorption assigned to Fe^{2+} and Fe^{3+} is shaded blue and red, respectively,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

40 mol% 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 Mg^{2+} and 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 Fe^{3+} in sixfold coordination is 0.645 Å (Shannon, 1976), which is between those of Mg^{2+} and Al^{3+} . This can explain why the FeAlO_3 component requires a higher abundance for the bridgmanite to the *LN*-type phase transition compared to the Al_2O_3 component. In addition, the closer similarity of ionic radii between Mg^{2+} and Fe^{3+} compared to Mg^{2+} and Al^{3+} allows less pressure for accommodation of the FeAlO_3 component than for Al_2O_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 MgSiO_3 and FeAlO_3 , since some Fe^{3+} was reduced to 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 Mg^{2+} and Fe^{2+} will be accommodated in the A site, whereas the tetravalent cation Si^{4+} will be accommodated in the B site. Secondly, the majority of Fe^{3+} cations will be accommodated in the A (Mg^{2+}) site, while the majority of Al^{3+} cations will be accommodated in the B

phase again (Figure 4b). In situ XRD observations clearly demonstrate that the 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 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 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 Al_2O_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 Al_2O_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/LiNbO₃-Type Phase

	Run. No.					
	IRIS483	IRIS428	IRIS517	IRIS427 ^a	IRIS461	IRIS493
	Composition					
	En ₉₀ FA ₁₀	En ₇₅ FA ₂₅	En ₆₀ FA ₄₀	En ₅₀ FA ₅₀	En ₂₅ FA ₇₅	En ₂₅ FA ₇₅ + ⁵⁷ Fe ₂ O ₃
	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 ₂ O ₃	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 ₂	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 ³⁺ 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 ³⁺	0.056 (9)	0.144 (9)	0.320 (12)	0.493 (9)	0.671 (10)	0.692 (16)
Fe ²⁺	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 ₃	88 (1)	77 (1)	57 (1)	49 (1)	20 (1)	20 (2)
FeSiO ₃	4 (2)	2 (1)	5 (1)	0	9 (3)	12 (0)
FeAlO ₃	6 (1)	11 (1)	29 (2)	49 (1)	65 (4)	63 (2)
AlAlO ₃	2 (2)	7 (1)	7 (1)	1 (1)	N	N
FeFeO ₃	N	N	N	N	0	1 (1)
MgAlO _{2.5}	N	N	N	N	6 (3)	N
MgFeO _{2.5}	N	N	N	N	N	4 (1)
Al _{2/3} SiO ₃	N	N	N	1 (1)	N	N
Fe _{2/3} SiO ₃	N	3 (2)	2 (2)	N	N	N
Total	100	100	100	100	100	100
Hyperfine parameters						
CS Fe ²⁺	1.04 (9)	1.13 (4)	1.12 (3)	N	1.01 (fixed)	0.94 (6)
QS Fe ²⁺	1.43 (13)	1.78 (6)	1.96 (7)	N	1.55 (fixed)	1.48 (9)
FWHM Fe ²⁺	0.67 (32)	1.01 (13)	0.59 (12)	N	1.10 (fixed)	0.63 (20)
CS Fe ³⁺	0.37 (3)	0.43 (1)	0.43 (1)	0.34 (1)	0.35 (1) ^b	0.35 (2)
QS Fe ³⁺	0.94 (6)	0.92 (1)	0.98 (1)	0.91 (1)	0.88 (1)	0.93 (3)
FWHM Fe ³⁺	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 = LiNbO₃-type phase; *n* = number of analysis points; N = not present; QS = quadrupole splitting (mm/s).

^aReported in Liu, Dubrovinsky, et al. (2019). ^bBroad magnetic Fe³⁺ component also present with CS = 0.25 mm/s, BHF (magnetic hyperfine field) = 8.3 (28) T, and FWHM = 3.5 (3) mm/s.

(Si⁴⁺) site based on the similar effective ionic radii of Fe³⁺ (0.645 Å) and Mg²⁺ (0.72 Å) and those of Al³⁺ (0.535 Å) and Si⁴⁺ (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 Fe³⁺ or Al³⁺ cations is too large for the A or B site, the rest of Fe³⁺ or Al³⁺ 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-Fe²⁺) is positive, an A-site vacancy will form as a Fe_{2/3}SiO₃ component. If the value of *d* is negative, the oxygen vacancy component MgAlO_{2.5} will form. Fourthly, the remaining Fe³⁺ and Al³⁺ will firstly form FeAlO₃, and then either FeFeO₃ or AlAlO₃ components if the amount of the remaining Fe³⁺ or Al³⁺ is not equal.

The results of our calculations are shown in Table 2. The trivalent and divalent components considered are MgSiO₃, FeSiO₃, FeAlO₃, MgAlO_{2.5}, MgFeO_{2.5}, AlAlO₃, FeFeO₃, and Fe_{2/3}SiO₃. The most important conclusion is that the maximum FeAlO₃ content reaches 65 mol% at our experimental conditions of 27 GPa and 2000 K. Bridgmanite thus accommodates a large amount of the FeAlO₃ component. Other important features are as follows: (1) At very low FeAlO₃ contents (En₉₀FA₁₀), bridgmanite is nearly stoichiometric; (2) at slightly higher FeAlO₃ contents (En₇₅FA₂₅ and En₆₀FA₄₀), the A-site vacancy component Al_{2/3}SiO₃

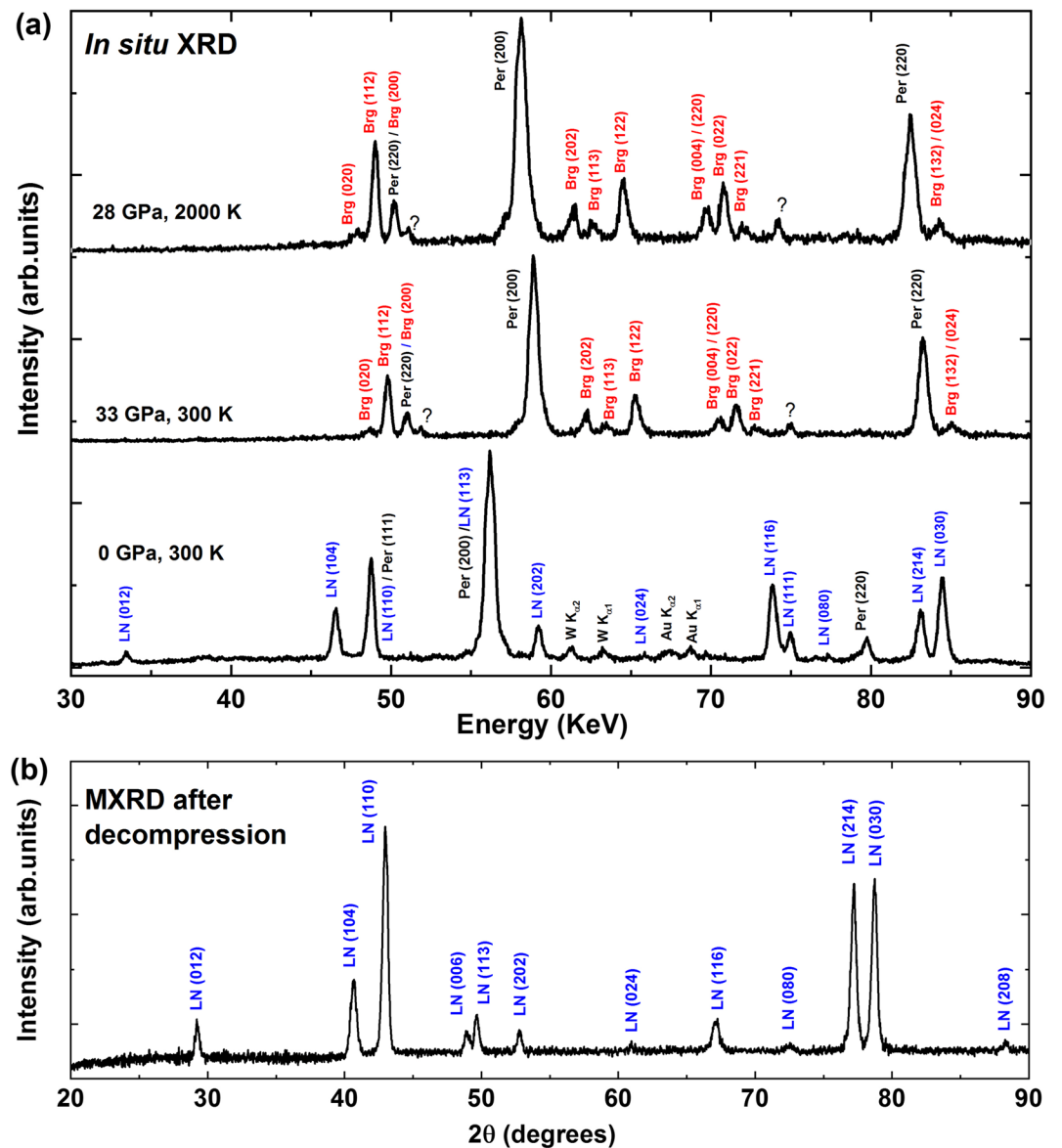


Figure 4. (a) In situ energy-dispersive XRD patterns of synthetic $En_{50}FA_{50}$ LN-type phase at different conditions. (b) MXRD of the recovered sample shown in (a). Brg = bridgmanite; LN = $LiNbO_3$ -type phase; Per = periclase from surrounding MgO sleeves.

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 LiNbO₃-Type Phase

Let.	Phases	MgO	Al ₂ O ₃	FeO	SiO ₂	Total	Mg	Al	Fe ³⁺	Si	O
IRIS461											
En ₂₅ FA ₇₅	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 ₁₀₀	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 ₁₀₀	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 ₂₅ FA ₇₅ + ⁵⁷ Fe ₂ O ₃	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 FeAlO₃ content was obtained at 27 GPa, which is much lower than 52 GPa. The easier accommodation of the FeAlO₃ component compared to the Al₂O₃ component can be explained by the more similar ionic radii between Mg and Fe³⁺ compared to Mg and Al³⁺ as discussed above.

Nishio-Hamane et al. (2005) reported that the amount of the FeAlO₃ 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 FeAlO₃ 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 FeAlO₃-rich starting compositions were not used. Furthermore, Mössbauer spectroscopy demonstrates that some fraction of Fe³⁺ 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 Fe³⁺/ΣFe and Al³⁺ in Bridgmanite

Previous data suggest that the Fe³⁺/ΣFe ratio in bridgmanite increases with increasing Al³⁺ 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% Fe³⁺/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% Fe³⁺/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 Fe³⁺/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 Fe³⁺ and Al³⁺ also depends on synthesis pressure and temperature, which will be discussed below. As mentioned above, however, the similar ionic radii of Al³⁺ and Si⁴⁺ promote substitution of Al³⁺ in the B site, which stabilizes Fe³⁺ in the A site even under reducing conditions to maintain charge balance. On other hand, oxidizing conditions stabilize Fe³⁺, so that the Fe³⁺ content is independent of Al³⁺ content. Although it is possible that part of Fe³⁺ might be reduced to Fe²⁺ by charge-coupled substitution with Si⁴⁺, there is no evidence for this possibility.

4.5. Partial Molar Volume of Bridgmanite

The molar volume of FeAlO₃-, AlAlO₃-, and FeSiO₃-bearing bridgmanite is shown in Figure 6a, and lattice parameters are given in Table 4. Our data for FeAlO₃-bearing bridgmanite agree with earlier data reported by Saikia et al. (2009) and Boffa Ballaran et al. (2012). To compare the effect of FeAlO₃, AlAlO₃, and FeSiO₃

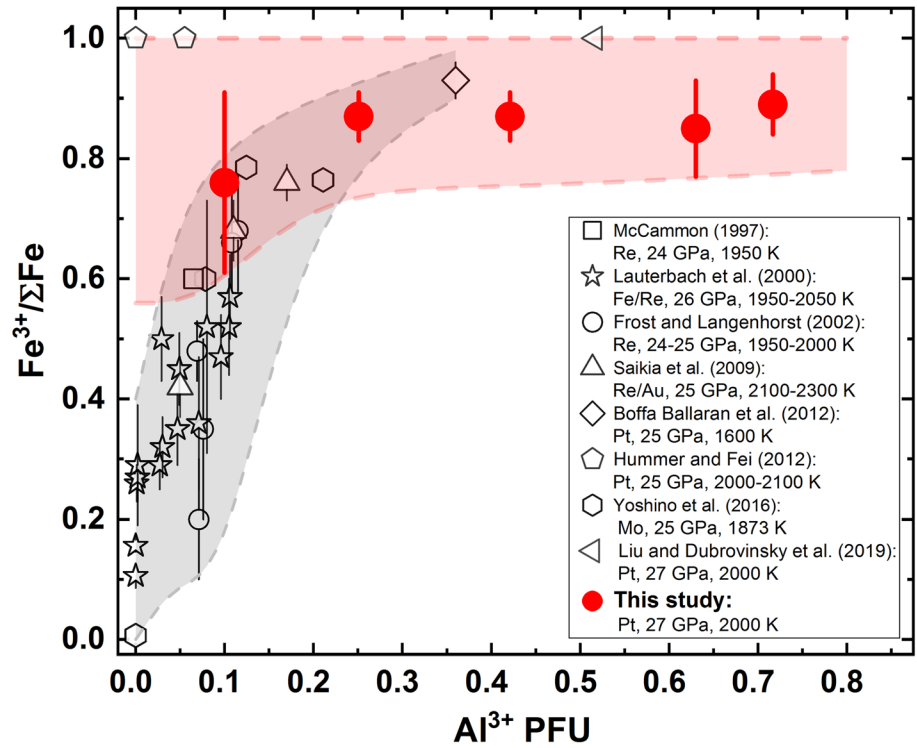


Figure 5. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of bridgmanite/*LN*-type phase as a function of its Al^{3+} content (PFU = atoms per formula unit with total cation number of two). Grey- and red-shaded regions represent estimated uncertainties of previous and present data, respectively.

components on the molar volume of bridgmanite, we fitted the current reported data using a linear function with molar volume of 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 cm^3/mol and $X_{\text{FeAlO}_3/\text{AlAlO}_3/\text{FeSiO}_3}$ is the FeAlO_3 or AlAlO_3 or 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 FeAlO_3 , AlAlO_3 , and 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 FeSiO_3 and AlAlO_3 components are 0.0094 ± 0.0003 and $0.0140 \pm 0.0003 \text{ cm}^3/\text{mol}^2$, respectively, leading to partial molar volumes of 25.38 ± 0.03 and $25.84 \pm 0.03 \text{ cm}^3/\text{mol}$. We have subtracted the effects of the FeSiO_3 and AlAlO_3 components from the present volume data to derive the partial molar volume of the pure FeAlO_3 component. Following this process, we obtained the molar volume of MgSiO_3 - 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 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 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

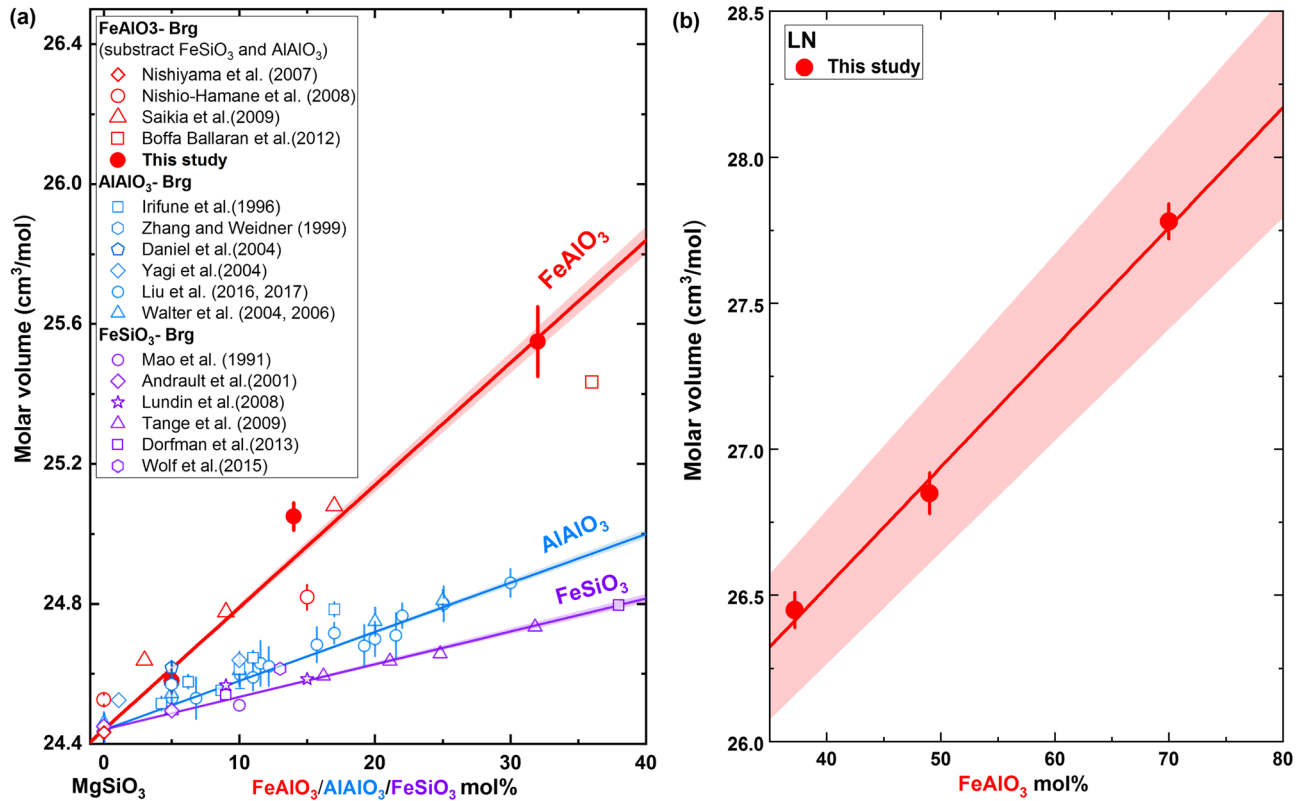


Figure 6. Molar volume of (a) FeAlO₃-, AlAlO₃-, and FeSiO₃-bearing bridgmanite and (b) LN-type phase in present and previous studies. The solid line shows the linear fitting results, while the shaded region indicates uncertainties of linear fitting. Brg = bridgmanite; LN = LiNbO₃-type phase.

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 FeAlO₃ 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 LiNbO₃-Type Phase

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

Abbreviations: Brg = bridgmanite; LN = LiNbO₃-type phase; V = volume.

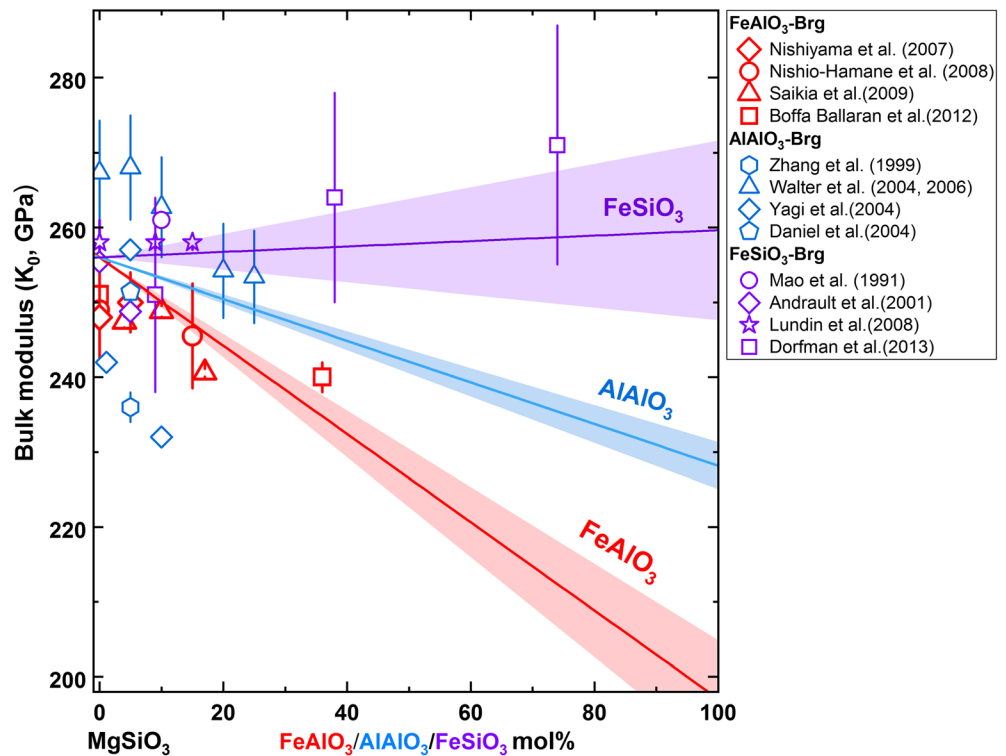


Figure 7. Bulk modulus of FeAlO_3 -, AlAlO_3 -, and FeSiO_3 -bearing bridgmanite. Solid lines show linear fits, while shaded regions indicate uncertainties of linear fitting. The blue line and its uncertainty are derived from the theoretical study by Panero et al. (2006). Brg = bridgmanite.

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 MgSiO_3 , FeAlO_3 , AlAlO_3 , and FeSiO_3 components are 24.44 , 27.94 ± 0.10 , 25.84 ± 0.03 and 25.38 ± 0.03 cm^3/mol , respectively. These values give Margules interaction parameters of MgSiO_3 - FeAlO_3 , MgSiO_3 - Al_2O_3 (i.e., AlAlO_3), and MgSiO_3 - FeSiO_3 solid solutions as 13.1 ± 0.3 , 5.2 ± 0.1 , and 3.4 ± 0.1 kJ/mol , respectively. Thus, non-ideality of the FeAlO_3 component is much larger than for the AlAlO_3 and FeSiO_3 components. The maximum Al_2O_3 and 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 MgSiO_3 - Al_2O_3 and MgSiO_3 - 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 MgSiO_3 - FeAlO_3 bridgmanite, and its compositional range extends to at least 67 mol% FeAlO_3 . We suggest that Al_2O_3 and 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 FeAlO_3 , AlAlO_3 , and FeSiO_3 components. We selected the value $K_0 = 256$ GPa for end-member 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 FeAlO_3 or AlAlO_3 or FeSiO_3 content in mol% in bridgmanite. The value of dK_0/dX for FeAlO_3 -bearing bridgmanite is derived to be -0.59 ± 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 FeSiO_3 -bridgmanite reported by Dorfman et al. (2013), the derived dK_0/dX for the 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_3 -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_3 and $\text{MgAlO}_{2.5}$ 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_3 component based on a theoretical study by Panero et al. (2006). The derived bulk modulus of hypothetical FeAlO_3 bridgmanite is 197 ± 8 GPa, which is significantly lower than that of FeSiO_3 (259 ± 12 GPa) and AlAlO_3 (255 GPa). The lower value suggests that a lower mantle dominated by FeAlO_3 -bridgmanite would be more compressible than if it were dominated by FeSiO_3 or AlAlO_3 -bridgmanite.

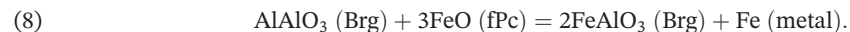
We derived the bulk sound velocity (V_ϕ) at ambient conditions based on estimated densities (ρ) and bulk moduli (K_0) of the three components for bridgmanite using the following equation:

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

The derived values of V_ϕ for FeAlO_3 , AlAlO_3 , and FeSiO_3 bridgmanite are 7.9 ± 0.3 , 9.8 ± 0.1 , and 8.6 ± 0.4 km/s, respectively. The FeAlO_3 component thus gives lower velocities than the AlAlO_3 and FeSiO_3 components, hence has a large effect on the elasticity of bridgmanite.

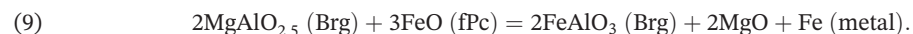
4.7. Expected Pressure Dependence of FeAlO_3 Solubility in Bridgmanite

Frost et al. (2004) proposed that bridgmanite coexists with ferropericlase and metallic iron in the lower mantle, so the incorporation of the FeAlO_3 component can be considered to occur by consumption of the AlAlO_3 component according to the following reaction:



Based on ambient conditions molar volumes of AlAlO_3 , FeO , FeAlO_3 , and Fe of 25.84, 12.06, 27.94, and 7.09 cm^3/mol , respectively, the molar volume change for reaction (8) is found to be 0.95 cm^3/mol . Therefore, we expect the maximum solubility of the FeAlO_3 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 $\text{MgAlO}_{2.5}$ 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_3 by consumption of $\text{MgAlO}_{2.5}$ as follows:



The molar volumes of MgO and the $\text{MgAlO}_{2.5}$ component in bridgmanite are 11.24 and 26.64 cm^3/mol , respectively (Liu, Akaogi, & Katsura, 2019), so the molar volume change for reaction (9) is -4.0 cm^3/mol . Therefore, we expect the amount of the $\text{MgAlO}_{2.5}$ component to decrease with increasing pressure in order to form the FeAlO_3 component, whose amount is expected to increase with increasing pressure. The rapid decrease in the amount of the $\text{MgAlO}_{2.5}$ component observed with increasing pressure in the MgSiO_3 - $\text{MgAlO}_{2.5}$ system (Liu, Akaogi, & Katsura, 2019) is thus strengthened by the presence of the FeAlO_3 component.

4.8. Implications for the Mineralogy of the Lower Mantle

We consider the amount of the FeAlO_3 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_3 , FeSiO_3 , and FeAlO_3 components and all excess MgO forms periclase, the ratio MgSiO_3 : FeSiO_3 : FeAlO_3 will be 0.85:0.06:0.09. Thus, the abundance of the FeAlO_3 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

MgSiO₃, FeAlO₃, and AlAlO₃ components and excess SiO₂ forms stishovite, their proportions will be 0.548:0.226:0.226. However, the solubility of the AlAlO₃ component in bridgmanite is only 12 mol% at 27 GPa and 2000 K, so the ratio of MgSiO₃, FeAlO₃, and AlAlO₃ components would change to 0.62:0.26:0.12. The amount of the FeAlO₃ 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 FeAlO₃ 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 FeAlO₃ in bridgmanite changes from 9 to 22 mol% in going from bulk pyrolitic mantle to basaltic slabs. Furthermore, a decrease in $\Sigma\text{Fe}^{3+}/\text{Fe}$ 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 FeAlO₃ 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 FeAlO₃ 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 FeAlO₃ component in bridgmanite may thus provide insight into seismically observed slab stagnation in the mid-lower mantle.

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