Stability of Fe,Al-bearing bridgmanite in the lower mantle and synthesis of pure Fe-bridgmanite

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The physical and chemical properties of Earth’s mantle, as well as its dynamics and evolution, heavily depend on the phase composition of the region. On the basis of experiments in laser-heated diamond anvil cells, we demonstrate that Fe,Al-bearing bridgmanite (magnesium silicate perovskite) is stable to pressures over 120 GPa and temperatures above 3000 K. Ferric iron stabilizes Fe-rich bridgmanite such that we were able to synthesize pure iron bridgmanite at pressures between ~45 and 110 GPa. The compressibility of ferric iron–bearing bridgmanite is significantly different from any known bridgmanite, which has direct implications for the interpretation of seismic tomography data.

INTRODUCTION

The lower mantle constitutes more than half of Earth’s interior by volume and is believed to consist predominantly of bridgmanite [perovskite-structured (Mg,Fe)(Si,Al)O3] with up to approximately 20% ferropericlase (Mg,Fe)O by volume (1, 2). Thus, the physical properties, crystal chemistry, and stability of bridgmanite at high pressures and temperatures are critical for understanding the structure and dynamics of our planet, as well as the interior of other terrestrial planets and exoplanets. Ever since the application of laser-heated diamond anvil cell (DAC) techniques and x-ray diffraction allowed the major components of the lower mantle to be identified (3), investigations of perovskite-structured silicates have been a popular focus of mineral physics studies. Over the decades, there have been several claims that bridgmanite undergoes structural transformations (4–6) or that the phase is not chemically stable at all conditions within the lower mantle (7–9). However, so far, only one phase transition in (Mg,Fe)(Si,Al)O3 bridgmanite has been unambiguously confirmed, namely, to a CaIrO3-type structure phase (often called post-perovskite) above ~125 GPa and at high temperatures (6). Earlier observations (4, 5) of decomposition were probably due to large temperature gradients, resulting in Soret or Gorsk effects arising from one-sided highly focused laser heating (9, 10). Recently, using more advanced setups for laser-heated DAC experiments, Zhang et al. (8) reported that Fe-bearing bridgmanite is unstable at pressures of 95 to 101 GPa and temperatures of 2200 to 2400 K, where it loses its iron component and decomposes into a nearly Fe-free MgSiO3 perovskite and a Fe-rich (Mg,Fe)SiO3 phase (“H-phase”) with a hexagonal structure not previously known, causing a small volume reduction in bridgmanite. The hexagonal phase can be synthesized at pressures as low as ~85 GPa. These findings may be of primary relevance for geophysical, geochemical, and geodynamic models of the lower mantle below depths of 2000 km. Changes in the pseudobinary MgSiO3–FeSiO3 phase relations could be associated with spin crossover of iron above ~60 GPa and drastic modifications of its crystal chemistry. However, structural data on (Mg,Fe)(Si,Al)O3 bridgmanite in the megabar pressure range and ~2000 K are very limited, and its possible decomposition with formation of the H-phase is inconsistent with some experimental observations and theoretical calculations (5, 11–14). Here, we apply single-crystal x-ray diffraction (SCXRD) in laser-heated DACs (see Materials and Methods and the Supplementary Materials) to study stability of iron (and aluminum)–bearing bridgmanite at conditions of the deep part of Earth’s lower mantle.

RESULTS

Single crystals of bridgmanite with different compositions, Mg0.83Fe0.17Al0.06Si0.94O3 (referred to below as FE17), Mg0.86Fe0.14Al0.05Si0.96O3 (FE14), and Mg0.90Fe0.40Si0.63Al0.37O3 (FE40), as determined from SCXRD structural refinement and microprobe analysis, were selected from samples synthesized in a multianvil (MA) apparatus at 25 GPa and 1300°C. According to Mössbauer spectroscopy, the ratio Fe3+/Fe is 0.93(3) (12) in FE40 and 0.20(3) in FE17 and FE14 (15). Before being loaded into a DAC, crystals with sizes from ~10 × 10 × 5 μm2 to ~20 × 20 × 7 μm2 were selected and tested with an in-house high-brilliance rotating anode diffractometer (16). X-ray diffraction measurements were carried out in angle-dispersive mode at the 13-IDD beamline (λ = 0.31 Å; beam size, 5 × 5 μm2) at the Advanced Photon Source (APS), United States, at the ID09a (λ = 0.41 Å; beam size, 10 × 10 μm2) and ID27 (λ = 0.37 Å; beam size, 3 × 3 μm2) beamlines at the European Synchrotron Radiation Facility (ESRF), France, and at the extreme conditions beamline P02.2 (λ = 0.2903 Å; beam size, 3 × 8 μm2) The Positron-Electron Tandem Ring Accelerator III (PETRA III), Deutsches Elektronen-Synchrotron (DESY), Germany (see Materials and Methods for more details). The samples were loaded at ~1.4 kbar in Ne pressure-transmitting medium, compressed to pressures ranging from 32 to 130 GPa (Fig. 1), and heated...
using a double-sided laser setup at temperatures between 2200 and 3100 K over relatively long time periods ranging from 20 to 100 min.

The only observed changes upon laser heating for all investigated samples were shifts in the positions of reflections due to variations in temperature and pressure (fig. S1). Detailed inspection of diffraction patterns (Fig. 2 and fig. S2) did not reveal the appearance of any unidentified reflections during or after heating. When pressure remained the same before and after laser heating (see, for example, table S1), the lattice parameters of bridgmanite also remained the same within experimental uncertainty, suggesting that the integrity of the material was not affected by prolonged laser heating. The data sets collected for temperature-quenched samples are of sufficient quality to perform accurate structure refinements, including the determination of the occupancy of iron at the two different distinct crystallographic sites of the perovskite-type structure [see the studies by Glazyrin et al. (12) and Bykova (17) for methodological details].

Perovskite-structured orthorhombic bridgmanite (space group $Pbmn$, no. 62) has two cation positions (fig. S3): one coordinated by a distorted bicapped prism ("A"-site) and one octahedrally coordinated ("B"-site). We found that in accordance with previous observations (12) and within the uncertainties of our method (about 5% of total iron content), there is no evidence for redistribution of Fe between the two crystallographic sites and there are no changes in the chemical composition (table S1).

The occurrence of an iron-rich H-phase at high pressures and temperatures may be related to the instability of pure iron bridgmanite [or pure ferrous iron bridgmanite (8)]. Indeed, the amount of the Fe$_2^+$SiO$_3$ component that can be accommodated by Mg,Fe bridgmanite ranges from about 12 mole percent (mol %) at 26 GPa (18) to 50 to 74 mol % at ~85 GPa (19–21). At pressures from ~20 to over 115 GPa, pure FeSiO$_3$ was reported to disproportionate into FeO and SiO$_2$ (22, 23). Ferrous iron end-member bridgmanite has never been synthesized so far, and the solubility limit of the Fe-bearing component in perovskite-structured silicate remains unknown. However, it is now widely accepted (2, 5, 12, 15, 24) that bridgmanite relevant to the lower mantle contains both ferrous and ferric iron. Thus, the relevant question is whether pure Fe$_2^+$Fe$_{3+}$-bridgmanite exists or not.

We used synthetic skiagite-majorite garnet as the starting material for experiments to study the high-pressure high-temperature behavior of Mg,Al-free Fe$_{3+}$-bearing silicate with the composition Fe$_{2.7}$(Fe$_{0.234(2)}$Fe$_{3+}$$_{1.532(1)}$Si$_{0.234(2)}$)$\text{SiO}_4$ (25), as determined from single-crystal diffraction and Mössbauer spectroscopy data (25). Our experiments using the MA apparatus up to 23 GPa and 1900 K demonstrate that above 12.5 GPa and 1700 K, skiagite-majorite garnet decomposes into SiO$_2$ and Fe oxides (Fig. 1 and fig. S4). Laser heating of skiagite-majorite garnet in the DAC up to ~40 GPa and 1500 to 2300 K resulted in decomposition into stishovite (SiO$_2$) and Fe$_4$O$_5$ (Fig. 1 and fig. S5) (26). Remarkably, in some runs, iron oxide crystallized in the form of single crystals (or polycrystalline domains), which gave diffraction data of sufficient quality for an accurate structure refinement of Fe$_4$O$_5$ (fig. S6 and table S4). Upon heating at pressures above ~45 GPa, we observed...
different sequences of transformations. For example, at 51(1) GPa and 1800(100) K, skiagite-majorite garnet decomposes into stishovite, high-pressure orthorhombic $h$-$\text{Fe}_3\text{O}_4$ (27), and one additional phase (fig. S5). At higher temperatures [2100(100) K; for example, fig. S5], diffraction lines of stishovite are absent, the intensity of reflections of $h$-$\text{Fe}_3\text{O}_4$ decreases, and the diffraction pattern is dominated by lines of the additional phase that can be easily indexed as orthorhombic. Analysis of single-crystal diffraction data allows unambiguous identification of this phase to be GdFeO$_3$-type perovskite structure (fig. S3 and table S2). The same phase was synthesized by heating skiagite-majorite

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**Fig. 2. Examples of parts of the two-dimensional wide-scan x-ray diffraction images of bridgmanite $\text{Mg}_{0.86}\text{Fe}_{0.14}\text{Al}_{0.04}\text{Si}_{0.96}\text{O}_3$.** (A to D) Data were collected (A) before and (B to D) after laser heating at the indicated temperatures and pressures. Indices are given for bridgmanite reflections (underlined by boxes). The only observed changes in diffraction patterns upon heating are due to development of additional domains of the same phase (marked in red). Large black spots are due to diamond (D) reflections. Diffraction rings of Ne (pressure transmitting medium), Re (gasket), and Au are also marked. Data were collected at IDD-13 at APS. Yellow circles indicate bad pixels of the detector. (Full high-resolution images are also given in the Supplementary Materials).
The crystal chemistry of ferric iron–bearing Fe-bridgmanite is remarkable (table S2). First, we observed that all iron is located in the A-site, and within the accuracy of determination of the occupancies of structural positions (better than 5%), there is no iron in the octahedra. This conclusion is robust because x-ray scattering factors of silicon and iron are very different, and agrees with recent studies on bridgmanite of different compositions (10, 12, 15). Therefore, it is obvious that the material synthesized between 50 and 100 GPa contains a significant amount of vacancies (about 12%) at the A-site according to the substitution scheme $3Fe^{3+}→2Fe^{3+} + vacancy$. The formation of materials with vacancies at high pressure is not unprecedented, particularly among $Fe^{3+}$-bearing oxides (28), but has not been expected for bridgmanite (29, 30). Nevertheless, on the basis of the summary of bridgmanite compositions known from the study by Liu et al. (31), it was reported that there are indications that an A-site vacancy is favored in Al-free bridgmanite, whereas an oxygen vacancy is dominant in Al-bearing bridgmanite.

The dependence of polyhedral volumes on the unit cell volume (Fig. 3) for Fe-bridgmanite is the same as for pure magnesium– and iron–aluminum–bearing bridgmanites. It confirms that the large iron cation does not enter the B-site because incorporation of any appreciable amount of iron cations in the octahedral site in Fe-bearing bridgmanite should significantly affect its compressibility.

The effect of pressure on the lattice parameters of $Fe^{3+}$-bearing Fe-bridgmanite is very different from the variation observed in any other silicate perovskites [see the studies by Dorfman et al. (10), Glazyrin et al. (12), Kupenko et al. (24), and Boffa Ballaran et al. (32) and references therein] in that the a and b axes are much more compressible (fig. S7). Thus, vacancies on the A-site lead to significant softening of the material; it has a bulk modulus of $K_{300} = 190(4)$ GPa [$K′ = 4$, $V_0 = 178.96(6) Å^3$ per unit cell; Fig. 3 and table S3], which is drastically lower than the values known for other Fe- or/and Al-rich bridgmanites (fig. S8) (10, 12, 21, 32, 33).

**DISCUSSION**

The elastic properties of Fe,Al-bearing bridgmanite reported in the literature are highly controversial, especially in cases where samples were synthesized in situ in laser-heated DACs [for discussion, see particularly the studies by Andrault (5), Dorfman et al. (10), Glazyrin et al. (12), Dorfman et al. (21), Boffa Ballaran et al. (32), and Saikia et al. (33)]. The large effect of $Fe^{3+}$ and vacancies on the bulk modulus of bridgmanite reported in the summary of bridgmanite compositions known from the study by Liu et al. (31) is expected for oxidized parts of the lower mantle (for example, subducted slabs) and for relevant chemical compositions, the variation of $Fe^{3+}/ΣFe$ and the structure of the material are known in detail.

A recent precise study of iron-bearing bridgmanite (30) demonstrates that in the case of the charge substitution mechanism, the density and bulk modulus of bridgmanite vary linearly with the Fe content. Using equations reported in the study by Dorfman and Duffy (34), at a representative mid-mantle depth of 1850 km (80 GPa), the density and bulk modulus of bridgmanite with composition Fe$_{0.88}$SiO$_3$ are estimated to be $ρ_{300} = 6.171(4) g/cm^3$ and $K_{300,300} = 556(24)$ GPa. Using our data, we obtained $ρ_{300} = 5.93(1) g/cm^3$ and $K_{300,300} = 480(15)$ GPa, and bulk velocity heterogeneity parameter $δlnV_p/δX_{Fe} = 0.16$ [versus $~0.10$ in the study by Glazyrin et al. (12) and Dorfman and Duffy (34), a parameter that is almost independent of temperature at Earth’s lower mantle pressures (12)]. Consequently, for oxidized parts of the lower mantle (for example, subducted slabs) and for relevant chemical compositions, the variation of $Fe^{3+}/ΣFe$ can lead to significant changes in the bulk sound velocity of bridgmanite (exceeding 2%), demonstrating the importance of iron oxidation state for interpreting seismic tomography data (12). Moreover, it is now generally accepted that variations in iron content may be one of the major sources of lateral seismic
heterogeneities in Earth’s lower mantle (35). Our results suggest that incorporation of ferric iron on the A-site of bridgmanite, accompanied by the formation of vacancies, considerably affects the bulk sound velocity and increases the heterogeneity parameter \( \delta \ln V_p/\delta X_{Fe} \) by about 60%. Thus, substantially smaller variations in iron content may be required to explain the seismic tomography data (35).

**MATERIALS AND METHODS**

**Materials**

The material used in this study consisted of single crystals of bridgmanite with different compositions: Mg0.83Fe0.17Al0.06Si0.94O3 (FE17), Mg0.36Fe0.14Al0.03Si0.99O3 (FE14), Mg0.05Fe0.60Si0.45Al0.35O3 (FE40), and skagia-majorite garnet (Fe2+0.64(2)Fe3+0.36(2)Si1.00(3)O3). The details of samples FE17, FE14, and FE40 were described elsewhere (12, 15, 36). Mg-Al-free Fe-bridgmanite was synthesized from skagia-majorite garnet from the same batch that was used in a previous study (25).

**MA experiments**

MA experiments for studying the stability of skagia were performed at Bayerisches Geoinstitut, Bayreuth, at pressures up to 23 GPa and temperatures up to 1800 K. The starting mixture with the skagia composition (Fe2+Fe3+Si1.0O1.5) was prepared from pure oxides Fe0.94O, Fe2O3, and SiO2. The mixtures were loaded into a Re capsule with a 1-mm diameter and 1.8-mm length and heated for 30 min. A W97Re3-W75Re25 anode diffractometer was used. The sample chamber was prepared using PerkinElmer flat panel laser-heating system, and temperatures were measured from both sides by spectroradiometry (38).

At the ESRF on beamline ID09A, we used a mar555 flat panel detector and an x-ray wavelength of 0.415 Å with a beam spot size of \( \sim 10 \times 10 \) μm², whereas on beamline ID27 the parameters were as follows: \( \lambda = 0.37 \) Å; beam size, \( 3 \times 3 \) μm²; using PerkinElmer flat panel detector. At the extreme conditions beamline P02.2 at PETRA III, we used an x-ray wavelength of \( \lambda = 0.2903 \) Å and PerkinElmer detector, and the beam size was \( 3 \times 8 \) μm². The positions of the detectors were calibrated using Si or CeO2 standards.

Single-crystal diffraction data were collected in two modes—by continuous rotation of the cell around the omega axis (“wide scans”) from \( -20^\circ \) to \( +20^\circ \) for in situ high-pressure, high-temperature data acquisition and from \( -38^\circ \) to \( +38^\circ \) (“step scans”) for the temperature-quenched sample (that is, without laser-heating setup) by narrow 0.5° omega scanning. Pressure was determined using the Ne equation of state (39). In some experiments, a small (linear dimensions less than 5 μm) piece of gold was loaded at the edge of the pressure chamber to allow an accurate alignment of the cell with respect to the goniometer rotational axis.

The two-dimensional (2D) diffraction images were first analyzed using Dioptas software (40). Data processing (peak intensity integration, background evaluation, cell parameters, space group determination, and absorption correction) was performed using CrysAlisPro 171.36.28 (41) software with implemented SCALE3 ABSPACK scaling algorithm. Structures were solved by the direct method using SHELXS (42) software implemented in an X-Seed package (43). Structure refinement of integrated intensities was performed using SHELXL. Full-profile refinement of powder patterns was conducted using GSAS (General Structure Analysis System) software with a graphical interface, EXPGUI (44). Polyhedral volumes were calculated in VESTA (Visualization for Electronic and Structural Analysis) software (45).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/7/e1600427/DC1

**fig. S1.** Parts of the integrated diffraction images of bridgmanite Mg0.96Fe0.04Si0.63Al0.37O3 (FE14) collected before (lower curve) and during (upper curve) laser heating.

**fig. S2.** Full high-resolution 2D wide-scan x-ray diffraction images of bridgmanite samples FE14, FE17, and FE40.

**fig. S3.** Representative polyhedral structural model of orthorhombic bridgmanite.

**fig. S4.** Backscattered electron image of skagia starting composition at 23 GPa and 1600°C (run S6151).

**fig. S5.** Typical powder x-ray diffraction patterns of skiagite-majorite garnet that was laser-heated in a DAC at 39(1) GPa and 2250(100) K (see table S4 for crystallographic data).

**fig. S6.** Crystal structure of Fe4O5 obtained as the product of decomposition of skiagite-majorite garnet in a laser-heated DAC at 39(1) GPa and 2250(100) K (see table S4 for crystallographic data).

**fig. S7.** Variation with pressure of the normalized unit-cell parameters for three bridgmanites—Fe-bridgmanite (this study), (Mg0.86Fe0.14Al0.04Si0.96O3 (FE14), Mg0.60Fe0.40Si0.63Al0.37O3 (FE40), and skagia-majorite garnet (Fe2+0.64(2)Fe3+0.36(2)Si1.00(3)O3). The details of samples FE17, FE14, and FE40 were described elsewhere (12, 15, 36). Mg-Al-free Fe-bridgmanite was synthesized from skagia-majorite garnet from the same batch that was used in a previous study (25).

**fig. S8.** Effect of Fe8Si12O42Fe3Al2FeO3 and Fe3Al2H2O3 substitutions in bridgmanite on the bulk modulus (A” and “B” denote structural positions; see table S3 for references).

**table S1.** Crystallographic data for Fe,Al bridgmanite samples FE14, FE17, and FE40 at selected pressures before and after laser heating at different temperatures.
table S2. Crystallographic data for Fe$_x$(Mg$_{1-x}$Fe)$_2$Si$_{2-x}$O$_7$, bridgmanite at selected pressures.

Table S3. Compressibility of bridgmanite with different compositions.

Table S4. Crystallographic data of Fe$_4$O$_5$.

REFERENCES AND NOTES


5. K. Glazyrin, T. Boffa Ballaran, D. J. Frost, C. McCammon, A. Kantor, M. Merlini, M. Hanfland, K. Funakoshi, N. Sata, Phase relations in the system MgO–FeO–SiO$_2$ to 50 GPa and 2000°C: An application of experimental techniques using shock-heating with the gas loading at APS. Portions of this research were carried out at the light source PETRA III at DESY. We thank I. Kantor for help with laser heating, and we acknowledge the ESRF for provision of synchrotron radiation facilities. We thank S. Thachev for the technical support with the gas loading at APS. Portions of this research were carried out at the light source PETRA III at DESY. We acknowledge the use of the DESY photon facility. Funding: L.D. and N.D. thank Deutsche Forschungsgemeinschaft (DFG) (project nos. DUS 456/6-2 and the Heisenberg Program and project no. DUS 189/6-1) and the Federal Ministry of Education and Research (BMBF), Germany (project no. SK13W3C), for financial support. A part of this study was performed at GeoSoilEnviROCS (Sector 13), APS, Argonne National Laboratory. GeoSoilEnviROCS is supported by the NSF–Earth Sciences (EAR-1128799) and Department of Energy (DOE)–Geosciences (DE-FG02-94ER14466). This research used resources of the APS, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, under contract no. DE-AC02-06CH11357. This study was partly supported by the Russian Foundation for Basic Research.
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