

# Does pressure promote Fe<sup>3+</sup>-Al disordering in lower mantle bridgmanite?

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Bridgmanite, perovskite-type (Mg,Fe,Al)(Si,Al,Fe)O<sub>3</sub>, is the most abundant mineral in the Earth's lower mantle, comprising more than 75 vol.% of pyrolitic and harzburgitic phase assemblages and ~25 vol.% of a basaltic assemblage [1,2]. At shallow lower mantle conditions and for Fe < Al, ferric iron is incorporated in the bridgmanite structure mainly through the Fe<sup>3+</sup>AlO<sub>3</sub> substitution mechanism. Due to its larger ionic radius, Fe<sup>3+</sup> is hosted in the pseudo-dodecahedral A-site, whereas Al in the octahedral B-site. At pressures above 40 GPa, evidence of disordering of Fe<sup>3+</sup> and Al in the A-site and B-site of bridgmanite after laser annealing in the diamond anvil cell was recently reported based on *in-situ* synchrotron Mössbauer spectroscopy measurements [3,4]. Disordering of Fe<sup>3+</sup> and Al could impact both the elastic behavior of bridgmanite and its partitioning of Fe with other lower mantle phases. However, the sample characterization in ref. 3 and 4 was not fully conclusive due to the relatively low signal-to-noise ratio of the Mössbauer spectra and the absence of X-ray structural analyses supporting the Fe<sup>3+</sup>-Al disordering. Here, we synthesized a suite of bridgmanite samples at 45 GPa and 2000 K using advanced multi-anvil techniques with tapered tungsten carbide anvils. The recovered samples were characterized at both room and high pressure using electron microprobe, synchrotron Mössbauer spectroscopy and synchrotron single-crystal X-ray diffraction. Structural refinements at ambient conditions and Mössbauer spectra at high pressure showed no evidence for Fe<sup>3+</sup>-Al disordering or the onset of a spin crossover of octahedrally coordinated Fe<sup>3+</sup>. This suggests that Fe<sup>3+</sup> incorporation in the octahedral site of bridgmanite observed in ref. 3 and 4 is either due to thermodiffusion of Fe, which would locally create regions with Fe<sup>3+</sup> > Al, or may revert to the lower-pressure configuration when quenched at rates that are typical of multi-anvil experiments.

[1] Ishii et al., *J Geophys Res Solid Earth* 124, 3491 (2019).

[2] Irifune et al., *Science* (1979) 327, 193 (2010).

[3] Kuppenko et al., *Earth Planet Sci Lett* 423, 78 (2015).