Equation of state and hyperfine parameters of high-spin bridgmanite in the Earth’s lower mantle by synchrotron X-ray diffraction and Mössbauer spectroscopy

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ABSTRACT

In this study, we performed synchrotron X-ray diffraction (XRD) and Mössbauer spectroscopy (SMS) measurements on two single-crystal bridgmanite samples [Mg₀.₉₀Fe₀.₁₀Fe₀.₉₀₂₃Al₀.₁₀₈₇Si₀.₉₀O₃ (Bm6) and Mg₀.₉₀₂₃Fe₀.₀₇Fe₀.₆₀Al₀.₁₁Si₀.₉₆O₃ (Al-Bm11)] to investigate the combined effect of Fe and Al on the hyperfine parameters, lattice parameters, and equation of state (EoS) of bridgmanite up to 130 GPa. Our SMS results show that Fe²⁺ and Fe³⁺ in Bm6 and Al-Bm11 are predominantly located in the large pseudo-dodecahedral sites (A-site) at lower-mantle pressures. The observed drastic increase in the hyperfine quadrupole splitting (QS) between 13 and 32 GPa can be associated with an enhanced local distortion of the A-site Fe²⁺ in Bm6. In contrast to Bm6, the enhanced lattice distortion and the presence of extremely high QS values of Fe²⁺ are not observed in Al-Bm11 at high pressures. Our results here support the notion that the occurrence of the extremely high QS component of approximately 4 mm/s in bridgmanite is due to the lattice distortion in the high-spin (HS) A-site Fe²⁺, instead of the occurrence of the intermediate-spin state. Both A-site Fe²⁺ and Fe³⁺ in Bm6 and Al-Bm11 remain in the HS state at lower-mantle pressures. Together with XRD results, we present the first experimental evidence that the enhanced lattice distortion of A-site Fe²⁺ does not cause any detectable variation in the EoS parameters, but is associated with anomalous variations in the bond length, tilting angle, and shear strain in the octahedra of Bm6. Analysis of the obtained EoS parameters of bridgmanite at lower-mantle pressures indicates that the substitution of Fe in bridgmanite will cause an enhanced density and a reduced bulk sound velocity (Vₐ), whereas the Al and Fe substitution has a reduced effect on density and a negligible effect on Vₐ. These experimental results provide new insight into the correlation between lattice, hyperfine, and EoS parameters of bridgmanite in the Earth’s lower mantle.

Keywords: Bridgmanite, lattice distortion, equation of state, Fe and Al, lower mantle, high spin

INTRODUCTION

Bridgmanite, (Mg,Fe)(Fe,Al,Si)O₃, is the most abundant mineral in the Earth’s lower mantle occupying approximately 75% by volume in a pyrolitic mantle composition or as high as ~93% in the chondritic Earth model with a Si-enriched lower mantle (Hirose 2002; Irfune et al. 2010; Murakami et al. 2012; Ringwood 1975). In the past few decades, physical properties of bridgmanite at relevant pressure and temperature (P-T) conditions of the lower mantle have attracted extensive research interest (e.g., Hemley and Cohen 1992; McCammon 1997; Stixrude and Cohen 1993; Tsujiya et al. 2004). In particular, recent experimental and theoretical studies have reported that Fe in lower-mantle bridgmanite undergoes spin pairing transitions, calling for investigations into the effect of Fe spin transition on the physical properties of bridgmanite at lower-mantle pressures (e.g., Cataldi et al. 2011, 2010; Goncharov et al. 2010; Hsu et al. 2012; Lin et al. 2008, 2012; Mao et al. 2011, 2015; McCammon et al. 2008; Tsujiya and Wang 2013). However, the spin and valence states of iron in bridgmanite remain controversial (e.g., see Lin et al. 2013 for a review).

Fe can exist as both Fe²⁺ and Fe³⁺ in lower-mantle bridgmanite in large pseudo-dodecahedral sites (A site) and small octahedral sites (B site) (Lin et al. 2013), complicating our understanding of the spin states of Fe in bridgmanite. Thus far, both experimental and theoretical studies are in agreement that Fe³⁺ in the B site will undergo the high-spin (HS) to low-spin (LS) transition at lower-mantle pressures, but the A-site Fe³⁺ will stay in the HS