

Single-Crystal X-ray Diffraction on the Structure of (Al,Fe)-bearing Bridgmanite in the Lower Mantle

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Abstract

The lattice parameters of (Al,Fe)-bearing bridgmanite, the most abundant lower-mantle mineral, are fundamental to our understanding of its thermoelastic and transport properties at high pressure and temperature (P-T). However, due to the complexity of Fe and Al substitution as well as the spin and valence states of Fe in the structure of bridgmanite, experimental refinements on its atomic positions are rather limited to relatively low pressure and/or to compositions not as relevant to the lower mantle. Here, we have performed single-crystal X-ray diffraction (SCXRD) experiments on two high-quality crystal platelets of (Al,Fe)-bearing bridgmanite ($\text{Mg}_{0.88}\text{Fe}^{3+}_{0.065}\text{Fe}^{2+}_{0.035}\text{Al}_{0.03}$)($\text{Al}_{0.11}\text{Si}_{0.90}$) O_3 (Fe10-Al14-Bgm), up to 64.6 GPa at room temperature in a Boehler-Almax type diamond anvil cell (DAC). Refinements on the collected SCXRD patterns reveal reliable structural information of single-crystal Fe10-Al14-Bgm, including unit-cell parameters, atomic coordinates, and anisotropic displacement parameters. The axial compressibility of Fe10-Al14-Bgm behaves a trend of $a > c > b$. Single-crystal refinements show that our sample contains ~6.5 mol% Fe^{3+} , 3.5 mol% Fe^{2+} , and 3 mol%

Al³⁺ in the large pseudo-dodecahedral site (A site), and ~11 mol% Al³⁺ in the small octahedral site (B site). This suggests that Al³⁺ preferentially occupies the B site and the excess Al³⁺ together with Fe ions stay in the A site in (Al,Fe)-bearing bridgmanite. Our results show that the primary pressure response of Fe10-Al14-Bgm structure is the compression of AO₈ polyhedra and BO₆ octahedra with monotonical decreases in A-O and B-O bonds. Further calculations indicate that the interatomic angles of B-O1-B and B-O2-B decrease from 145.2-145.8° at 4.2 GPa to 143.3-143.5° at 64.6 GPa. Quantitative analyses on two distortion-related parameters, the observed tolerance factor (t_{obs}) and octahedral tilting angles (Φ), show that t_{obs} decreases and Φ increases smoothly with pressure. These results indicate an increased distortion of the Fe10-Al14-Bgm structure with pressure, which might be related to the distortion of A-site Fe²⁺. The local environmental changes of A-site Fe²⁺ in bridgmanite could help explain previous results on the hyperfine parameters, abnormal lattice thermal conductivity, mean force constant of iron bonds and other physical properties, which in turn provide insights into our understanding on the geophysics and geochemistry of the planet.

Keywords: (Al,Fe)-bearing bridgmanite, crystal structure, single-crystal X-ray diffraction, lower mantle, high pressure

INTRODUCTION

Bridgmanite, (Mg,Fe)(Si,Al)O₃, is believed to be the most abundant mineral in the lower mantle, ranging from 75 to 90 vol% (Irifune et al., 2010; Murakami et al., 2012; Ringwood, 1975). Under the lower-mantle P-T conditions, bridgmanite has an orthorhombic structure with a space group of *Pbnm* (Liu, 1974). Extensive experimental studies have shown that about 10 mol% Fe and Al could be incorporated into the structure of bridgmanite in the lower mantle via two crystallographic occupancy sites: the large pseudo-dodecahedral Mg²⁺ site (A site) and the small octahedral Si⁴⁺ site (B site) (Horiuchi et al., 1987; Irifune et al., 2010; Lin et al., 2016;

Ringwood, 1975). Current consensus is that Fe^{3+} can occupy both A and B sites, while Fe^{2+} will only exist in A site (Hirose et al., 2017; Lin et al., 2013; Shukla and Wentzcovitch, 2016). However, the incorporation of Al^{3+} into bridgmanite further complicates the site occupancy and studies suggested a charge-coupled substitution of $\text{Mg}_A^{2+} + \text{Si}_B^{4+} \leftrightarrow \text{Fe}_A^{3+} + \text{Al}_B^{3+}$, where Al^{3+} replaces Si^{4+} to occupy the B site and Fe^{3+} enters the A site (e.g., Huang et al., 2021; Hummer and Fei, 2012; Lin et al., 2016). Due to the compositional and structural complexities as well as Fe valence states, direct experimental refinements on atomic structures of (Al,Fe)-bearing bridgmanite with a composition relevant to the lower-mantle mineralogical model at high pressure are still rare.

The technical development of miniature diamond anvil cells (DACs) with a large optical opening (above 70°) coupled with synchrotron single-crystal X-ray diffraction(SCXRD) method (Boehler, 2006; Kantor et al., 2012) allows some studies to resolve the high-pressure structure of bridgmanite (Dubrovinsky et al., 2010; Fiquet and Reynard, 1999; Ismailova et al., 2016; Ross et al., 1990; Sugahara et al., 2006; Vanpeteghem et al., 2006). Pure MgSiO_3 bridgmanite end member has shown to experience an increased structure distortion with pressure up to 15 GPa at 300 K (Ross et al., 1990; Sugahara et al., 2006). Furthermore, Dubrovinsky et al. (2010) examined the crystal structure of single-crystal (Al,Fe)-rich bridgmanite, $(\text{Mg}_{0.62}\text{Fe}_{0.38})(\text{Al}_{0.36}\text{Si}_{0.64})\text{O}_3$ (Fe38-Al36-Bgm), up to 84.1 GPa at room temperature, suggesting that the enrichment of Fe and Al in bridgmanite would greatly increase its unit-cell lattices as well as the degree of distortion. Ismailova et al. (2016) reported the synthesis of single-crystal $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{Al}_{0.06}\text{Si}_{0.94}\text{O}_3$ (Fe17-Al6-Bgm), $\text{Mg}_{0.86}\text{Fe}_{0.14}\text{Al}_{0.04}\text{Si}_{0.96}\text{O}_3$ (Fe14-Al4-Bgm), and $\text{Fe}^{2+}_{0.64}\text{Fe}^{3+}_{0.24}\text{SiO}_3$ bridgmanite as well as crystal structure refinements up to 130 GPa. Considering the relevant pressure-temperature and compositional (P-T-X) conditions in the lower mantle (23-130 GPa, 1800-2500 K, and ~10 mol% Fe and Al in bridgmanite) (Irifune et al., 2010; Katsura et al., 2010; Ringwood, 1975),

it is thus critical to investigate the single-crystal structures of bridgmanite with a lower-mantle relevant composition. However, the quantitative understanding of the Fe and Al effects of the atomic structures of bridgmanite with a composition relevant to the lower mantle requires high-quality single crystals for the high-pressure structural refinements which are still lacking.

Experimental and theoretical studies have indicated that Fe ions, potentially occupying A and B crystallographic sites of bridgmanite, can have different electronic spin and valence states at high pressure, which can affect its chemical and physical properties (Catalli et al., 2011; Catalli et al., 2010; Dorfman et al., 2015; Hsu et al., 2011; Hsu et al., 2010; Hsu et al., 2012; Lin et al., 2008; Mao et al., 2017; Shukla et al., 2016; Tsuchiya and Wang, 2013). For instance, the B-site Fe^{3+} in bridgmanite is shown to undergo a high-spin to low-spin transition at 40-60 GPa, which is associated with an abrupt volume collapse and a drastic softening in compressional wave velocity (Catalli et al., 2011; Catalli et al., 2010; Fu et al., 2018; Hsu et al., 2011; Lin et al., 2012; Mao et al., 2015; Shukla et al., 2016). In contrast, both Fe^{2+} and Fe^{3+} in the A-site remain in the high-spin state throughout the lower-mantle pressure (Dorfman et al., 2015; Hsu et al., 2010; Li et al., 2004; Lin et al., 2016; Shukla et al., 2015). In contrast to the A-site Fe^{3+} , the A-site Fe^{2+} in Fe-bearing bridgmanite displays extremely high quadrupole splitting (QS) at pressures above ~20 GPa, which has been attributed to the local site distortion (Hsu et al., 2011; Hsu et al., 2010; Jackson et al., 2005; Mao et al., 2017). Some earlier studies using X-ray emission and Mossbauer results suggested the occurrence of the intermediate-spin state in the A-site Fe^{2+} (Lin et al., 2008; McCammon et al., 2010; Narygina et al., 2010), but the high QS value of the A-site Fe^{2+} was theoretically suggested to result from the lattice distortion (Hsu et al., 2011).

The changes in the A site configuration can not only influence the aforementioned hyperfine parameters, but also other physical properties of bridgmanite at high pressure. For instance, Yang et al. (2019) found a drastic softening of 21% in mean force constants of iron

bonds in Fe-bearing and (Al,Fe)-bearing bridgmanite at 40-60 GPa from nuclear resonant inelastic X-ray scattering measurements, which is attributed to the effect of the A-site distortion from low to high QS states. In addition, a recent study measured lattice thermal conductivity of bridgmanite up to 120 GPa at room temperature using laser pump-probe spectroscopy (Hsieh et al., 2017). The observed 20% drop of thermal conductivity in Fe-bearing bridgmanite at ~45 GPa could possibly result from the pressure-induced distortion of the A-site Fe^{2+} (Hsieh et al., 2017). However, atomistic scale evidence for these macroscopic-scale observations remains limited. Further quantitative analyses on the atomistic structure of (Al,Fe)-bearing bridgmanite, such as site occupancies of Fe ions and Al^{3+} and atomic coordinates, are required to provide insights into the physical properties of bridgmanite and to model lower-mantle geophysics and geodynamics (Garnero et al., 2007; Lin et al., 2013; Mao et al., 2017; Masters et al., 2000).

In this study, we have carried out SCXRD experiments on (Al,Fe)-bearing bridgmanite, $(\text{Mg}_{0.88}\text{Fe}^{3+}_{0.065}\text{Fe}^{2+}_{0.035}\text{Al}_{0.03})(\text{Al}_{0.11}\text{Si}_{0.90})\text{O}_3$ (Fe10-Al14-Bgm), up to 64.6 GPa using a Boehler-Almax type DAC with synchrotron radiations. The use of two crystal platelets allows us to collect up to 230-300 reflection peaks with intensities (I) of $I > 3\sigma(I)$ at each experimental pressure to derive its high-pressure lattice parameters and atomic coordinates. These data are analyzed to help understand site occupancies of Fe^{2+} , Fe^{3+} , and Al^{3+} in Fe10-Al14-Bgm as well as to determine its high-pressure structural variations, including bond lengths and angles, octahedral tilting, and degree of lattice distortion. These results could provide important clues for understanding the effect of local iron environment on the physical and chemical properties of bridgmanite.

EXPERIMENTAL DETAILS

High-quality (Al,Fe)-bearing bridgmanite was synthesized at ~24 GPa and ~1800 °C for 20 h in the presence of hydrous melt using the 5000-ton Kawai-type multi-anvil apparatus with

a run number of 5K2667 at the Institute for Planetary Materials at Okayama University. Details of sample synthesis and characterizations have been well documented in early studies (Fu et al., 2019; Fu et al., 2022). Further electron microprobe analysis and Mössbauer spectroscopy results show that the synthesized bridgmanite has a homogenous composition of $\text{Mg}_{0.88}\text{Fe}_{0.1}\text{Al}_{0.14}\text{Si}_{0.90}\text{O}_3$ (Fe10-Al14-Bgm) with $\text{Fe}^{3+}/\Sigma\text{Fe} \sim 0.65$ (Fu et al., 2019). Synchrotron XRD results on the sample show sharp diffraction spots with lattice parameters of $a = 4.7875(3)$ Å, $b = 4.9423(2)$ Å, $c = 6.9205(6)$ at ambient conditions in a $Pbnm$ space group, confirming its high quality for SCXRD experiments (Figure 1).

A short symmetric DAC equipped with a pair of 250- μm Boehler-Almax type anvils was used for high-pressure SCXRD experiments (Boehler, 2006). One anvil glued onto a cubic boron nitride (cBN) seat was used to face the upstream incident beam while the other anvil glued onto a tungsten-carbide seat with a large opening angle up to 70° (4θ) was used as the downstream side for diffraction collections. The upstream cBN seat absorbs a noticeable degree of X-rays and avoids producing powder diffraction signals from the backing plate (Dera et al., 2013). A 250- μm thick Re gasket was pre-indented to ~ 25 GPa or 25-30 μm thickness, and a hole with a diameter of 150 μm was drilled in the pre-indented area to be used as a sample chamber. Knowing that each bridgmanite platelet in the DAC can only give rise to certain parts of the reciprocal space of the crystal lattice, the use of several crystal platelets in different crystallographic orientations in single-crystal DAC experiments is highly desirable for collections of more reflection spots and thus better statistics in the structural refinements (Ross et al., 1990). Here, we double-side polished two random orientations of bridgmanite platelets that were $\sim 20 \mu\text{m} \times 20 \mu\text{m}$ big and $\sim 5\text{-}7 \mu\text{m}$ thick. These two clean platelets were loaded into the sample chamber, together with a piece of Au as pressure calibrant (Figure 1c insert). The Au and two bridgmanite platelets were intentionally placed as a triangular geometry to minimize pressure differences in the sample chamber during high-pressure experiments. Neon

was loaded into the sample chamber as a pressure medium using a gas loading system in the Mineral Physics Laboratory of the Department of Geological Sciences at the University of Texas at Austin.

In situ high-pressure synchrotron SCXRD experiments were performed on Fe₁₀-Al₁₄-Bgm up to 64.6 GPa with a pressure interval of ~3 GPa at the beamline 13ID-D GeoSoilEnviroCARS (GSECARS) of the Advanced Photon Source (APS), Argonne National Laboratory. An incident X-ray beam with an energy of 42 keV and a wavelength of 0.2952 Å was focused to a beam size of approximately 3 µm × 3 µm on the sample. Single-crystal XRD step-scan measurements were conducted on each platelet by rotating ±30° of the DAC about the vertical axis of the sample stage with a step size of 0.5° and an exposure time of 1 or 2 s/step. A total of 120 XRD frames were collected for each platelet by a Pilatus 1M CdTe detector at each experimental pressure. Pressures and pressure uncertainties were determined by measuring the unit-cell volume of Au right before and after each SCXRD measurement (Fei et al., 2007). These single-crystal patterns were processed for data reduction using the CrysAlisPro software (Diffraction, 2019). This procedure enables us to determine the lattice parameters, extract the intensity of each hkl reflection, and perform absorption corrections. Single-crystal refinements on the high-pressure atomic structure of Fe₁₀-14-Bgm were further carried out on the combined reflection datasets of two platelets by using the JANA software (Petříček et al., 2014). These structure refinements eventually resolve atomic coordinates and anisotropic displacement parameters of each atom in the sample (Table 1, supporting information cif files). Residual *R*-factor (*R* and *wR* in %) were used to evaluate the quality of the refinement, defined as:

$$R(\%) = \left[\frac{\sum |F_o^2 - F_c^2|}{\sum w F_o^2} \right]^{1/2} \times 100 \quad (1)$$

$$wR(\%) = \left[\frac{\sum w|F_o^2 - F_c^2|}{\sum wF_o^2} \right]^{1/2} \times 100 \quad (2)$$

where F_o and F_c are observed and calculated structure factor amplitudes, respectively, and w is a weighting factor (Figure 2 and Table 1). We used the VESTA software to view and graph the refined crystal structure of Fe10-Al14-Bgm at high pressure (Momma and Izumi, 2011).

RESULTS AND DATA ANALYSES

Figure 1 shows representative raw SCXRD patterns of both platelets ($\pm 30^\circ$) at ~ 52.7 GPa. The circular and round diffraction spots with an average FWHM of 0.07° - 0.10° confirm the high-quality of our single-crystal Fe10-Al14-Bgm without apparent development of cleavage or texture at high pressure with neon as a transmitting pressure medium. Our individual analyses on the total 120 XRD frames of each platelet using the CrysAlisPro software (Diffraction, 2019) show that both loaded platelets have high-quality reflections (Figure 2a) and similar unit-cell parameters ($<0.2\%$) at each experimental pressure. The obtained lattice parameters (a , b , c) and unit-cell volume (V) of Fe10-Al14-Bgm decrease monotonically with pressure up to 64.6(6) GPa (Table 1 and Figure 3). Third-order Birch-Murnaghan equation of state (EoS) is used to evaluate the high-pressure axial and bulk incompressibility of Fe10-Al14-Bgm. The best fits to pressure-volume (P - V) data yield $K_{T0} = 256 \pm 2$ GPa, $K'_{T0} = 4$ (fixed), or $K_{T0} = 259 \pm 4$ GPa, $K'_{T0} = 3.8 \pm 0.2$, with a fixed V_0 of $163.75(3) \text{ \AA}^3$.

Refinements were conducted to resolve the structure of single-crystal Fe10-Al14-Bgm by initially setting the atomic coordinates of A-site, B-site, O1, and O2 atoms as those of MgSiO₃ bridgmanite (space group: $Pbnm$) (Horiuchi et al., 1987). The total abundances of Mg²⁺, Si⁴⁺, Al³⁺, Fe ions were fixed from the EPMA results, and the relative ratio of Fe²⁺ and Fe³⁺ was obtained from Mössbauer measurements on the same sample (Fu et al., 2019). Regarding the site occupancy of different ions, we fixed 88 mol% Mg²⁺ and 90 mol% Si⁴⁺ in the A and B

sites, respectively, and we considered that Fe ions and Al^{3+} can stay in both A and B sites. The refinement process assumes the same atomic coordinates for ions in the same site and the software does not distinguish Fe ions between Fe^{2+} and Fe^{3+} . It should be noted that theoretical calculations have suggested the atomic positions of different Fe^{2+} and Fe^{3+} components in the same site are similar and indistinguishable in bridgmanite (Hsu et al., 2011; Hsu et al., 2010), supporting the aforementioned assumptions in the structure refinements using the JANA software (Petříček et al., 2014).

During the refinement, we relaxed the following parameters, including abundances of Fe ions and Al^{3+} in both A and B sites, atomic coordinates of each site and anisotropic displacement parameters of each atom. The best fits to combined reflection peaks of the two platelets show that our (Al,Fe)-bearing bridgmanite sample has a chemical composition of $(\text{Mg}_{0.88}\text{Fe}^{3+}_{0.065}\text{Fe}^{2+}_{0.035}\text{Al}_{0.03})(\text{Al}_{0.11}\text{Si}_{0.90})\text{O}_3$ with all the Fe ions and ~ 3 mol% Al^{3+} in the A site and ~ 11 mol% Al^{3+} in the B site. The residual R -factors, wR , is about 3.2% at the initial pressure of 4.2(1) GPa (Figure 2b), indicating reliable constraints on the structure of single-crystal Fe10-Al14-Bgm (Toby, 2006). Although the number of diffraction peaks decreases with increasing pressure, the use of two platelets allows over 230 peaks with $I > 3\sigma(I)$ for the structure refinements even at the highest experimental pressure of 64.6(6) GPa. The low R and wR values indicate small uncertainties of our refinements (Figure 2 and Table 1). We conducted several synthetic tests to fix a certain amount of Fe ions in the B site, however, the resultant wR is unreasonably high, $>20\%$, even at 4.2(1) GPa. These tests rule out the possibility of Fe ions occupying the B site within uncertainties of the structure refinements.

DISCUSSION

Lattice parameters of (Al,Fe)-bearing bridgmanite at high pressure

Compared with literature reports on bridgmanite with different Fe and Al contents, the unit-cell parameters of Fe10-Al14-Bgm are comparable to those of $\text{Mg}_{0.89}\text{Fe}^{2+}_{0.024}\text{Fe}^{3+}_{0.096}\text{Al}_{0.11}\text{Si}_{0.89}\text{O}_3$ (Fe12-Al11-Bgm) (Mao et al., 2017), slightly greater than those of pure MgSiO_3 bridgmanite end member (Boffa Ballaran et al., 2012), and much lower than those of (Al,Fe)-rich bridgmanite, $(\text{Mg}_{0.60}\text{Fe}^{2+}_{0.03}\text{Fe}^{3+}_{0.38})(\text{Al}_{0.36}\text{Si}_{0.62})\text{O}_3$ (Fe41-Al36-Bgm) (Boffa Ballaran et al., 2012), Fe38-Al36-Bgm (Dubrovinsky et al., 2010), and $\text{Fe}^{2+}_{0.64}\text{Fe}^{3+}_{0.24}\text{SiO}_3$ bridgmanite (Ismailova et al., 2016) (Figure 3a-c). This indicates that incorporation of Fe and Al into bridgmanite significantly increases its unit-cell lattice parameters mainly due to the larger size of Fe ions compared to Mg^{2+} and Si^{4+} . In addition, our analyses show that the axial compressibility of Fe10-Al14-Bgm shows a trend of $a > c > b$ (Figure 3d-f), consistent with those of MgSiO_3 and $\text{Fe}^{2+}_{0.64}\text{Fe}^{3+}_{0.24}\text{SiO}_3$ bridgmanite end members (Boffa Ballaran et al., 2012; Ismailova et al., 2016). In contrast, Boffa Ballaran et al. (2012) reported that c axis of Fe41-Al36-Bgm is the most compressible axis, suggesting that intermediate Fe and Al in bridgmanite may change the direction of the maximum axial compressibility. Additionally, early studies reported noticeable volume collapses of 0.5-0.8% in pure Fe-bearing bridgmanite at 40-60 GPa (Fu et al., 2018; Mao et al., 2015) because of the spin transition of B-site Fe^{3+} . Our Fe10-Al14-Bgm does not display apparent volume collapses, supporting our refinements on the site occupancies that all Fe ions stay in the A site (without any observable B-site Fe^{3+}) and remain in the high-spin state up to 64.6(6) GPa. These results are also consistent with early theoretical modeling on the spin and valences of the A-site and B-site Fe ions in bridgmanite and their effects on unit-cell volumes (Hsu et al., 2011; Hsu et al., 2010; Shukla et al., 2016).

Bond lengths and angles in (Al,Fe)-bearing bridgmanite at high pressure

The obtained atomic coordinates of Fe10-Al14-Bgm can be used to precisely determine its structural response to compression, such as interatomic distances and bond angles among atoms

(Table 2). For an ideal perovskite structure, the A and B sites will have twelvefold and sixfold coordination to form AO_{12} dodecahedra and BO_6 octahedra, respectively. Kudoh et al. (1987) observed that in MgSiO_3 bridgmanite, the application of pressure up to 9.6 GPa changes the A-site polyhedral configuration towards eightfold coordination (AO_8 polyhedron) rather than twelvefold coordination. Each AO_8 polyhedron shares two faces, four edges, and two corners with the eight surrounding BO_6 octahedra. Here we calculated mean interatomic distances between A-site (B-site) atoms and O within an eight (six) coordination, denoted as $\langle\text{A-O}\rangle_8$ ($\langle\text{B-O}\rangle$), using the derived high-pressure atomic coordinates (Figures 4 and 5a). The average interatomic distances between A-site cations and O within an AO_{12} pseudo-dodecahedron ($\langle\text{A-O}\rangle_{12}$) were also calculated for comparison. Results show that $\langle\text{A-O}\rangle_8$, $\langle\text{A-O}\rangle_{12}$, and $\langle\text{B-O}\rangle$ of the single-crystal Fe10-Al14-Bgm decrease smoothly with pressure from 2.192(1), 2.471(1), and 1.795(1) Å, respectively at 4.2(1) GPa to 2.052(5), 2.347(5), and 1.715(3) Å, respectively at 64.6(6) GPa. Furthermore, variations of bond lengths in the BO_6 octahedra decrease with pressure, suggesting the BO_6 octahedra is approaching to form an ideal octahedra at high pressure (Figure 4). Comparisons with literature data on bridgmanite with different compositions (Dubrovinsky et al., 2010; Ross et al., 1990; Sugahara et al., 2006) show that incorporation of 36 mol% Al and 38 mol% Fe into its structure will increase $\langle\text{B-O}\rangle$ and $\langle\text{A-O}\rangle_{12}$ by approximately 2.1% and 1.7%, respectively, but affects $\langle\text{A-O}\rangle_8$ little, less than 0.5%. That is, the incorporation of Fe and Al into bridgmanite has a stronger effect on the BO_6 octahedron than the AO_8 polyhedron.

We have also calculated two angles between O and B-site atoms, B-O1-B and B-O2-B, which have been served as helpful indicators on the tilting of the BO_6 octahedra (Andrault and Poirier, 1991). Specifically, the B-O1-B and B-O2-B represent the tilting of the BO_6 octahedra in the *b-c* plane and the *a-b* plane, respectively. Calculations show that B-O1-B and B-O2-B of Fe10-Al14-Bgm are about 145.2(2)° and 145.8(2)°, respectively, at 4.2(1) GPa, which

gradually decrease to about $143.3(3)^\circ$ and $143.5(3)^\circ$, respectively, at 64.6(6) GPa (Figure 5b-c). This indicates an increasing tilt of the BO_6 octahedra with pressure. The pressure effect on tilting angles of the BO_6 octahedra in both b - c and a - b planes in Fe10-Al14-Bgm is consistent with those of Fe38-Al35-Bgm (Dubrovinsky et al., 2010) and pure MgSiO_3 bridgmanite end member (Sugahara et al., 2006). Furthermore, we have noticed that with increasing Fe and Al contents from Fe10-Al14-Bgm to Fe38-Al36-Bgm in bridgmanite, both angles of B-O1-B and B-O2-B decrease 1.4-1.6%, showing a strong Fe and Al incorporation effect on the distortion of the BO_6 octahedra.

Structural distortion of (Al,Fe)-bearing bridgmanite at high pressure

To quantitatively evaluate the distortion of the bridgmanite structure in the lower-mantle pressure, we followed literature procedures to calculate two relevant parameters, the observed tolerance factor (t_{obs}) and octahedral tilting angles (Φ), using the refined atomic structure of Fe10-Al14-Bgm from a microscopic approach (Ross et al., 1990; Sugahara et al., 2006; Zhao et al., 1993a). The t_{obs} is initially used to systematically describe the tilting and distortion in GdFeO_3 -type perovskite (Sasaki et al., 1983), calculated as:

$$t_{\text{obs}} = \frac{\langle A - O \rangle_{12}}{\langle B - O \rangle} \quad (3)$$

where $\langle A - O \rangle_{12}$ ($\langle B - O \rangle$) is the mean interatomic distance between A-site (B-site) atoms and O within a twelvefold (sixfold) coordination. According to the definition, an ideal cubic GdFeO_3 perovskite will have t_{obs} as one. Our calculations show that the t_{obs} of Fe10-Al14-Bgm is about 0.974(1) at 4.2(1) GPa and decreases with pressure to $\sim 0.968(4)$ at 64.6(6) GPa (Figure 6). Thus, there is an increasing degree of the lattice distortion in Fe10-Al14-Bgm from an ideal cubic symmetry in the orthorhombic system with pressure. In addition, compared to literature reports on bridgmanite with different compositions, the t_{obs} of Fe10-Al14-Bgm is slightly lower than those of MgSiO_3 end member (Ross et al., 1990; Sugahara et al., 2006) and higher than

288 those of Fe₃₈-Al₃₅-Bgm (Dubrovinsky et al., 2010), suggesting an increased structure
 289 distortion in (Al,Fe)-rich bridgmanite.

290 Taking advantage of the obtained atomic coordinates of the single-crystal Fe₁₀-Al₁₄-Bgm
 291 in this study, we can reliably calculate the titling angles of the octahedron (Φ) to describe the
 292 distortion degree of bridgmanite at high pressure. In this method, the octahedron in the structure
 293 of bridgmanite is assumed as a pseudo-cubic unit cell with a length (a_p) approximately
 294 described as: $a_p \approx \sqrt{2}a/2 \approx \sqrt{2}b/2 \approx c/2$ (Figure 7a). Φ is defined as titling of the octahedron
 295 about the pseudo-cubic [111] direction. Alternatively, Φ can be viewed as a combination of
 296 titling about the pseudo-cubic [110] direction (angle θ) and the pseudo-cubic [001] direction
 297 (angle φ) in the pseudo-cubic unit cell (Figure 7b), calculated using:

$$\cos \Phi = \cos \theta \cos \varphi \quad (4)$$

$$\tan \theta = 4 \sqrt{u_{O1}^2 + v_{O1}^2} / c \quad (5)$$

$$\tan \varphi = 4 \sqrt{u_{O2}^2 + v_{O2}^2} / \sqrt{a^2 + b^2} \quad (6)$$

298 where u_{O1} , u_{O2} , v_{O1} , and v_{O2} are parameters derived from refined atomic coordinates using:

$$u_{O1} = ax_{O1} \quad (7)$$

$$v_{O1} = b(0.5 - y_{O1}) \quad (8)$$

$$u_{O2} = a(0.25 - x_{O2}) \quad (9)$$

$$v_{O2} = b(y_{O2} - 0.25) \quad (10)$$

299 where x_{On} and y_{On} are atomic coordinates of the n th oxygen atom (Zhao et al., 1993a).
 300 Calculations show that Φ of Fe₁₀-Al₁₄-Bgm gradually increases with pressure from $\sim 21.0(1)^\circ$
 301 at 4.2(1) GPa to $\sim 22.5(3)^\circ$ at 64.6(6) GPa (Figure 8), indicating an increasing distortion.

Comparison with literature results suggests that Φ of bridgmanite also increases with increasing Fe and Al contents (Dubrovinsky et al., 2010; Ross et al., 1990; Sugahara et al., 2006). We note that, due to the experimental difficulties in obtaining reliable high-pressure atomic structure of bridgmanite, some early studies attempted to estimate the value of Φ from its unit-cell parameters in a macroscopic approach by assuming regular octahedra in the structure, calculated as: $\cos \Phi = \sqrt{2}a^2/bc$ (Mao et al., 2017; O'keeffe et al., 1977). Comparisons of the calculated Φ from both macroscopic and microscopic approaches (Boffa Ballaran et al., 2012; Mao et al., 2017) show that the macroscopic approach typically underestimates Φ (Figure 8). This is due to the fact that the macroscopic approach simply assumes that the octahedron in bridgmanite is rigid and the octahedral angles are small (Zhao et al., 1993a; Zhao et al., 1993b).

The calculated t_{obs} and Φ show a consistent trend that the distortion degree of the Fe10-Al14-Bgm structure increases with pressure (Figures 6 and 8). Our SCXRD refinements reveal that all the Fe ions in our Fe10-Al14-Bgm, about 6.5 mol% Fe^{3+} and 3.5 mol% Fe^{2+} , occupy the A site within uncertainties of the refinements. Therefore, the observed high-pressure distortion in Fe10-Al14-Bgm should be closely related to changes of local A-site Fe ions environment. Both earlier theoretical and experimental studies indicate that the A-site Fe^{2+} and Fe^{3+} remain in the high-spin state throughout the lower-mantle pressure, and the A-site Fe^{2+} can experience an enhanced distortion at 40-60 GPa with extremely high QS (Hsu et al., 2011; Hsu et al., 2010; Mao et al., 2017). Theoretical calculations also show that the small changes in the local structure and d -orbital occupations of Fe^{2+} in bridgmanite can greatly affect its QS (Bengtson et al., 2009; Hsu et al., 2010). Therefore, we attribute the increased SiO_6 octahedron tilting angles and distortion degree in Fe10-Al14-Bgm to the increased distortion of the A-site Fe^{2+} at high pressures. These local changes of A-site Fe^{2+} environment in bridgmanite can result in high QS values as observed experimentally (Jackson et al., 2005; Mao et al., 2017).

We note that the abundance of Fe^{3+} in our Fe10-Al14-Bgm is much higher than that of Fe^{2+} , which might weaken the distortion degree of A-site Fe^{2+} and result in smooth increase in t_{obs} and Φ with pressure. Moreover, Mao et al. (2017) observed the existence of both high and low QS A-site Fe^{2+} components in the Fe12-Al11-Bgm at 0-130 GPa and suggest that the presence of Al may play a key role in decreasing the differences between high and low QS A-site Fe^{2+} .

IMPLICATIONS

Approximately 5-7 wt% Al_2O_3 can be dissolved into (Al,Fe)-bearing bridgmanite via the decomposition of majoritic garnet at the topmost lower mantle (~660-770 km in depth) (Hummer and Fei, 2012; Irifune et al., 2010; Lin et al., 2016). Our refined crystal structure of the Fe10-Al14-Bgm suggests that Al^{3+} would preferentially occupy the B site and all the Fe ions stay in the A site in (Al,Fe)-bearing bridgmanite. That is, the lower-mantle (Al,Fe)-bearing bridgmanite is not expected to contain the B-site Fe^{3+} , and thus, will not experience the B-site spin transition as well as the associated thermoelastic anomalies as discussed in the previous reports (Fu et al., 2018; Hsu et al., 2011; Mao et al., 2015; Shukla et al., 2016).

Studies have shown that the enhanced distortion of A-site Fe^{2+} in bridgmanite does not cause detectable anomalies in unit-cell volumes (Boffa Ballaran et al., 2012; Mao et al., 2017) but could be linked with enhanced hyperfine parameters and softening in some macroscopic properties, such as lattice thermal conductivity and mean force constants of iron bonds (Hsieh et al., 2017; Yang et al., 2019). For instance, Hsieh et al. (2017) found that MgSiO_3 , Fe-bearing $\text{Mg}_{0.96}\text{Fe}_{0.07}\text{Si}_{0.98}\text{O}_3$ (Fe7-Bgm), and (Al,Fe)-bearing $\text{Mg}_{0.89}\text{Fe}^{2+}_{0.024}\text{Fe}^{3+}_{0.096}\text{Al}_{0.11}\text{O}_3$ $\text{Si}_{0.89}\text{O}_3$ (Fe12-Al11-Bgm) have comparable and increasing lattice thermal conductivities with pressure below 40 GPa. This can be explained by the pressure-induced shortening of the interatomic distances in the bridgmanite structure (Figure 5). While the thermal conductivity of Fe7-Bgm drops by ~20% at 40-45 GPa and then changes little with further increasing pressure. Such a

drop in the conductivity is likely related to the distortion of the A-site Fe^{2+} occurring in the same pressure range. The lattice distortion can increase the phonon-defect and reduce the phonon-phonon scattering contribution in bridgmanite (Ladd et al., 1986; Schelling et al., 2002) consequently leading to the reduced lattice thermal conductivity at high pressure. Because of the trade-offs between the positive effect of shortened interatomic distances and the negative effect of the A-site Fe^{2+} distortion, the pressure dependence of the lattice thermal conductivity in Fe7-Bgm is almost flat above 45 GPa (Hsieh et al., 2017). In comparison, Fe12-Al11-Bgm displays a moderate thermal conductivity between MgSiO_3 and Fe7-Bgm above 40 GPa (Hsieh et al., 2017). Due to the relative abundance of Fe^{2+} and Fe^{3+} as well as the presence of Al^{3+} in (Al,Fe)-bearing bridgmanite, the A-site Fe^{2+} distortion is likely weakened, and thus, its decreasing effect on thermal conductivity will be weakened. This trend is consistent with our observations on the gradual distortion instead of abrupt anomalies with pressure in Fe10-Al14-Bgm. Similarly, the drastic softening in force constants of (Al,Fe)-bearing bridgmanite at 40-60 GPa observed by Yang et al. (2019) might be caused by the A-site Fe^{2+} distortion: the weak pressure dependence of force constants above 60 GPa is possibly a result of the combined effect between the shorten interatomic bond lengths and A-site Fe^{2+} distortion at high pressure, which has positive and negative effects on force constants, respectively. Thermal conductivity and force constants of lower-mantle candidate minerals are key for understanding geophysics and geochemistry of our planet, such as the heat flux across the core-mantle boundary and isotope fractionation in an early magma ocean (Hofmeister, 1999; Poitrasson et al., 2004). Therefore, the softening effect of the A-site Fe^{2+} distortion could greatly affect our views on mantle convection flow and evolution history of the planet. Considering that our study is limited to room temperature on (Al,Fe)-bearing bridgmanite with low A-site Fe^{2+} , further examinations of the thermal effect on atomic structures of Fe^{2+} -rich (Al,Fe)-bearing bridgmanite at high

pressure are still needed to better interpret the lower-mantle geochemistry, geophysics, and geodynamics.

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Data availability

All the high-pressure cif files of the single-crystal bridgmanite in this study are provided in supplementary materials.

Competing interests

The authors declare no competing interests.

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Figures and Tables:

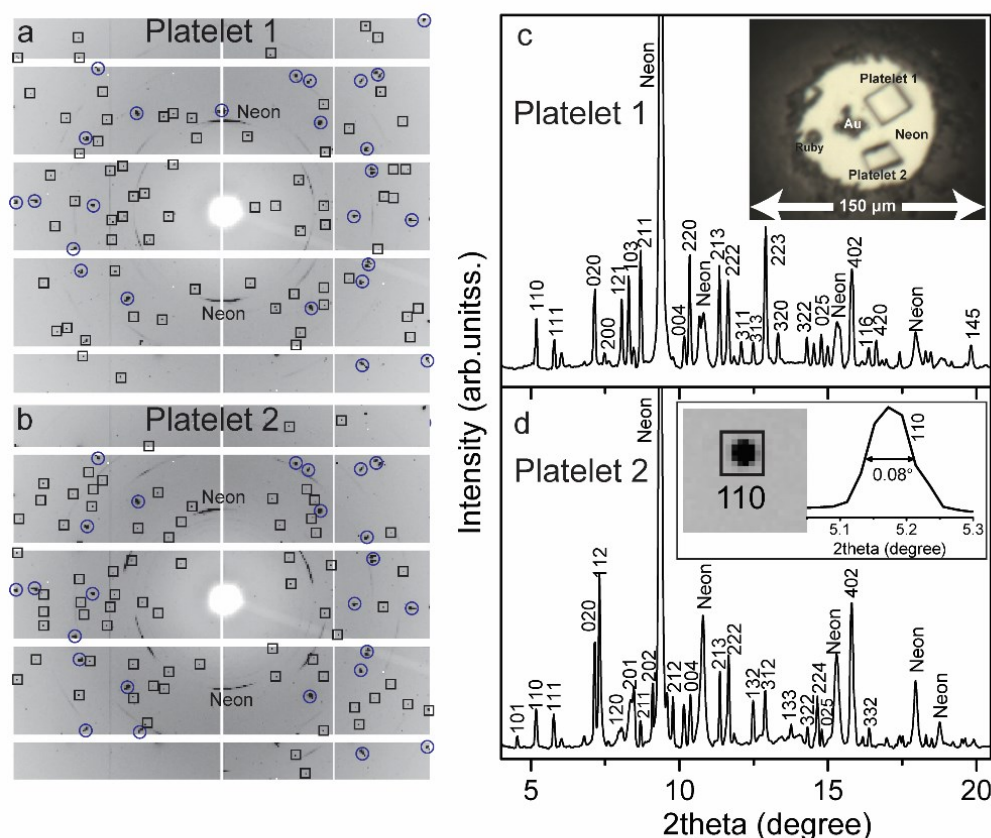
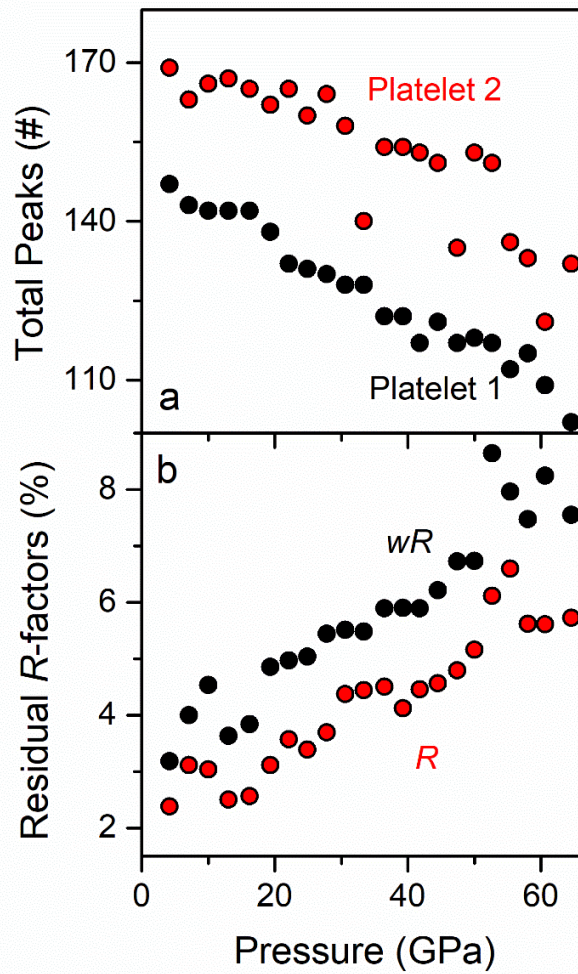
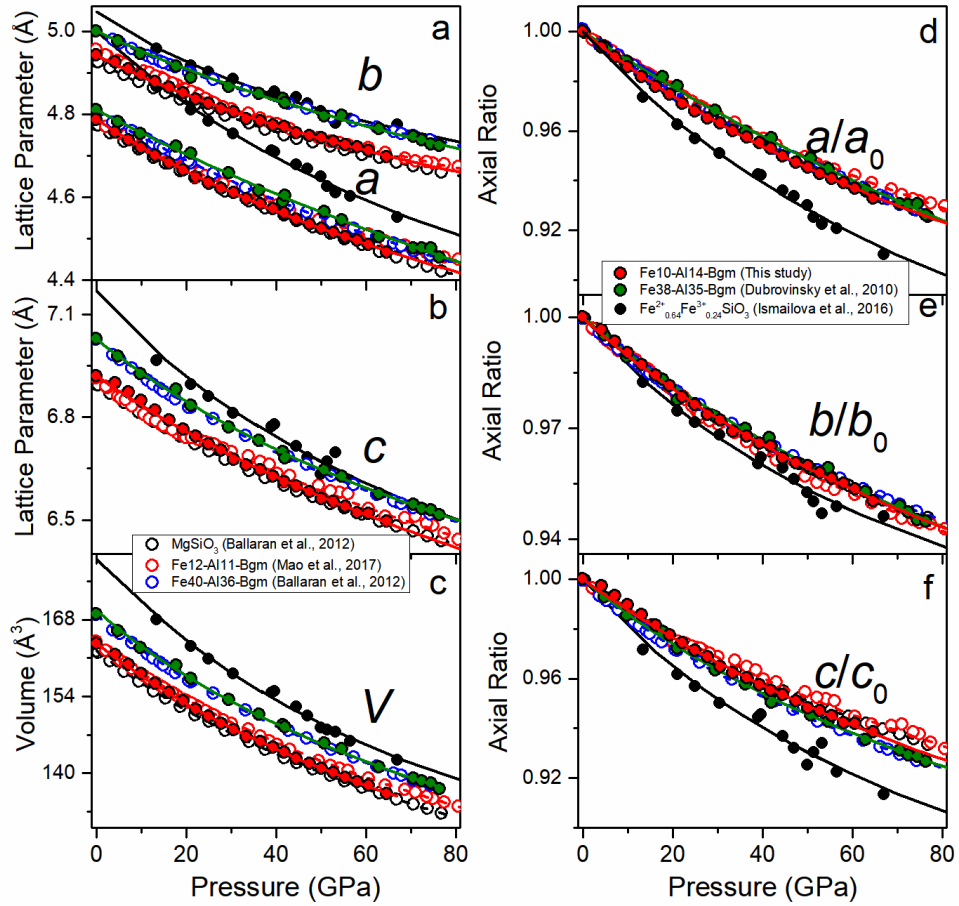


Figure 1. Representative single-crystal X-ray diffraction results of Fe₁₀-Al₁₄-Bgm at ~52.7 GPa and room temperature. **a** and **b** Original XRD patterns of platelets 1 and 2, respectively. The black squares and blue circles mark reflection spots from bridgmanite and diamonds, respectively. Diffraction rings show signals from solid neon medium, labeled with “Neon”. **c** and **d** Corresponding integrated XRD patterns of platelets 1 and 2, respectively. Miller indices (hkl) of bridgmanite are labeled close to the top of diffraction peaks. The average FWHM of these peaks is ~0.08°. The insert in **c** shows an image of the sample chamber with two Fe₁₀-Al₁₄-Bgm platelets and Au pressure calibrant. The insert in **d** is a round 110 reflection spot and its integrated peak. The wavelength of the incident X-ray beam is 0.2952 Å.



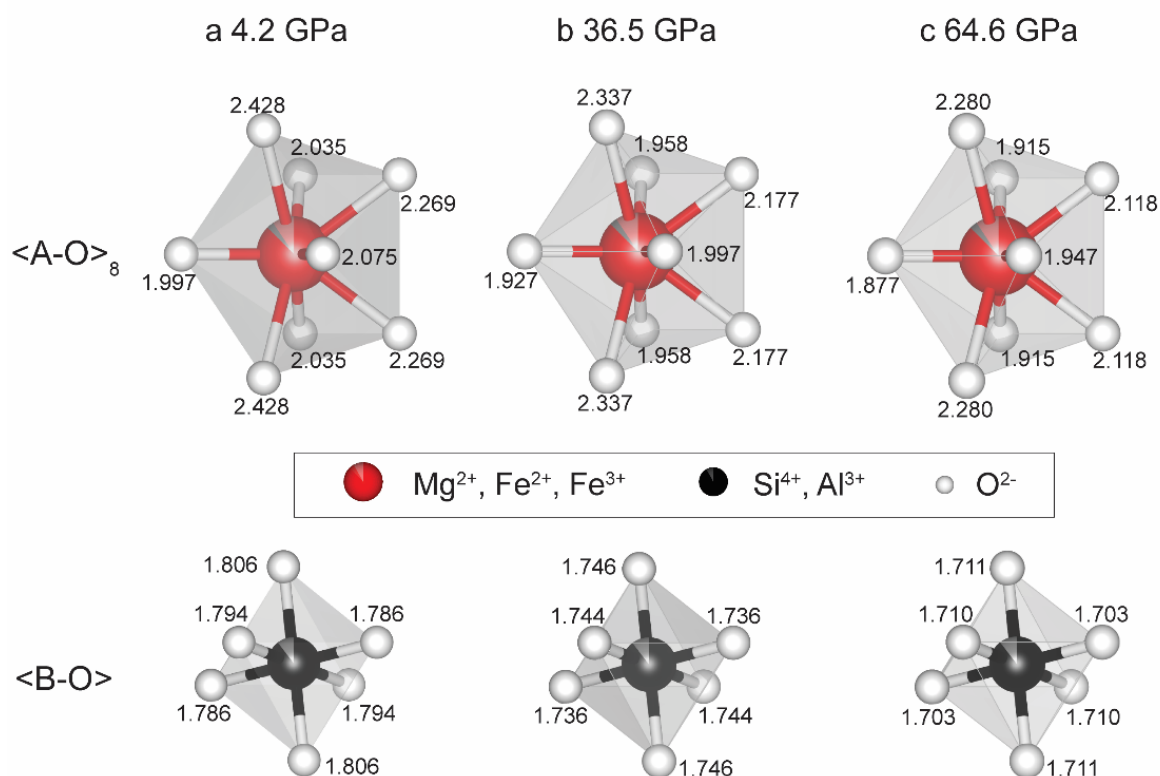
566

567 **Figure 2.** Data analyses on single-crystal XRD patterns of Fe10-Al14-Bgm at high pressure. **a** The
 568 number of high-quality reflection peaks of each bridgmanite platelet used for structure refinements.
 569 These reflections were selected with intensities (I) of $I > 3\sigma(I)$. Solid black and red circles are for platelets
 570 1 and 2, respectively. **b** Residual R -factors during the refinements to derive the atomic structure of
 571 Fe10-Al14-Bgm using JANA software (Petříček et al., 2014). Solid black and red circles show weighted
 572 R -factor ($wR(F^2)$) and R -factor ($R(F^2 > 2\sigma(F^2))$) in percentages, respectively.



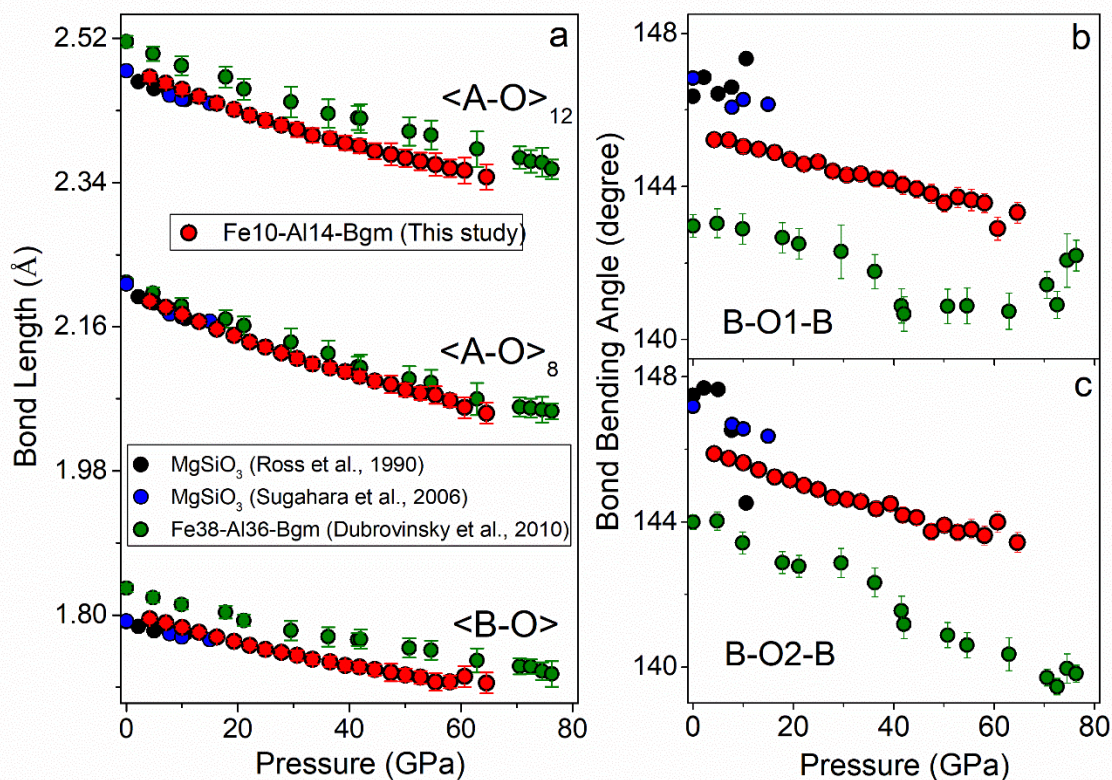
573

574 **Figure 3.** Unit-cell parameters of single-crystal Fe10-Al14-Bgm at high pressure. **a-c** Lattice
575 parameters (a , b , c) and unit-cell volume (V). **d-f** Normalized lattice parameters (a/a_0 , b/b_0 , and c/c_0 ,
576 respectively). Solid red circles are results of Fe10-Al14-Bgm in this study, and representative previous
577 data on bridgmanite with different Fe and Al contents are plotted for comparisons (Boffa Ballaran et
578 al., 2012; Dubrovinsky et al., 2010; Ismailova et al., 2016; Mao et al., 2017). Particularly, solid symbols
579 are single-crystal XRD data on bridgmanite with well-resolved atomic coordinates (Dubrovinsky et al.,
580 2010; Ismailova et al., 2016), while open symbols are on samples derived from integrated XRD patterns
581 (Boffa Ballaran et al., 2012; Mao et al., 2017).



582

583 **Figure 4.** Local atomic configurations and bond lengths around the A-site and B-site atoms in single-
 584 crystal Fe₁₀-Al₁₄-Bgm at high pressure. **a** 4.2 GPa. **b** 36.5 GPa. **c** 64.6 GPa. Red, black, and white
 585 balls represent A-site, B-site, and oxygen atoms, respectively. These structures are viewed and graphed
 586 from *a* axis. The upper and lower panels show configurations of A-site and B-site atoms, respectively.
 587 Numbers next to the oxygen atoms are respective bond lengths with a unit of Å.



588

589 **Figure 5.** Interatomic distances and angles in the structure of single-crystal Fe10-Al14-Bgm as a
590 function of pressure. **a** Atomic distances of the A-site and B-site atoms with respect to oxygen atoms.
591 $\langle A-O \rangle_{12}$ and $\langle A-O \rangle_8$ are average distances between O and A-site atoms in eightfold and twelvefold
592 coordination, respectively, while $\langle B-O \rangle$ are average distances between O and B-site atoms in sixfold
593 coordination. **b** and **c** Variations of BO₆ octahedral tilt angles in the *b-c* plane and the *a-b* plane, given
594 by B-O1-B and B-O2-B, respectively. Solid red circles are results of single-crystal Fe10-Al14-Bgm in
595 this study, and previous data on bridgmanite with different compositions are plotted for comparisons
596 (Dubrovinsky et al., 2010; Ross et al., 1990; Sugahara et al., 2006). The decrease of B-O1-B and B-O2-
597 B angles with pressure indicates an increased distortion of the orthorhombic structure.

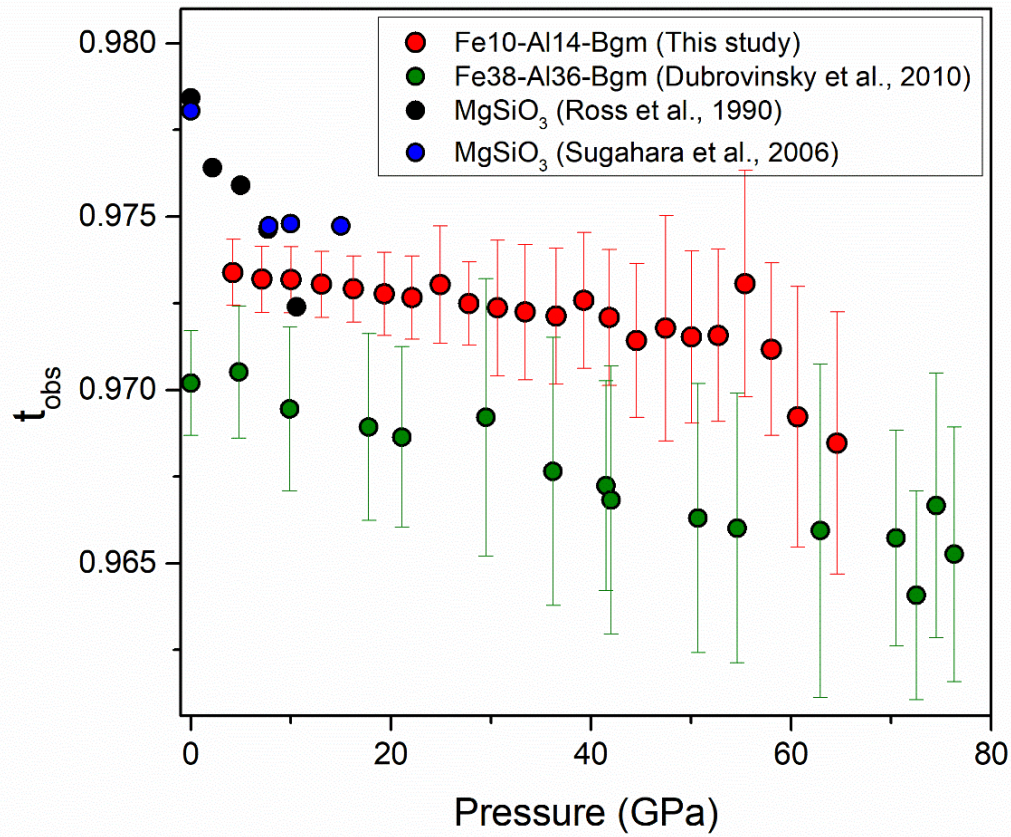


Figure 6. The tolerance factors (t_{obs}) of single-crystal Fe10-Al14-Bgm as function of pressure. Solid red circles are results from this study, and literature data on bridgmanite with different compositions are plotted for comparisons (Dubrovinsky et al., 2010; Ross et al., 1990; Sugahara et al., 2006). Deviations of t_{obs} from one indicate a distortion of the bridgmanite structure from an ideal GdFeO_3 -type cubic symmetry (Sasaki et al., 1983).

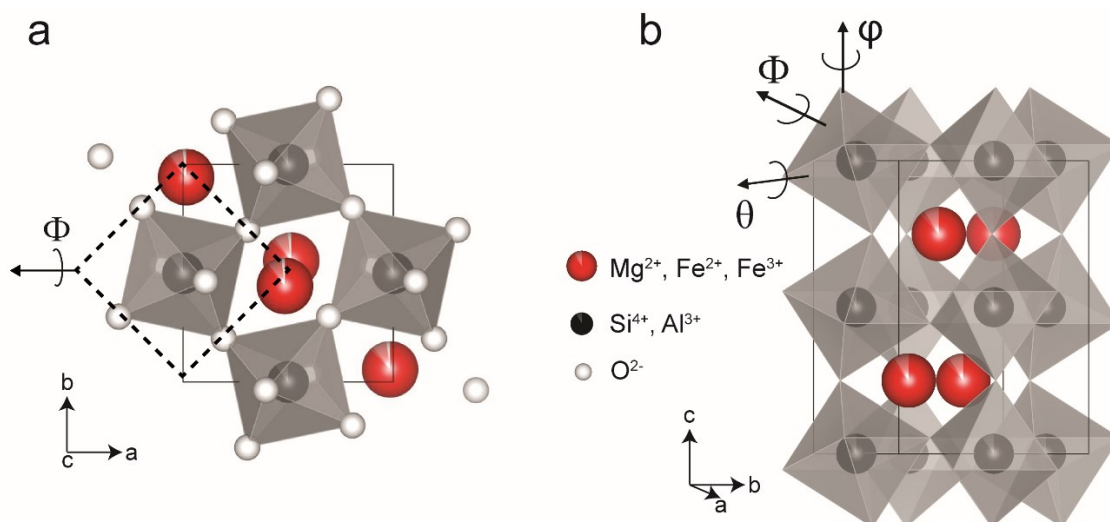


Figure 7. Schematic illustrations of the octahedral tilting angles (Φ) in the structure of single-crystal Fe10-Al14-Bgm at 64.6 GPa. **a** Top view from c axis; **b** Side view. The octahedron in bridgmanite structure can be assumed as a pseudo-cubic unit cell, shown as dashed square in **a**. Φ is defined as tilting of the octahedron about the pseudo-cubic $[111]$ direction. Φ can be also viewed as a combination of tilting about the pseudo-cubic $[110]$ direction (angle θ) and the pseudo-cubic $[001]$ direction (angle ϕ), shown in **b**. Refer to Figure 4 for detailed geometry of the octahedron in single-crystal Fe10-Al14-Bgm viewing from a axis at different high pressures.

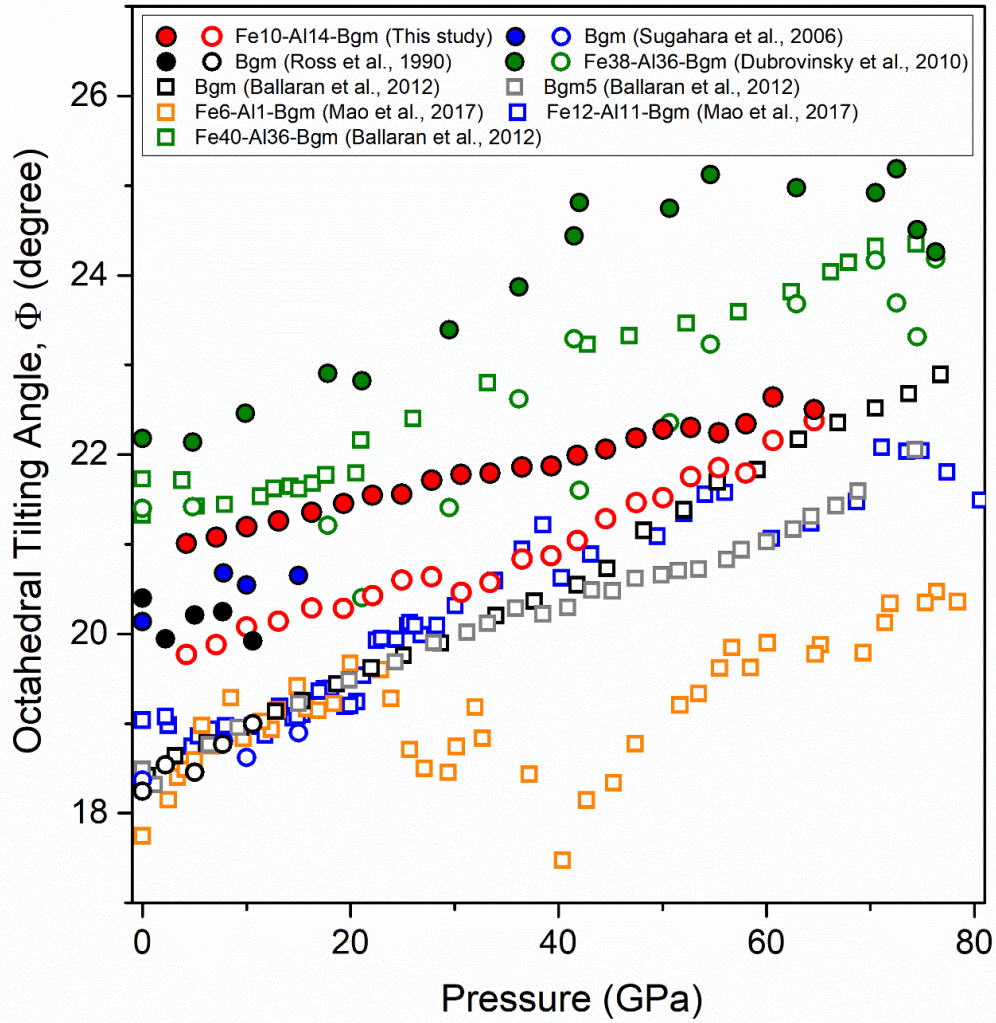


Figure 8. Octahedral titling angles in the single-crystal Fe10-Al14-Bgm as a function of pressure. Red circles are results of Fe10-Al14-Bgm in this study, and literature reports on bridgmanite with different compositions are plotted for comparisons (Boffa Ballaran et al., 2012; Dubrovinsky et al., 2010; Mao et al., 2017; Ross et al., 1990; Sugahara et al., 2006). Solid symbols are derived from the quantitatively refined atomic coordinates in a microscopic approach, while open symbols are calculations from lattice parameters in a macroscopic approach. Bgm denotes MgSiO_3 bridgmanite end member.

Table 1. Refined unit-cell parameters and atomic coordinates of single-crystal Fe10-Al14-Bgm at high pressures

Pressure (GPa)	Evaluation parameters		Unit-cell parameters			A site				B site				O1				O2			
	*Total peaks (#)	wR (%)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	x	y	z	U	x	y	z	U	x	y	z	U	x	y	z	U
4.2(1)	316	3.2	4.7564(7)	4.9263(4)	6.9005(9)	0.5149(1)	0.5583(1)	0.25	0.0066(2)	0.5	0	0.5	0.0041(2)	0.1068(2)	0.4631(2)	0.25	0.0056(4)	0.1943(2)	0.1994(1)	0.5548(2)	0.0060(3)
7.1(2)	306	4.0	4.7378(10)	4.9098(4)	6.8742(9)	0.5151(1)	0.5588(2)	0.25	0.0056(3)	0.5	0	0.5	0.0031(2)	0.1070(3)	0.4633(2)	0.25	0.0048(5)	0.1939(2)	0.1992(2)	0.5548(2)	0.0051(4)
10.0(2)	308	4.5	4.7191(7)	4.8949(4)	6.8493(9)	0.5154(1)	0.5594(2)	0.25	0.0053(3)	0.5	0	0.5	0.0029(2)	0.1076(3)	0.4629(2)	0.25	0.0042(5)	0.1935(2)	0.1985(2)	0.5550(2)	0.0049(4)
13.1(2)	309	3.6	4.7006(6)	4.8792(4)	6.8205(15)	0.5157(1)	0.5601(2)	0.25	0.0052(2)	0.5	0	0.5	0.0030(2)	0.1079(2)	0.4631(2)	0.25	0.0043(4)	0.1931(2)	0.1983(1)	0.5554(2)	0.0047(3)
16.3(2)	307	3.8	4.6816(7)	4.8648(4)	6.7918(12)	0.5159(1)	0.5609(2)	0.25	0.0063(2)	0.5	0	0.5	0.0043(2)	0.1082(2)	0.4632(2)	0.25	0.0055(4)	0.1926(2)	0.1978(1)	0.5556(2)	0.0060(3)
19.3(2)	300	4.8	4.6657(9)	4.8511(5)	6.7648(11)	0.5162(1)	0.5614(2)	0.25	0.0049(3)	0.5	0	0.5	0.0031(2)	0.1088(3)	0.4633(2)	0.25	0.0045(5)	0.1922(2)	0.1978(2)	0.5557(2)	0.0042(4)
22.1(3)	297	5.0	4.6492(14)	4.8362(6)	6.7435(11)	0.5164(1)	0.5620(2)	0.25	0.0047(3)	0.5	0	0.5	0.0031(2)	0.1093(3)	0.4635(2)	0.25	0.0042(5)	0.1917(2)	0.1975(2)	0.5558(2)	0.0044(4)
24.9(3)	291	5.0	4.6342(8)	4.8257(4)	6.7225(11)	0.5166(1)	0.5627(2)	0.25	0.0044(3)	0.5	0	0.5	0.0027(2)	0.1091(3)	0.4635(2)	0.25	0.0036(6)	0.1916(2)	0.1972(2)	0.5560(2)	0.0036(4)
27.8(3)	294	5.4	4.6208(11)	4.8127(12)	6.7035(11)	0.5169(1)	0.5635(2)	0.25	0.0046(3)	0.5	0	0.5	0.0029(2)	0.1100(3)	0.4633(2)	0.25	0.0038(6)	0.1909(2)	0.1968(2)	0.5563(2)	0.0040(4)
30.6(3)	286	5.5	4.6107(20)	4.8054(7)	6.6765(15)	0.5172(2)	0.5639(2)	0.25	0.0036(3)	0.5	0	0.5	0.0024(2)	0.1101(3)	0.4633(3)	0.25	0.0041(6)	0.1908(2)	0.1965(2)	0.5562(2)	0.0031(4)
33.4(7)	268	5.5	4.5955(14)	4.7896(6)	6.6595(14)	0.5174(2)	0.5645(2)	0.25	0.0032(4)	0.5	0	0.5	0.0016(2)	0.1103(3)	0.4635(3)	0.25	0.0038(6)	0.1905(2)	0.1966(2)	0.5563(2)	0.0033(5)
36.5(4)	276	5.9	4.5835(17)	4.7832(10)	6.6450(18)	0.5177(2)	0.5647(2)	0.25	0.0040(4)	0.5	0	0.5	0.0029(2)	0.1110(4)	0.4637(3)	0.25	0.0044(7)	0.1900(3)	0.1963(2)	0.5566(3)	0.0038(5)
39.3(4)	276	5.9	4.5725(15)	4.7743(8)	6.627(12)	0.5178(2)	0.5655(3)	0.25	0.0053(4)	0.5	0	0.5	0.0033(2)	0.1111(4)	0.4639(3)	0.25	0.0050(8)	0.1902(3)	0.1963(2)	0.5565(3)	0.0048(6)
41.8(4)	270	5.9	4.5618(23)	4.7698(9)	6.6100(20)	0.5182(2)	0.5660(3)	0.25	0.0058(5)	0.5	0	0.5	0.0042(2)	0.1113(4)	0.4637(3)	0.25	0.0057(8)	0.1897(3)	0.1959(3)	0.5570(3)	0.0055(6)
45.6(5)	272	6.2	4.5470(14)	4.7546(8)	6.5990(22)	0.5184(2)	0.5661(3)	0.25	0.0061(5)	0.5	0	0.5	0.0046(2)	0.1122(5)	0.4641(3)	0.25	0.0063(7)	0.1893(3)	0.1957(3)	0.5569(3)	0.0062(6)
47.5(5)	242	6.7	4.5353(12)	4.7480(7)	6.5820(15)	0.5186(2)	0.5668(3)	0.25	0.0070(5)	0.5	0	0.5	0.0058(2)	0.1125(5)	0.4635(4)	0.25	0.0067(8)	0.1883(4)	0.1953(2)	0.5577(4)	0.0066(7)
50.1(4)	271	6.7	4.5254(14)	4.7436(9)	6.5620(23)	0.5188(2)	0.5677(3)	0.25	0.0068(4)	0.5	0	0.5	0.0059(2)	0.1133(4)	0.4638(3)	0.25	0.0064(7)	0.1883(3)	0.1953(2)	0.5572(3)	0.0065(5)
52.7(4)	268	8.6	4.5142(12)	4.7342(7)	6.5530(14)	0.5190(2)	0.5677(3)	0.25	0.0067(5)	0.5	0	0.5	0.0063(2)	0.1130(6)	0.4641(4)	0.25	0.0055(9)	0.1874(4)	0.1951(3)	0.5574(4)	0.0054(7)
55.4(5)	235	8.0	4.5044(17)	4.7268(8)	6.5395(13)	0.5193(3)	0.5684(4)	0.25	0.0103(6)	0.5	0	0.5	0.0096(2)	0.1128(6)	0.4632(5)	0.25	0.0100(9)	0.1891(4)	0.1951(3)	0.5577(5)	0.0097(8)
58.0(5)	240	7.5	4.4962(12)	4.7206(7)	6.5215(18)	0.5194(3)	0.5687(3)	0.25	0.0063(5)	0.5	0	0.5	0.0055(2)	0.1136(5)	0.4642(4)	0.25	0.0058(8)	0.1878(4)	0.1949(3)	0.5579(5)	0.0059(7)
60.6(6)	193	8.2	4.4858(12)	4.7127(8)	6.5190(19)	0.5195(3)	0.5691(4)	0.25	0.0046(8)	0.5	0	0.5	0.0045(2)	0.1156(8)	0.4642(6)	0.25	0.0053(12)	0.1876(5)	0.1948(4)	0.5576(6)	0.0052(5)
64.6(6)	234	7.6	4.4669(15)	4.6972(9)	6.4955(24)	0.5199(3)	0.5701()	0.25	0.0059(6)	0.5	0	0.5	0.0039(2)	0.1148(6)	0.4643(5)	0.25	0.0066(10)	0.1878(4)	0.1944(4)	0.5580(5)	0.0066(8)

*: The total number of used peaks on two crystal platelets together. The reflections have intensities (*I*) of $I > 3\sigma(I)$ for structure refinements. Refer to Figure 2a for the number of used peaks on individual platelet.

Table 2. Selected interatomic distances (Å) and angles (°) in the structure of single-crystal Fe10-Al14-Bgm at high pressures

Pressure (GPa)	B-O1 × 2 (Å)	B-O2 × 2 (Å)	B-O2 × 2 (Å)	Mean <B-O> (Å)	A-O1 × 1 (Å)	A-O1 × 1 (Å)	A-O1 × 1 (Å)	A-O1 × 1 (Å)	A-O2 × 2 (Å)	A-O2 × 2 (Å)	A-O2 × 2 (Å)	A-O2 × 2 (Å)	Mean <A-O>viii (Å)	Mean <A-O>xii (Å)	B-O1-B (°)	B-O2-B (°)
4.2(1)	1.806(1)	1.794(1)	1.786(1)	1.795(1)	1.997(1)	2.854(2)	2.988(1)	2.075(1)	3.141(2)	2.269(1)	2.428(2)	2.035(1)	2.192(1)	2.471(1)	145.2(2)	145.9(2)
7.1(2)	1.801(1)	1.789(1)	1.781(1)	1.790(1)	1.990(2)	2.843(2)	2.981(1)	2.068(1)	3.135(2)	2.262(1)	2.419(2)	2.028(1)	2.184(1)	2.464(1)	145.2(2)	145.7(2)
10.0(2)	1.795(1)	1.783(1)	1.776(1)	1.785(1)	1.981(2)	2.834(2)	2.977(1)	2.059(1)	3.129(2)	2.253(1)	2.408(2)	2.021(2)	2.176(1)	2.456(1)	145.0(2)	145.6(2)
13.1(2)	1.788(1)	1.778(1)	1.770(1)	1.779(1)	1.975(1)	2.824(1)	2.970(1)	2.050(1)	3.123(1)	2.242(1)	2.399(1)	2.012(1)	2.166(1)	2.447(1)	145.0(2)	145.4(2)
16.3(2)	1.781(1)	1.773(1)	1.765(1)	1.773(1)	1.967(1)	2.813(1)	2.965(1)	2.042(1)	3.117(1)	2.232(1)	2.389(2)	2.003(1)	2.157(1)	2.439(1)	144.9(2)	145.2(2)
19.3(2)	1.775(2)	1.768(1)	1.760(1)	1.767(2)	1.960(2)	2.806(2)	2.959(1)	2.035(1)	3.110(2)	2.223(2)	2.379(2)	1.996(2)	2.149(2)	2.431(2)	144.7(2)	145.1(2)
22.1(3)	1.770(1)	1.763(1)	1.754(1)	1.762(1)	1.951(2)	2.798(2)	2.953(2)	2.028(1)	3.105(2)	2.215(1)	2.371(2)	1.988(1)	2.141(2)	2.424(2)	144.6(2)	145.0(2)
24.9(3)	1.764(2)	1.758(1)	1.751(1)	1.757(2)	1.948(2)	2.787(2)	2.950(2)	2.020(2)	3.100(2)	2.207(2)	2.363(2)	1.983(2)	2.134(3)	2.418(3)	144.6(2)	144.9(2)
27.8(3)	1.760(1)	1.755(1)	1.746(1)	1.754(1)	1.941(2)	2.783(2)	2.947(2)	2.012(2)	3.098(2)	2.200(2)	2.356(2)	1.976(2)	2.127(3)	2.410(3)	144.4(2)	144.7(2)
30.6(3)	1.753(2)	1.751(1)	1.744(1)	1.750(2)	1.938(2)	2.776(2)	2.944(2)	2.008(2)	3.092(2)	2.193(2)	2.348(3)	1.969(2)	2.120(3)	2.406(2)	144.3(2)	144.6(2)
33.4(7)	1.749(1)	1.747(1)	1.737(1)	1.745(1)	1.932(2)	2.767(2)	2.938(2)	1.999(2)	3.086(2)	2.185(2)	2.340(2)	1.965(2)	2.113(3)	2.399(3)	144.3(2)	144.6(2)
36.5(4)	1.746(2)	1.744(2)	1.735(1)	1.742(2)	1.926(2)	2.761(2)	2.935(2)	1.997(2)	3.085(2)	2.177(2)	2.337(3)	1.958(2)	2.109(4)	2.394(4)	144.2(2)	144.4(2)
39.3(4)	1.741(2)	1.739(2)	1.732(1)	1.737(2)	1.923(2)	2.755(3)	2.932(2)	1.991(2)	3.078(3)	2.172(2)	2.328(3)	1.958(2)	2.104(3)	2.389(3)	144.2(2)	144.5(2)
41.8(4)	1.737(2)	1.738(2)	1.730(2)	1.735(2)	1.919(3)	2.750(3)	2.933(3)	1.987(2)	3.079(3)	2.166(2)	2.323(3)	1.950(2)	2.098(4)	2.385(4)	144.0(2)	144.2(2)
45.6(5)	1.735(2)	1.733(2)	1.725(2)	1.732(2)	1.910(2)	2.743(2)	2.923(2)	1.983(2)	3.073(3)	2.161(2)	2.318(3)	1.944(2)	2.092(4)	2.379(4)	143.9(2)	144.1(2)
47.5(5)	1.731(2)	1.733(2)	1.722(2)	1.728(2)	1.907(3)	2.737(3)	2.925(2)	1.976(2)	3.075(3)	2.154(2)	2.314(4)	1.936(2)	2.088(4)	2.375(4)	143.8(2)	143.7(2)
50.1(4)	1.727(3)	1.728(2)	1.719(2)	1.725(2)	1.900(2)	2.735(3)	2.925(2)	1.972(2)	3.068(3)	2.149(2)	2.304(4)	1.936(2)	2.081(4)	2.370(4)	143.6(2)	143.9(3)
52.7(4)	1.724(3)	1.727(2)	1.715(2)	1.722()	1.899(3)	2.725(3)	2.920(3)	1.968(3)	3.066(3)	2.148(3)	2.299(4)	1.930(3)	2.077(3)	2.366(3)	143.7(3)	143.7(3)
55.4(5)	1.721(3)	1.719(3)	1.716(2)	1.717(3)	1.898(3)	2.719(3)	2.922(3)	1.959(3)	3.062(4)	2.136(3)	2.298(5)	1.929(3)	2.075(4)	2.362(3)	143.6(3)	143.8(3)
58.0(5)	1.716(3)	1.719(3)	1.712(2)	1.717(3)	1.891(3)	2.715(3)	2.915(2)	1.960(2)	3.059(4)	2.133(3)	2.292(4)	1.922(3)	2.068(4)	2.358(4)	143.6(3)	143.6(3)
60.6(6)	1.719(3)	1.716(2)	1.705(2)	1.723(3)	1.875(4)	2.722(4)	2.915(3)	1.958(3)	3.052(4)	2.135(3)	2.279(5)	1.928(4)	2.059(5)	2.355(5)	142.9(3)	144.0(3)
64.6(6)	1.711(3)	1.710(2)	1.703(2)	1.715(3)	1.878(3)	2.702(3)	2.908(3)	1.947(3)	3.052(4)	2.118(3)	2.279(5)	1.915(3)	2.052(5)	2.347(5)	143.3(3)	143.4(3)