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(FE, AL)-BEARING BRIDGMANITE IN A SUBDUCTING MID-OCEAN RIDGE BASALT

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Studies on crystal chemistry of minerals have provided a lot of substantial knowledge of transformations, phase relations, physical properties, and dynamics in the Earth's interior. In particular, precise atomic-level knowledge of bridgmanite (simplified formula MgSiO₃), occupying about 80 volume percent of the Earth's lower mantle, is indispensable for a detailed understanding of the deep mantle. Because Fe and Al are important major elements in the mantle composition after Mg and Si, their incorporation effects into the bridgmanite structure (FIG. 1A) have attracted much attention because of their great influence on the lowermantle dynamics. Bridgmanite formed from a mid-ocean ridge basalt (MORB) component of subducting slabs contains much larger amounts of Fe and Al than that formed from a pyrolytic composition (Hirose and Fei 2002). Different bridgmanite compositions can produce different incorporation mechanisms of both cations into the crystal structure between subducting slabs and the surrounding lower-mantle. This should cause heterogeneity in the physical properties and rheology of the lower mantle. Elucidating the crystal chemistry of bridgmanite that forms from the MORB composition is thus a key to solve this issue. We focused on the incorporation effects of Fe and Al into bridgmanite and investigated the crystal chemistry of its single-crystal form with both cation contents expected in MORB using a combination of X-ray diffraction structure analysis, synchrotron ⁵⁷Fe-Mössbauer spectroscopy, and electron probe microanalysis (Nakatsuka et al. 2021). In particular, ⁵⁷Fe-Mössbauer spectroscopy is a powerful probe to distinguish the valence- and spin-states of Fe, which cannot directly be observed by X-ray diffraction.

Bridgmanite single- crystals were synthesized in a bulk composition with the Fe- and Al-contents expected for bridgmanite formed from the MORB composition at 28 GPa and 1873 K, using a Kawai-type multianvil apparatus. The zero-pressure/room-temperature crystal structure was determined and refined on the basis of single-crystal X-ray diffraction intensities collected using a four-circle diffractometer with a laboratory MoK α -radiation source. Energy-domain synchrotron ⁵⁷Fe-Mössbauer spectroscopy at room temperature using a nuclear Bragg monochromator was conducted at the BL10XU beamline of SPring-8 (Japan).

The electron probe microanalyses of the synthesized crystals gave a chemical composition of Mg_{0.642(7)}Fe_{0.341(6)}Si_{0.656(10)}Al_{0.356(4)}O₃, agreeing excellently with Mg_{0.662(3)}Fe_{0.338(3)}Si_{0.662(3)}Al_{0.338(3)}O₃ from the structure refinement. The measured Mössbauer spectrum (FIG. 1B) gave 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 trivalent high-spin (HS) state. In consideration of the cation ratio from the electron probe microanalyses, this shows that Al³⁺ ions exclusively occupy the sixfold coordinated B-site and there are no vacancies. These cation distributions were also confirmed from the structure refinement. We thus conclude that the charge-coupled substitution ${}^{A}Mg^{2+} + {}^{B}Si^{4+} \leftrightarrow {}^{A}Fe^{3+}(HS) + {}^{B}Al^{3+}$ is predominant in the incorporation of Fe and Al into our bridgmanite, where the superscripts "A" and "B" represent the occupied sites.

Some studies (Meade et al. 1995; Shim et al. 2001) suggested that bridgmanite could transform to another perovskite phase with a different symmetry before the phase transition to the post-perovskite phase, associated with the D" seismic discontinuity. In terms of the



FIGURE 1 (A) Crystal structure of our (Fe³⁺, Al)-bearing bridgmanite. The structure has the two cation sites: a larger eightfold (nominally 12-fold) coordinated A-site and a smaller sixfold coordinated B-site, consisting of a network of corner-linked BO₆ octahedra with A-site atoms located at the centers of cavities in the network and being distorted largely from the ideal cubic perovskite structure owing to the tilting of BO₆ octahedra. In the MgSiO₃ bridgmanite, the A and B sites are occupied only by Mg²⁺ and Si⁴⁺, respectively. In our (Fe³⁺, Al)-bearing bridgmanite, parts of Mg²⁺ and Si⁴⁺ are replaced with high-spin Fe³⁺ and Al³⁺, respectively, via the charge-coupled substitution. (B) Mössbauer spectrum of our (Fe³⁺, Al)-bearing bridgmanite single- crystal and (C) the fitting residuals. In (B), the pale-blue dots and red curve are the experimental data and fitting result, respectively. Taking some constraints required from the crystal structure into account, the measured Mössbauer spectrum can be interpreted as one asymmetric doublet.

compressibility ratio β_B/β_A (Angel et al. 2005), we conclude that this possibility cannot be ruled out and suggest that the phase transition to another perovskite phase, if present, might be found in slabs that have fallen/subducted into the lowermost mantle, where β_A and β_B are the compressibility of AO₁₂ (practically AO₈) and BO₆ polyhedra, respectively. We also revealed that β_B/β_A increases depending only on the rigidity of the BO₆ octahedron by the incorporation of Fe³⁺ and Al via the charge-coupled substitution. Because such an increase in β_B/β_A can correspond to a reduction of the bulk modulus, the bulk sound velocity would decrease with increasing contents of both cations. This crystallographic approach can be effective for gaining important insights into the seismic properties within the lower mantle.

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