Crystal chemistry of bridgmanite in a subducting mid-ocean ridge basalt: incorporation mechanism of Fe and Al

Bridgmanite (simplified formula $MgSiO_3$) is the most abundant constituent in the Earth's lower mantle and crystallizes in an orthorhombic perovskite-type structure with space group *Pbnm* (Fig. 1). Pressure, temperature, and chemical dependences of its physical and crystal-structure properties provide essential information for a detailed understanding of the lower mantle. In particular, the effects of the incorporation of Fe and Al, the next major mantle elements after Mg and Si, into bridgmanite can have a large effect on the physical properties and rheology of the lower mantle.

Bridgmanite formed from a mid-ocean ridge basalt (MORB) component of subducting slabs contains larger amounts of Fe and Al than that formed from a pyrolytic composition [1]. This difference in bridgmanite composition can cause a difference in the incorporation mechanism of Fe and Al into the crystal structure between subducting slabs and their surrounding lower mantle. This should cause heterogeneity in the physical properties and rheology of the lower mantle. Elucidating the crystal chemistry of bridgmanite formed from the MORB composition is a key to resolving this issue. The precise crystal chemistry examined employing a single crystal is, therefore, significant for gaining a detailed understanding of lower-mantle dynamics. In particular, the use of ^{57}Fe-Mössbauer spectroscopy is indispensable for distinguishing the valence and spin states of Fe, which cannot be directly observed by X-ray diffraction. For this purpose, we characterized a bridgmanite single-crystal with the Fe and Al contents expected in MORB, by a combination of single-crystal X-ray diffraction, synchrotron ^{57}Fe-Mössbauer spectroscopy, and electron probe microanalysis (EPMA) [2].

Single crystals of bridgmanite were synthesized at 28 GPa and 1873 K using a Kawai-type multianvil apparatus. The experiment was conducted in a bulk composition of $0.650MgO \cdot 0.175Fe_2O_3 \cdot 0.650SiO_2 \cdot 0.175Al_2O_3$, which is close to that reported for bridgmanite formed from the MORB composition. The zero-pressure/room-temperature crystal structure was determined and refined using single-crystal X-ray diffraction intensities collected with a four-circle diffractometer having a laboratory Mo-$K\alpha$ radiation source. Energy-domain synchrotron ^{57}Fe-Mössbauer spectroscopy measurements at room temperature using a nuclear Bragg monochromator were conducted at SPring-8 **BL10XU**.

The EPMA of synthesized crystals gave a chemical composition of $Mg_{0.642(7)}Fe_{0.341(6)}Si_{0.656(10)}Al_{0.356(4)}O_3$, which is in excellent agreement with $Mg_{0.662(3)}Fe_{0.338(3)}Si_{0.662(3)}Al_{0.338(3)}O_3$ obtained from the structure refinement.

The measured Mössbauer spectrum seems to consist of two absorption peaks with different intensities (Fig. 2(a)). These peaks were interpreted to be one asymmetric doublet on the basis of the following constraints: the coordination environments around the possible occupied sites of Fe are largely distorted, which should yield quadrupole splitting; the doublets measured using a single crystal can be asymmetric. The best fit based on this interpretation showed no significant residuals (Fig. 2(b)), resulting in an isomer shift of 0.40(3) mm/s and a quadrupole splitting of 0.86(4) mm/s, indicating that Fe ions exclusively occupy the eightfold (nominally 12-fold) coordinated A-site in the trivalent high-spin (HS) state. From the cation ratio indicated by EPMA, this leads to the conclusion that Al^{3+} ions exclusively occupy the sixfold-coordinated B-site and there are no vacancies. These cation distributions were also confirmed from the results of structure refinement ($R = 0.0189$, $wR = 0.0146$). In the present case where relatively large and equal amounts of Fe and Al are present, the following charge-coupled substitution is concluded to be predominant in the incorporation of both cations into bridgmanite:

$$^{A}Mg^{2+} + {}^{B}Si^{4+} \leftrightarrow {}^{A}Fe^{3+}(HS) + {}^{B}Al^{3+} \qquad (1),$$
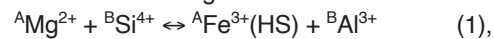
where the superscripts "A" and "B" represent the occupied sites. The incorporation of Fe^{3+} and Al via this substitution decreases the mean cation size on the A site ($<r_A>$) and increases that on the B site ($<r_B>$). We found that this incorporation of Fe^{3+} and Al enhances the structural distortion due to the tilting of BO_6 octahedra (Fig. 3(a)), yielding the unusual expansion of the mean <A−O> bond length owing to the flexibility of A−O bonds to the structural distortion (Fig. 3(b)), in contrast to the mean <B−O> bond length, which depends on the cation-size effect (Fig. 3(c)).
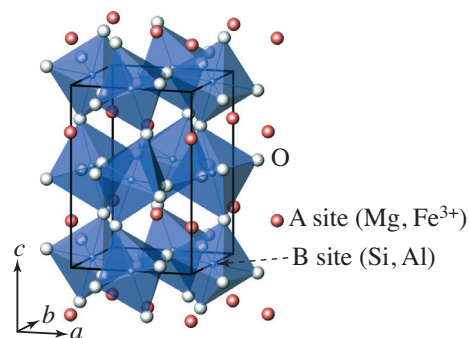

Fig. 1. Crystal structure of our (Fe^{3+}, Al)-bearing bridgmanite. Some of the Mg^{2+} on the eightfold (nominally 12-fold) coordinated A-site and Si^{4+} on the sixfold coordinated B-site are replaced with high-spin Fe^{3+} and Al^{3+}, respectively.

At the lowermost mantle, bridgmanite is believed to transform to the post-perovskite phase, associated with the D″ seismic discontinuity. However, a perovskite phase with a different symmetry can intervene between the *Pbnm* perovskite phase and the post-perovskite phase, as suggested for $(Mg, Fe)SiO_3$ bridgmanite at 64 GPa and 1850 K [3] and for $MgSiO_3$ bridgmanite above 83 GPa and 1700 K [4]. To examine the possibility of such phase transitions in perovskites at high pressures and high temperatures, it is effective to discuss the compressibility ratios (β_B/β_A) of the two coordination polyhedra [5], given by the rigidity ratio M_A/M_B defined from bond valence, where the subscripts "A" and "B" represent the AO_{12} and BO_6 polyhedra, respectively. In perovskites exhibiting zone-boundary phase transitions, such as bridgmanite, Clapeyron slopes (dP/dT_c) for the phase boundary are positive when $M_A/M_B < 1$ because the phase transition temperature T_c increases with pressure owing to the increased tilting of BO_6 octahedra, and they are negative when $M_A/M_B > 1$ because T_c decreases with increasing pressure owing to the decreased octahedral tilting [5]. The calculated M_A/M_B ratios under ambient conditions are 0.67 for the reported $MgSiO_3$ bridgmanite and 0.72 for our (Fe^{3+}, Al)-bearing bridgmanite. If a bridgmanite transforms to another perovskite phase under mantle conditions, its phase boundary has a positive Clapeyron slope. In addition, as described above, the incorporation of Fe^{3+} and Al increases the octahedral tilting (Fig. 3(a)). These show that the higher pressure and the higher Fe^{3+} and Al contents would raise T_c, implying that bridgmanites in subducting slabs have a much higher T_c than previously suggested ones [3,4] if the suggested phase transitions exist. The phase transition to another perovskite phase might be observed in slabs that have fallen/subducted into the lowermost mantle.
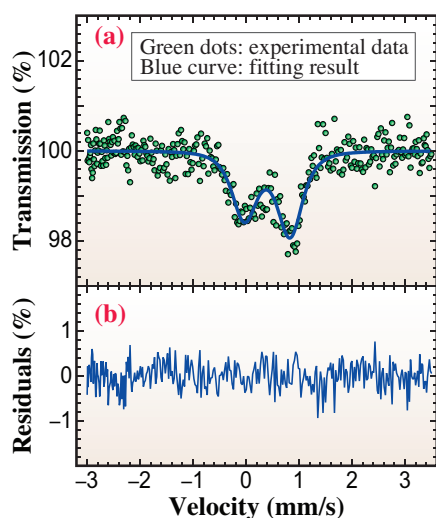
We also revealed that the incorporation of Fe^{3+} and Al via substitution (1) does not change M_A, decreases M_B, and consequently increases β_B/β_A. The increase in β_B/β_A depends only on M_B and may correspond to the decrease in the bulk modulus K. The bulk sound velocity $V_B = \sqrt{K/\rho}$ would thus decrease with increasing Fe^{3+} and Al contents, which agrees with the reported results of theoretical calculation for (Fe^{3+}, Al)-bearing bridgmanite. This crystallographic approach can be effective for gaining important insights into the seismic properties within the lower mantle.
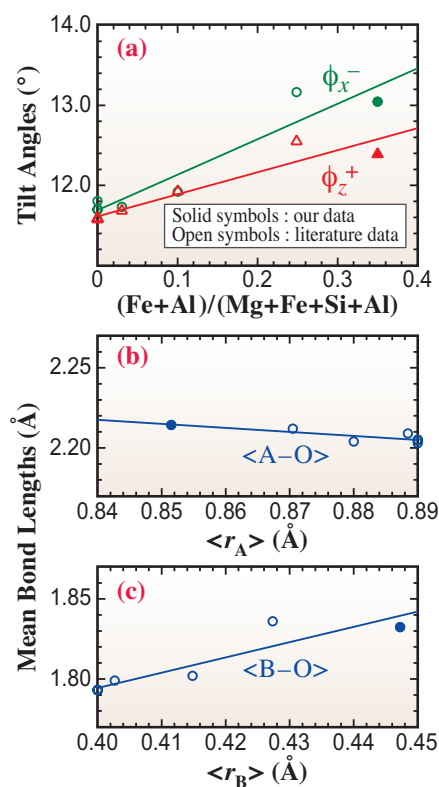
Fig. 3. **(a)** Tilt angles ϕ_x^- and ϕ_z^+ of BO_6 octahedra as functions of the ratio (Fe+Al)/(Mg+Fe+Si+Al), **(b)** mean <A–O> bond length as a function of the mean cation size on A site ($<r_A>$), and **(c)** mean <B–O> bond length as a function of the mean cation size on B site ($<r_B>$). Refer to [2] for details of tilt angles.

Fig. 2. **(a)** Mössbauer spectrum of our (Fe^{3+}, Al)-bearing bridgmanite single-crystal and **(b)** the fitted residuals.

Akihiko Nakatsuka

Graduate School of Sciences and Technology for Innovation, Yamaguchi University

Email: tuka@yamaguchi-u.ac.jp

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