



RESEARCH LETTER

10.1002/2015GL064400

Key Points:

- The spin transition of Fe³⁺ is observed in Pv10 at 18–25 GPa using XRD
- The spin transition causes a sudden decrease in the volume and increase in K
- The effect of Fe and Al on the density and K of bridgmanite is discussed

Supporting Information:

- Supporting Information S1

Correspondence to:

Z. Mao,
zhumao@ustc.edu.cn

Citation:

Mao, Z., J.-F. Lin, J. Yang, T. Inoue, and V. B. Prakapenka (2015), Effects of the Fe³⁺ spin transition on the equation of state of bridgmanite, *Geophys. Res. Lett.*, 42, 4335–4342, doi:10.1002/2015GL064400.

Received 28 APR 2015

Accepted 15 MAY 2015

Accepted article online 18 MAY 2015

Published online 4 JUN 2015

Effects of the Fe³⁺ spin transition on the equation of state of bridgmaniteZhu Mao^{1,2,3}, Jung-Fu Lin^{1,4}, Jing Yang¹, Toru Inoue⁵, and Vitali B. Prakapenka⁶

HPSTAR
161-2015

¹Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA, ²Laboratory of Seismology and Physics of Earth's Interior, School of Earth and Planetary Sciences, University of Science and Technology of China, Hefei, China, ³National Geophysics Observatory at Mengcheng, Mengcheng, China, ⁴Center for High Pressure Science and Advanced Technology Research (HPSTAR), Shanghai, China, ⁵Geodynamics Research Center, Ehime University, Matsuyama, Japan, ⁶GeoSoilEnviroCARS, University of Chicago, Chicago, Illinois, USA

Abstract We have investigated the equation of state of Fe-bearing bridgmanite, (Mg_{0.9}Fe_{0.1})SiO₃, using synchrotron X-ray diffraction in diamond anvil cells up to 125 GPa and 300 K. Combined with previous synchrotron Mössbauer spectroscopy results, we have found that the occurrence of the low-spin Fe³⁺ in the octahedral sites (B site) of bridgmanite has produced a 0.5(±0.1)% reduction in the unit cell volume at 18–25 GPa and has increased the isothermal bulk modulus to 284(±4) GPa, consistent with recent theoretical calculations. Together with literature results, we note that the addition of Fe can cause an increase in the density, bulk modulus, and bulk sound velocity in both Al-free and Al-bearing bridgmanite at lower mantle pressures. The presence of Fe³⁺ in the B site of bridgmanite can further enhance this increase. The observed spin transition of B site Fe³⁺ in bridgmanite is thus important for understanding the density and velocity structures of the lower mantle.

1. Introduction

Earth's lower mantle is believed to mainly consist of bridgmanite [(Mg,Fe)(Al,Si)O₃] and ferropericlase [(Mg,Fe)O] with approximately 10% Fe in bridgmanite and 17% Fe in ferropericlase [Ringwood, 1975]. Of particular importance is the electronic spin transition of Fe in ferropericlase and bridgmanite which has been reported to affect a number of physical properties, including density, sound velocity, electronic conductivity, etc. [e.g., Badro et al., 2003; Crowhurst et al., 2008; Goncharov et al., 2006; Lin et al., 2013; Mao et al., 2010, 2011a, 2014]. Experimental and theoretical studies on the spin transition of Fe in ferropericlase and bridgmanite thus provide new insights on the physical, chemical, and dynamic states of the lower mantle [e.g., Badro et al., 2004; Cammarano and Romanowicz, 2007; Lin et al., 2005; Wentzcovitch et al., 2009].

A review of recent theoretical and experimental results shows that the spin and valence states of iron can affect its stability in different crystallographic sites in bridgmanite [Lin et al., 2013]. For example, Fe²⁺ in bridgmanite is reported to exist in the large dodecahedral sites (A site), while Fe³⁺ can occupy both the A and octahedral sites (B site). Although previous Mössbauer spectroscopic studies have shown an abnormal increase in the quadrupole splitting of Fe²⁺ in the A site of bridgmanite at high pressures, it is still debated whether this change is associated with the high-spin (HS) to intermediate-spin transition of Fe²⁺ in bridgmanite or the change is only a result of the enhanced lattice distortion that does not involve the spin transition [Hsu et al., 2010; Lin et al., 2012, 2013; McCammon et al., 2008]. On the other hand, Fe³⁺ has been reported to occupy both the dodecahedral A site and the octahedral B site in bridgmanite. It has been shown that only Fe³⁺ in the B site can undergo the HS to low-spin (LS) transition at lower mantle pressures [Bengtson et al., 2009; Hsu et al., 2010; Lin et al., 2013]. It is worth noting that the B site Fe³⁺ is only reported to be present in the polycrystalline bridgmanite samples, which have been observed to coexist with stishovite (excess silica environment) but is absent in single-crystal bridgmanite [Ballaran et al., 2012; Catalli et al., 2010, 2011; Glazyrin et al., 2014; Lin et al., 2012; Potapkin et al., 2013]. Fe³⁺ in the B site of bridgmanite is theoretically predicted to be metastable and only occur at high pressures and high temperatures [Hsu et al., 2012]. Future investigations are needed to clarify the effects of the synthesis conditions (e.g., excess silica and oxygen fugacity) and substitution mechanisms on the presence of B site Fe³⁺ in bridgmanite.

Recent theoretical studies have shown that the HS to LS transition of Fe^{3+} in bridgmanite occurs at approximately 50 GPa, leading to a volume reduction, softening of the bulk modulus, and anomalous variation in the thermal expansion coefficient, heat capacity, and the Grüneisen parameter [Hsu *et al.*, 2011; Tsuchiya and Wang, 2013]. Meanwhile, elevating the temperature will broaden the width of the Fe^{3+} spin transition [Tsuchiya and Wang, 2013]. The spin transition of Fe^{3+} in bridgmanite has also been identified in experimental studies [Catalli *et al.*, 2010, 2011; Lin *et al.*, 2012], yet the effect of the Fe^{3+} spin transition on the volume and density of bridgmanite is highly debated and unclear in recent experimental results probably due to the use of inadequate starting samples and pressure medium as well as limited data points. Catalli *et al.* [2011] have shown an anomalous collapse in the volume of an Al-bearing bridgmanite at ~ 70 GPa where the spin transition of Fe^{3+} occurs, although the Al-bearing bridgmanite is expected to predominantly contain Fe^{3+} in the A site, which is theoretically predicted to be stable in the HS state [Hsu *et al.*, 2012].

In this study, we have conducted in situ synchrotron X-ray diffraction (XRD) experiments on bridgmanite with 10 mol.% Fe up to 125 GPa and 300 K. Compared to previous studies which did not constrain the spin and valence states of Fe in bridgmanite [Andrault *et al.*, 2001; Ballaran *et al.*, 2012; Dorfman *et al.*, 2013], our XRD results obtained from well-characterized bridgmanite samples, together with previous synchrotron Mössbauer spectroscopy (SMS) results, help to better constrain the effects of the Fe spin transition on the equation of state (EoS) of bridgmanite at lower mantle pressures. Using the obtained results, we have discussed the effect of the Fe spin transition and the variation of Fe and Al content on the density, bulk modulus, and bulk sound velocity of the lower mantle, which aids in understanding the effect of compositional variation on the density and sound velocity of the lower mantle.

2. Experiments

Bridgmanite with 10 mol.% Fe (Pv10) was synthesized from enstatite powder, $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$, which was synthesized by mixing powders of the oxides MgO, SiO_2 , and $^{57}\text{Fe}_2\text{O}_3$ according to the appropriate ratios (see supporting information for details) [Lin *et al.*, 2012]. The synthesized bridgmanite sample was examined by X-ray diffraction, electron microscope, and Mössbauer spectroscopy (Figure S1 in the supporting information) [Lin *et al.*, 2012]. Here we used the same batch of the bridgmanite sample as Lin *et al.* [2012] which has been examined by the conventional Mössbauer spectroscopy at ambient conditions and synchrotron Mössbauer spectroscopy measurements (SMS) at high pressures to determine the spin and valence states of Fe. These measurements indicate approximately 20% of the total Fe as Fe^{3+} occupying the octahedral sites and the remaining 80% as Fe^{2+} in the pseudododecahedral sites.

High-pressure XRD experiments of Pv10 were performed at GeoSoilEnviroConsortium for Advanced Radiation Sources (GSECARS) sector of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The Pv10 samples were polished down to 10–15 μm thick disks which were then loaded into symmetric diamond anvil cells (DACs) with a Re gasket and Ne pressure medium for high-pressure diffraction experiments. Pt powder was placed next to the sample as the pressure calibrant [Fei *et al.*, 2007a]. We have made three runs of XRD measurements, each ranging from 1 bar to 125 GPa (Figure 1 and Table S1 in the supporting information). In each run starting at approximately 30 GPa, both the sample and the Pt powder were annealed at ~ 1500 K by laser heating at every 8–15 GPa pressure step up to 125 GPa in order to reduce the potential deviatoric stress in the sample chamber. Compared to previous studies which synthesized bridgmanite in laser-heated DACs, using well-characterized bridgmanite samples presynthesized from a multi-anvil apparatus helped to avoid potential chemical inhomogeneities in the laser-annealed samples [Andrault *et al.*, 2001; Catalli *et al.*, 2010, 2011; Dorfman *et al.*, 2013; Mao *et al.*, 2011b; Sinmyo *et al.*, 2014]. The diffraction patterns were collected every 2–4 GPa with an X-ray beam of $5 \times 7 \mu\text{m}$.

3. Results

High-pressure XRD experiments on bridgmanite with 10 mol.% Fe were performed at up to 125 GPa and 300 K using DACs (Figures S1 and S2 in the supporting information). The obtained XRD patterns of Pv10 match the diffraction lines of bridgmanite (Figure S1 in the supporting information). Several weak peaks are identified as diffraction lines of stishovite (Figure S1 in the supporting information). About 10–12 diffraction lines were used to calculate the unit cell volume of bridgmanite at each pressure. Comparing the obtained pressure-volume (P - V) data of Fe-bearing bridgmanite to that of pure MgSiO_3 -bridgmanite clearly shows

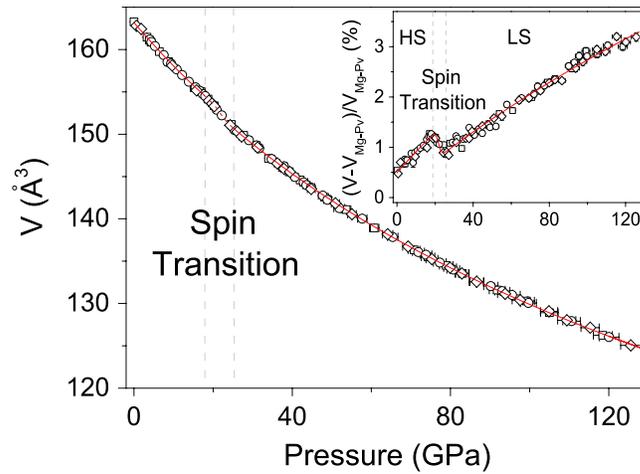


Figure 1. Pressure–volume relations of silicate bridgmanite. Square, circle, and diamonds: experimental data for the first, second, and third runs, respectively; red lines: EoS of bridgmanite; red dashed lines: bridgmanite with mixed HS and LS Fe³⁺. The vertical grey dashed lines indicate the region with mixed HS and LS Fe³⁺. The insert figure shows the variation of the unit cell volume of bridgmanite with pressure using end-member MgSiO₃ bridgmanite as the reference, $(V - V_{\text{Mg-Pv}}) / V_{\text{Mg-Pv}}$ [Ballaran *et al.*, 2012]. Errors are smaller than symbols when not shown.

an abnormal reduction of 0.5(±0.1)% in the unit cell volume between 18 and 25 GPa, which has been confirmed by three individual runs of experiments (Figure 1 and Table S1 in the supporting information). The abnormal volume reduction is consistent with previous theoretical predictions, which could be associated with the HS to LS transition of Fe³⁺ in the B site of bridgmanite [Hsu *et al.*, 2011; Tsuchiya and Wang, 2013]. Meanwhile, comparing the high-pressure XRD results in this study with previous SMS results that used the same bridgmanite sample indicates that the observed reduction in volume can be mainly associated with the spin transition of the B site Fe³⁺ in bridgmanite, although the effect of the local site distortion of the A site Fe²⁺ that concurs with the B site spin transition remains to be further understood [Lin *et al.*, 2012]. We compare the *P*-*V* relation of Pv10 to pure MgSiO₃-bridgmanite,

which helps to define the width of the spin transition. The LS fraction of bridgmanite with increasing pressure is calculated as follows (Figure 2) [Wentzcovitch *et al.*, 2009]:

$$n_{\text{LS}} = \frac{1}{1 + \exp(\Delta G(P, T)^* / T)} \quad (1)$$

where n_{LS} is the LS fraction, $\Delta G(P, T)^*$ is the normalized difference of the Gibbs free energy between the LS and HS state (see supporting information for details) [Tsuchiya *et al.*, 2006; Wentzcovitch *et al.*, 2009]. These analyses show that the spin transition starts at 18 GPa and completes at 25 GPa (Figure 2). Using the derived width of the spin transition, the *P*-*V* data above 25 GPa fitted to the third-order Birch-Murnaghan EoS yield the isothermal bulk modulus, $K_{T0} = 284 (\pm 4)$ GPa, and unit cell volume, $V_0 = 162.6 (\pm 0.3) \text{ \AA}^3$, with a fixed $K_{T0}' = 4$ for Pv10 with the LS B site Fe³⁺.

4. Discussion and Geophysical Implications

Our high-pressure XRD measurements have shown that a sudden collapse in the unit cell volume of Pv10 by 0.5(±0.1)% occurs between 18 and 25 GPa, which corresponds to a 0.6(±0.2)% increase in density. Combining our XRD results with previous SMS results that used the same bridgmanite sample allows us to thoroughly investigate the potential cause for this volume reduction. The high-pressure SMS measurements have shown that the B site Fe³⁺ undergoes an electronic spin transition at approximately 13–25 GPa, while the A site experiences strong lattice distortions [Lin *et al.*, 2012]. The enhanced volume reduction observed in our XRD measurements is more likely to be associated with the HS to LS transition of Fe³⁺, consistent with previous theoretical studies, although the effect of the increase in the lattice distortion of the A site Fe²⁺ remains to be further understood [Hsu *et al.*, 2011; Tsuchiya and Wang, 2013]. Moreover, our results support recently predicted theoretical results in which bridgmanite having 6.25–12.5% Fe³⁺/(Fe²⁺+Fe³⁺) in the B site undergoes the Fe³⁺ spin transition with a 0.7–1.2% volume reduction at 40–50 GPa (Figure 2) [Hsu *et al.*, 2011; Tsuchiya and Wang, 2013]. Although two experimental studies have also documented the spin transition of Fe³⁺ in bridgmanite, the effect of the potential Fe³⁺ spin transition on the EoS of bridgmanite cannot be quantitatively evaluated because of the limited data points and the stiffer pressure medium used (Figure 2) [Catalli *et al.*, 2010, 2011]. It should be noted that all of the samples used in this study were well characterized and were loaded with Ne, a softer pressure medium as compared to the previous experimental studies [Catalli

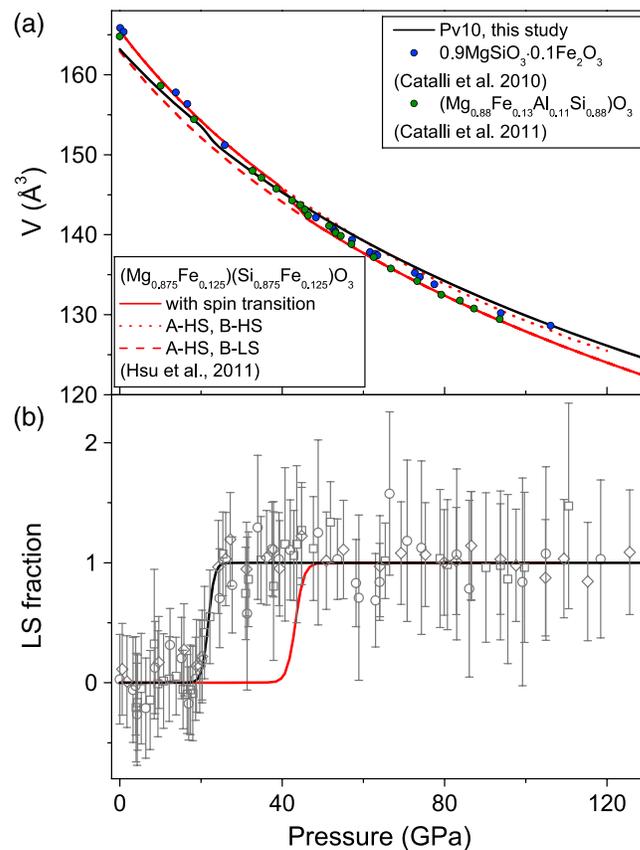


Figure 2. (a) Pressure-volume relations and (b) low-spin fraction of silicate bridgmanite (Pv10) compared with previous experimental and theoretical calculations. (a) Black line: Pv10, this study; red lines: $(\text{Mg}_{0.875}\text{Fe}_{0.125})(\text{Si}_{0.875}\text{Fe}_{0.125})\text{O}_3$ -bridgmanite [Hsu et al., 2011]; green and blue circles: experimental results [Catalli et al., 2010; Catalli et al., 2011] (Figure 2a). (b) Open square, circle, and diamonds: experimental LS fraction of Fe^{3+} in bridgmanite in the first, second, and third runs, respectively (this study); black lines: fitting results for the LS fraction of Fe^{3+} in bridgmanite (this study); red line: theoretically calculated LS fraction of Fe^{3+} in Pv25 [Hsu et al., 2011] (Figure 2b).

Bengtson et al. [2008] predicted that the spin transition pressure of Fe^{3+} in bridgmanite is independent of the Fe content up to 25%, previous XRD and SMS measurements have shown that the onset pressure of the Fe^{2+} spin transition for ferropicriole and the Fe^{3+} spin transition for bridgmanite increases with the Fe content [Catalli et al., 2010, 2011; Fei et al., 2007b; Jackson et al., 2005; Lin et al., 2012]. The onset pressure of the spin transition could be much lower than that in literature reports because of much lower Fe^{3+} content in our bridgmanite [Catalli et al., 2010, 2011; Hsu et al., 2011; Tsuchiya and Wang, 2013]. It is also worth noting that Fe^{3+} enters the lower mantle bridgmanite either by the coupled substitution of Mg^{2+} and Si^{4+} by Al^{3+} and Fe^{3+} or the self-disproportionation of Fe^{2+} to Fe^{3+} plus metallic iron [Frost et al., 2004; Hummer and Fei, 2012; Zhang and Oganov, 2006]. Although the lower mantle Fe^{3+} in bridgmanite could be as high as 60% [$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$], most of the Fe^{3+} will be located in the A site, while only a small amount of Fe^{3+} could be in the B site [Ballaran et al., 2012; Frost et al., 2004; Hummer and Fei, 2012; McCammon, 1997]. This will be particularly true when the dissolution of Al-bearing majorite into Al-bearing bridgmanite occurs at pressures of 25–30 GPa of the top lower mantle [Irifune et al., 2010]. A previous study has shown that the amount of Al will increase in bridgmanite at the pressure of the top lower mantle together with an increase in the Fe content with the coupled substitution [Irifune et al., 2010]. Since Al will be located in the B site of bridgmanite, the addition of Fe^{3+} in bridgmanite at the top lower mantle will be mainly located in the A site. Fe^{3+} in the B site of bridgmanite is thus significantly limited by the addition of Al in bridgmanite. Since the amount

et al., 2010, 2011]. In order to better understand the effects of the B site Fe^{3+} spin transition on the EoS parameters of Fe-bearing bridgmanite, we have used bridgmanite samples which were presynthesized from enstatite powder using the large-volume pressure. The spin and valence states of Fe as well as chemical homogeneity of the bridgmanite sample have been characterized using Mössbauer spectroscopy, X-ray diffraction, and electron microprobe analyses at ambient conditions, while synchrotron Mössbauer spectroscopy results of the sample at high pressures have revealed the B site Fe^{3+} spin transition at approximately 13–24 GPa that can be directly combined with our EoS data. We should note that although there have been a number of previous in situ studies on the spin and valence states of iron and their effects on the EoS of bridgmanite, some of these previous studies had used bridgmanite samples synthesized using laser heating from polycrystalline enstatite or glass starting samples [Catalli et al., 2010, 2011], which could develop rather complex chemistry and iron valence states due to laser heating conditions.

The onset pressure of the spin transition could be much lower than that in literature reports because of much lower Fe^{3+} content in our bridgmanite (Figure 2) [Catalli et al., 2010, 2011; Hsu et al., 2011; Tsuchiya and Wang, 2013]. Although

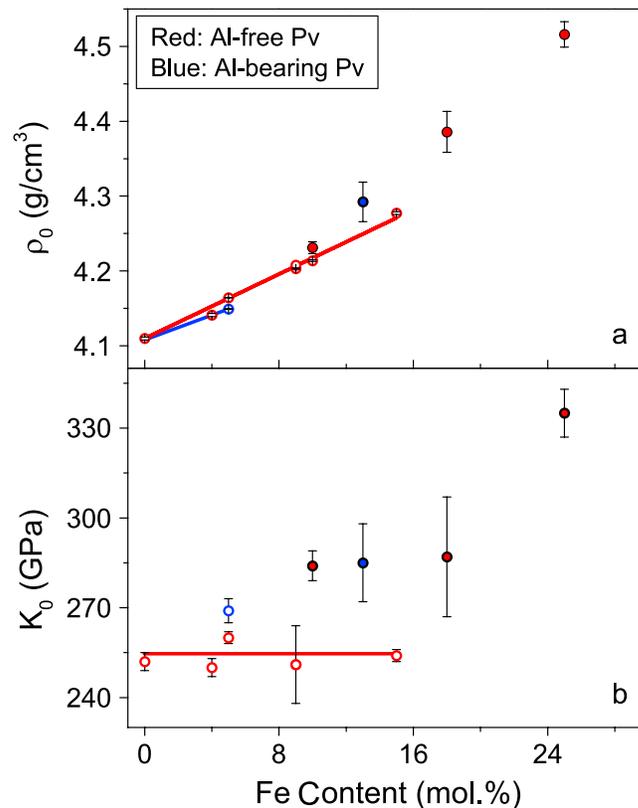


Figure 3. (a) Density, ρ_0 , and (b) bulk modulus, K_0 , of bridgmanite at ambient conditions. Red open circles and line: Al-free bridgmanite in literature without an apparent abnormal change in the P - V data [Ballaran *et al.*, 2012; Dorfman *et al.*, 2013; Fiquet *et al.*, 2000; Lundin *et al.*, 2008]; red solid circles: Al-free bridgmanite with LS Fe³⁺ (this study) [Catalli *et al.*, 2010; Mao *et al.*, 2011b]; blue open circles and line: Al-bearing bridgmanite without an apparent abnormal change in the P - V data [Andraut *et al.*, 2001]; blue solid circles: Al-bearing bridgmanite with LS Fe³⁺ [Catalli *et al.*, 2011]. Results for bridgmanite with LS Fe³⁺ are derived using experimental data at pressures above the spin transition (this study) [Catalli *et al.*, 2010, 2011; Mao *et al.*, 2011b]. Errors are smaller than symbols when not shown.

2001; Lundin *et al.*, 2008]. On the other hand, the use of the Fe³⁺-containing starting material may also promote the presence of LS B site Fe³⁺ [Catalli *et al.*, 2010, 2011]. Mao *et al.* [2011b] reported the observation of LS B site Fe³⁺ in the Fe-enriched bridgmanite. Although Dorfman *et al.* [2013] studied two Fe-rich bridgmanite, the spin and valence states of Fe in their synthesized bridgmanite samples were unknown. The pressure-temperature dependent substitution mechanism of Fe in the bridgmanite's lattice, such as the charge-coupled substitution, vacancies, and/or charge transfer, together with the starting material on the spin states of Fe in bridgmanite remains to be further investigated in future studies.

We have further examined the effect of Fe content on the density (ρ_0) and bulk modulus (K_0) of bridgmanite at ambient conditions (Figure 3 and supporting information Figure S4 and Table S2) [Andraut *et al.*, 2001; Ballaran *et al.*, 2012; Catalli *et al.*, 2010, 2011; Dorfman *et al.*, 2013; Lundin *et al.*, 2008; Mao *et al.*, 2011b]. Although Dorfman *et al.* [2013] reported the EoS of bridgmanite with up to 74% Fe, we focus on the Fe-dilute systems in Figure 3 because of the coexistence of bridgmanite with other Fe-bearing phases in Dorfman *et al.* [2013], which could lead to the depletion of Fe in their synthesized bridgmanite. Here the Fe content defined as Fe/(Fe + Mg) refers to the total molar percentage of Fe. It is worth noting that a long-standing problem in comparing the equation of state parameters of mantle minerals to literature results is that different studies use different pressure calibrants and scales. Although most previous studies for the EoS of bridgmanite used Au as the pressure calibrant, which is different from the Pt calibrant used here, we have recalculated the pressure in literature using the Au

of B site Fe³⁺ in the lower mantle bridgmanite is low, the onset pressure of the Fe³⁺ spin transition could also be low in the lower mantle, similar to that shown in our study [Catalli *et al.*, 2010, 2011; Hsu *et al.*, 2011; Tsuchiya and Wang, 2013].

We have noted that the spin transition of Fe³⁺ in the B site of bridgmanite has only been reported in a few high-pressure studies which used powder bridgmanite samples synthesized at high pressures using Fe³⁺-bearing material or Fe-rich material as the starting sample in laser-heated DACs for XRD and/or SMS experiments, in which the SMS results play a critical role in identifying the LS Fe³⁺ in the synthesized bridgmanite [Catalli *et al.*, 2010, 2011; Mao *et al.*, 2011b]. In single-crystal studies, Fe³⁺ tends to be located in the large A site in bridgmanite [Ballaran *et al.*, 2012; Glazyrin *et al.*, 2014; Potapkin *et al.*, 2013]. It is possible that the substitution of Fe³⁺ in the octahedral sites in bridgmanite powder samples is related to the starting material, synthesis conditions, and/or pressure-temperature environments of the experiments. Even with an Fe²⁺-bearing starting material, polycrystalline bridgmanite synthesized at large-volume pressure which is in a more O₂ open environment may be more likely to have LS Fe³⁺ than that synthesized in DACs [Andraut *et al.*,

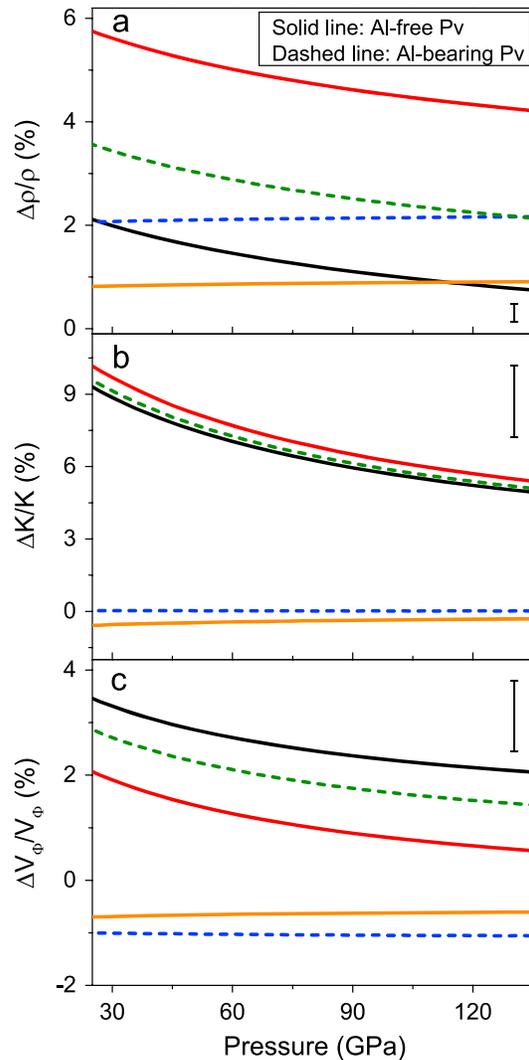


Figure 4. (a) Variation of density, (b) bulk modulus, and (c) bulk sound velocity of bridgmanite at lower mantle pressures using MgSiO_3 bridgmanite as the reference. Solid lines: Al-free bridgmanite; dashed lines: Al-bearing bridgmanite; orange line: Al-free bridgmanite with 4 mol % Fe [Ballaran et al., 2012]; black line: Al-free bridgmanite with the LS Fe^{3+} (Pv10), this study; red line: Al-free bridgmanite with the LS Fe^{3+} [Catalli et al., 2010]; blue dashed line: $(\text{Mg}_{0.9}\text{Fe}_{0.1})(\text{Al}_{0.1}\text{Si}_{0.9})\text{O}_3$ bridgmanite without the LS Fe^{3+} ; green dashed line: Al-bearing bridgmanite with the LS Fe^{3+} [Catalli et al., 2011].

system, the density of Al-bearing bridgmanite is slightly lower than that of Al-free bridgmanite with the same Fe content [Andraut et al., 2001]. The relationship between K_0 and the Fe content is difficult to be evaluated quantitatively because only Andraut et al. [2001] studied the EoS of bridgmanite in the Al-dilute system. It is interesting to note that Glazyrin et al. [2014] studied the EoS of Fe^{3+} - and Al^{3+} -enriched bridgmanite at lower mantle pressure and temperature conditions. Addition of Fe^{3+} in the A site together with the presence of Al^{3+} in the B site can result in a great reduction in K_0 , indicating the importance of exploring the effect of oxidation state on the EoS of lower mantle bridgmanite in future studies [Glazyrin et al., 2014]. In contrast, the spin transition of the B site Fe^{3+} can cause an increase in both ρ_0 and K_0 in Al-bearing bridgmanite, which is similar to that shown in Al-free bridgmanite [Catalli et al., 2011].

pressure scale in Fei et al. [2007a], which reported an internally consistent pressure scale for Pt and Au (Table S2 in the supporting information) Catalli et al., 2010, 2011; Dorfman et al., 2013; Lundin et al., 2008; Mao et al., 2011b). In addition, Andraut et al. [2001] and Ballaran et al. [2012] used Ruby as the pressure calibrant. Pressures in these two studies were recalibrated using the pressure scales from Dewaele et al. [2004], which is in a good agreement with the metal pressure scales in Fei et al. [2007a]. Relevant literature P - V data were reanalyzed using a third-order Birch-Murnaghan EoS with a fixed $K_0' = 4$ in order to have a more consistent, direct comparison of ρ_0 and K_0 from different studies (Table S2 in the supporting information and Figure 3). The term ρ_0 is directly measured by XRD in most previous studies, although these studies did not report the spin transition of Fe^{3+} in bridgmanite [Andraut et al., 2001; Ballaran et al., 2012; Lundin et al., 2008]. For bridgmanite with the LS B site Fe^{3+} , ρ_0 is derived by fitting the experimental P - V data using the third-order Birch-Murnaghan EoS, which suffers from a well-known trade-off between the derived K_0 and K_0' values [Catalli et al., 2010, 2011; Mao et al., 2011b]. The confidence ellipses are constructed for bridgmanite with the LS B site Fe^{3+} to better understand the trade-off between the derived ρ_0 (V_0) and K_0 values (Figure S5 in the supporting information).

For Al-free bridgmanite without abnormal changes in the P - V data, ρ_0 linearly increases with the Fe content, while K_0 is independent of the Fe content when taking the uncertainties into consideration (Figure 3). The spin transition of the B site Fe^{3+} in bridgmanite is found to enhance ρ_0 and K_0 to above the linear relation. The increase in ρ_0 of our Pv10 is less than that in Catalli et al. [2010] and Mao et al. [2011b], which could be due to a lower LS Fe^{3+} content in our Pv10. Because of limited experimental studies available, ρ_0 and K_0 of Al-bearing bridgmanite are not as well constrained as those in the Al-free counterparts [Andraut et al., 2001; Ballaran et al., 2012; Catalli et al., 2011; Glazyrin et al., 2014]. In the Al-dilute

We have modeled the variation of ρ , K , and bulk sound velocity (V_{Φ}) of bridgmanite at lower mantle pressures and 300 K using MgSiO_3 bridgmanite as the reference (Figure 4) (see supporting information for details). For Al-free bridgmanite without abnormal changes in the P - V data, the difference in density between Al free and MgSiO_3 bridgmanite is almost constant with pressure because K_0 is independent of Fe content (Figure 4). Since the spin transition of the B site Fe^{3+} increases the stiffness of bridgmanite, the difference in density between bridgmanite with the LS Fe^{3+} and MgSiO_3 end-member exhibits a decrease with increasing pressure. At pressures corresponding to the lowermost mantle, ρ of our Pv10 with the LS Fe^{3+} is undistinguishable from that of Pv4 within uncertainties of the EoS modeling [Ballaran *et al.*, 2012]. Furthermore, raising the amount of the LS Fe^{3+} in bridgmanite may increase the density difference between the Fe-bearing and MgSiO_3 end-members (Figure 4) [Catalli *et al.*, 2010]. On the other hand, K and V_{Φ} of our Pv10 with the LS Fe^{3+} in the B site are 6–9(\pm 3)% and 2–3.5(\pm 1.5)% greater than those of MgSiO_3 bridgmanite at lower mantle pressures, respectively (Figure 4). These values are also much greater than that of Al-free bridgmanite in literature which does not clearly exhibit an abnormal change in the unit cell volume at high pressures. To better understand the effect of Fe and Al on the EoS of bridgmanite, we also compute the variation of ρ , K , and V_{Φ} of $(\text{Mg}_{0.9}\text{Fe}_{0.1})(\text{Al}_{0.1}\text{Si}_{0.9})\text{O}_3$ bridgmanite. In the analyses, we assumed that all of the Fe was in the HS state, the same K_0 as the MgSiO_3 end-member, and used the linear relation in Figure 3 to derive the density. Comparing the variation of ρ , K , and V_{Φ} of $(\text{Mg}_{0.9}\text{Fe}_{0.1})(\text{Al}_{0.1}\text{Si}_{0.9})\text{O}_3$ bridgmanite without the LS Fe^{3+} to results in Catalli *et al.* [2011] provides a first-order estimation on the effect of LS Fe^{3+} in Al-bearing bridgmanite. It is shown that Al-bearing bridgmanite with the LS Fe^{3+} in the B site also has a greater ρ , K , and V_{Φ} at lower mantle pressures than bridgmanite without the LS Fe^{3+} at lower mantle pressures (Figure 4). Since the EoS of the Al-bearing bridgmanite is not as well constrained as the Fe-bearing ones, more reliable data are needed in the future to provide a better understanding of the combined effects of Fe spin state as well as Fe and Al content on the density profiles and velocity structures of the lower mantle.

Our study here has shown that the spin transition of Fe^{3+} can cause a sudden reduction in the volume and an increase in the bulk modulus of lower mantle bridgmanite, which is consistent with recent theoretical predictions. Using a well-characterized bridgmanite sample by combining XRD, conventional Mössbauer spectroscopy, and SMS allows us to better constrain the spin and valence states of Fe in bridgmanite and understand the effect of spin transition on the density and bulk modulus of bridgmanite. Based on our current understanding of the phase diagram of the (Al,Fe)-bearing MgSiO_3 - Mg_2SiO_4 system at mantle P - T conditions, bridgmanite starts to contain a more significant amount of Al at pressures above approximately 28 GPa where majoritic garnet, the major host of Al in the transition zone and very top of the lower mantle, becomes unstable and forms solid solution with bridgmanite [Irfune *et al.*, 2010]. Therefore, it is possible that the B site Fe^{3+} can exist in the bridgmanite's lattice at conditions of the topmost lower mantle but would become much less abundant at higher pressures when Al extensively dissolves into the bridgmanite. The effects of the spin transition of B site Fe^{3+} in bridgmanite observed here are thus most applicable to understand the properties of the topmost lower mantle, where the spin transition can lead to more enhanced density and elevated bulk sound velocity in bridgmanite than previously thought for a high-spin bridgmanite. However, if the amount of B site Fe^{3+} in the lower mantle bridgmanite is less than that in our bridgmanite sample containing 20% B site Fe^{3+} , the effect of Fe^{3+} spin transition on the density and bulk sound velocity of bridgmanite could be greatly reduced or even become negligible geophysically. Future studies are expected to explore how the Fe^{3+} content and temperature affects the onset pressure of the spin transition and the thermoelastic properties of bridgmanite, which is of particular importance for understanding the density states, velocity structure, and dynamic behaviors of the lower mantle.

Acknowledgments

We acknowledge J. Liu for experimental assistance and M. Matheny, L. A. Kuang, and L. Dafov for editing the manuscript. We thank GSECARS, HPCAT, APS, and ANL for providing X-ray diffraction facilities for the study. Z.M. acknowledges financial support from the National Natural Science Foundation of China (41374092) and the Fundamental Research Funds for the Central Universities in China (WK2080000052). J.F.L. acknowledges financial support from the U.S. National Science Foundation (EAR-0838221 and EAR-1053446) and the Carnegie/DOE Alliance Center (CDAC). APS is supported by DOE-BES, under contract DE-AC02-06CH11357. GeoSoilEnviroCARS is supported by the National Science Foundation—Earth Sciences (EAR-1128799) and Department of Energy Geosciences (DE-FG02-94ER14466). Experimental data and parameters for modeling Figures 3 and 4 are available in the supporting information.

The Editor thanks an anonymous reviewer for assisting in the evaluation of this paper.

References

- Andrault, D., N. Bolfan-Casanova, and N. Guignot (2001), Equation of state of lower mantle (Al,Fe)- MgSiO_3 perovskite, *Earth Planet. Sci. Lett.*, *193*, 501–508.
- Badro, J., G. Fiquet, F. Guyot, J. P. Rueff, V. V. Struzhkin, G. Vanko, and G. Monaco (2003), Iron partitioning in Earth's mantle: Toward a deep lower mantle discontinuity, *Science*, *300*, 789–791.
- Badro, J., J. P. Rueff, G. Vanko, G. Monaco, G. Fiquet, and F. Guyot (2004), Electronic transitions in perovskite: Possible nonconvecting layers in the lower mantle, *Science*, *305*, 383–386.
- Ballaran, T. B., A. Kurnosov, K. Glazyrin, D. J. Frost, M. Merlini, M. Hanfland, and R. Caracas (2012), Effect of chemistry on the compressibility of silicate perovskite in the lower mantle, *Earth Planet. Sci. Lett.*, *333*, 181–190.
- Bengtson, A., K. Persson, and D. Morgan (2008), *Ab initio* study of the composition dependence of the pressure-induced spin crossover in perovskite $(\text{Mg}_{1-x}\text{Fe}_x)\text{SiO}_3$, *Earth Planet. Sci. Lett.*, *265*, 535–545.

- Bengtson, A., J. Li, and D. Morgan (2009), Mössbauer modeling to interpret the spin state of iron in (Mg,Fe)SiO₃ perovskite, *Geophys. Res. Lett.*, *36*, L15301, doi:10.1029/2009GL038340.
- Cammarano, F., and B. Romanowicz (2007), Insights into the nature of the transition zone from physically constrained inversion of long-period seismic data, *Proc. Natl. Acad. Sci. U.S.A.*, *104*, 9139–9144.
- Catalli, K., S. H. Shim, V. B. Prakapenka, J. Y. Zhao, W. Sturhahn, P. Chow, Y. M. Xiao, H. Z. Liu, H. Cynn, and W. J. Evans (2010), Spin state of ferric iron in MgSiO₃ perovskite and its effect on elastic properties, *Earth Planet. Sci. Lett.*, *289*, 68–75.
- Catalli, K., S. H. Shim, P. Dera, V. B. Prakapenka, J. Y. Zhao, W. Sturhahn, P. Chow, Y. M. Xiao, H. Cynn, and W. J. Evans (2011), Effects of the Fe³⁺ spin transition on the properties of aluminous perovskite—New insights for lower-mantle seismic heterogeneities, *Earth Planet. Sci. Lett.*, *310*, 293–302.
- Crowhurst, J. C., J. M. Brown, A. F. Goncharov, and S. D. Jacobsen (2008), Elasticity of (Mg,Fe)O through the spin transition of iron in the lower mantle, *Science*, *319*, 451–453.
- Dewaele, A., P. Loubeyre, and M. Mezouar (2004), Equations of state of six metals above 94 GPa, *Phys. Rev. B*, *70*, 094112.
- Dorfman, S., Y. Meng, V. Prakapenka, and T. S. Duffy (2013), Effect of Fe-enrichment on the equation of state and stability of (Mg,Fe)SiO₃ perovskite, *Earth Planet. Sci. Lett.*, *361*, 246–257.
- Fei, Y. W., A. Ricolleau, M. Frank, K. Mibe, G. Y. Shen, and V. Prakapenka (2007a), Toward an internally consistent pressure scale, *Proc. Natl. Acad. Sci. U.S.A.*, *104*, 9182–9186.
- Fei, Y. W., L. Zhang, A. Corgne, H. Watson, A. Ricolleau, Y. Meng, and V. Prakapenka (2007b), Spin transition and equations of state of (Mg,Fe)O solid solutions, *Geophys. Res. Lett.*, *34*, L17307, doi:10.1029/2007GL030712.
- Fiquet, G., A. Dewaele, D. Andraut, M. Kunz, and T. Le Bihan (2000), Thermoelastic properties and crystal structure of MgSiO₃ perovskite at lower mantle pressure and temperature conditions, *Geophys. Res. Lett.*, *27*, 21–24, doi:10.1029/1999GL008397.
- Frost, D. J., C. Liebske, F. Langenhorst, C. A. McCammon, R. G. Tronnes, and D. C. Rubie (2004), Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle, *Nature*, *428*, 409–412.
- Glazyrin, K., T. B. Ballaran, D. J. Frost, C. McCammon, A. Kantor, M. Merlini, M. Hanfland, and L. Dubrovinsky (2014), Magnesium silicate perovskite and effect of iron oxidation state on its bulk sound velocity at the conditions of the lower mantle, *Earth Planet. Sci. Lett.*, *393*, 182–186.
- Goncharov, A. F., V. V. Struzhkin, and S. D. Jacobsen (2006), Reduced radiative conductivity of low-spin (Mg, Fe)O in the lower mantle, *Science*, *312*, 1205–1208.
- Hsu, H., K. Umamoto, P. Blaha, and R. M. Wentzcovitch (2010), Spin states and hyperfine interactions of iron in (Mg,Fe)SiO₃ perovskite under pressure, *Earth Planet. Sci. Lett.*, *294*, 19–26.
- Hsu, H., P. Blaha, M. Cococcioni, and R. M. Wentzcovitch (2011), Spin-state crossover and hyperfine interactions of ferric iron in MgSiO₃ perovskite, *Phys. Rev. Lett.*, *106*, 118501.
- Hsu, H., Y. G. Yu, and R. M. Wentzcovitch (2012), Spin crossover of iron in aluminous MgSiO₃ perovskite and post-perovskite, *Earth Planet. Sci. Lett.*, *359–360*, 34–39.
- Hummer, D. R., and Y. W. Fei (2012), Synthesis and crystal chemistry of Fe³⁺-bearing (Mg,Fe³⁺)(Si,Fe³⁺)O₃ perovskite, *Am. Mineral.*, *97*, 1915–1921.
- Irfune, T., T. Shinmei, C. A. McCammon, N. Miyajima, D. C. Rubie, and D. J. Frost (2010), Iron partitioning and density changes of pyrolyte in Earth's lower mantle, *Science*, *327*, 193–195.
- Jackson, J. M., W. Sturhahn, G. Y. Shen, J. Y. Zhao, M. Y. Hu, D. Errandonea, J. D. Bass, and Y. W. Fei (2005), A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO₃ perovskite up to 120 GPa, *Am. Mineral.*, *90*, 199–205.
- Lin, J. F., V. V. Struzhkin, S. D. Jacobsen, M. Y. Hu, P. Chow, J. Kung, H. Z. Liu, H. K. Mao, and R. J. Hemley (2005), Spin transition of iron in magnesiowüstite in the Earth's lower mantle, *Nature*, *436*, 377–380.
- Lin, J. F., E. E. Alp, Z. Mao, T. Inoue, C. McCammon, Y. M. Xia, P. Chow, and J. Y. Zhao (2012), Electronic spin states of ferric and ferrous iron in the lower-mantle silicate perovskite, *Am. Mineral.*, *97*, 592–597.
- Lin, J. F., S. Speziale, Z. Mao, and H. Marquardt (2013), Effects of the electronic spin transitions of iron in lower-mantle minerals: Implications to deep-mantle geophysics and geochemistry, *Rev. Geophys.*, *51*, 244–275, doi:10.1002/rog.20010.
- Lundin, S., K. Catalli, J. Santillan, S. H. Shim, V. B. Prakapenka, M. Kunz, and Y. Meng (2008), Effect of Fe on the equation of state of mantle silicate perovskite over 1 Mbar, *Phys. Earth Planet. Inter.*, *168*(1–2), 97–102.
- Mao, Z., J. F. Lin, C. Jacobs, H. C. Watson, Y. Xiao, P. Chow, E. E. Alp, and V. B. Prakapenka (2010), Electronic spin and valence states of Fe in CaIrO₃-type silicate post-perovskite in the Earth's lowermost mantle, *Geophys. Res. Lett.*, *37*, L22304, doi:10.1029/2010GL045021.
- Mao, Z., J. F. Lin, J. Liu, and V. B. Prakapenka (2011a), Thermal equation of state of lower-mantle ferropericlasite across the spin crossover, *Geophys. Res. Lett.*, *38*, L23308, doi:10.1029/2011GL049915.
- Mao, Z., J. F. Lin, H. P. Scott, H. C. Watson, V. B. Prakapenka, Y. Xiao, P. Chow, and C. McCammon (2011b), Iron-rich perovskite in the Earth's lower mantle, *Earth Planet. Sci. Lett.*, *309*, 179–184.
- Mao, Z., et al. (2014), (Fe, Al)-bearing post-perovskite in the Earth's lower mantle, *Earth Planet. Sci. Lett.*, *403*, 157–165.
- McCammon, C. (1997), Perovskite as a possible sink for ferric iron in the lower mantle, *Nature*, *387*, 694–696.
- McCammon, C., I. Kantor, O. Narygina, J. Rouquette, U. Ponkratz, I. Sergueev, M. Mezouar, V. Prakapenka, and L. Dubrovinsky (2008), Stable intermediate-spin ferrous iron in lower-mantle perovskite, *Nat. Geosci.*, *1*, 684–687.
- Potapkin, V., et al. (2013), Effect of iron oxidation state on the electrical conductivity of the Earth's lower mantle, *Nat. Commun.*, *4*, doi:10.1038/ncomms2436.
- Ringwood, A. E. (1975), *Composition and Petrology of the Earth's Mantle*, 618 pp., McGraw-Hill, New York.
- Sinmyo, R., G. Pesce, E. Greenberg, C. McCammon, and L. Dubrovinsky (2014), Lower mantle electrical conductivity based on measurements of Al, Fe-bearing perovskite under lower mantle conditions, *Earth Planet. Sci. Lett.*, *393*, 165–172.
- Tsuchiya, T., and X. Wang (2013), Ab initio investigation on the high-temperature thermodynamic properties of Fe³⁺-bearing MgSiO₃ perovskite, *J. Geophys. Res. Solid Earth*, *118*, 83–91, doi:10.1029/2012JB009696.
- Tsuchiya, T., R. M. Wentzcovitch, C. R. S. da Silva, and S. de Gironcoli (2006), Spin transition in magnesiowüstite in Earth's lower mantle, *Phys. Rev. Lett.*, *96*, 198501.
- Wentzcovitch, R. M., J. F. Justo, Z. Wu, C. R. S. da Silva, D. A. Yuen, and D. Kohlstedt (2009), Anomalous compressibility of ferropericlasite throughout the iron spin cross-over, *Proc. Natl. Acad. Sci. U.S.A.*, *106*(21), 8447–8452.
- Zhang, F. W., and A. R. Oganov (2006), Mechanisms of Al³⁺ incorporation in MgSiO₃ post-perovskite at high pressures, *Earth Planet. Sci. Lett.*, *248*(1–2), 69–76.