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Recoil-free fractions of iron in aluminous bridgmanite from temperature-dependent Mössbauer spectra†

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Abstract

Aluminous bridgmanite (Al-Bm) is the dominant phase in the Earth's lower mantle. In this study, the Mössbauer spectra of an Al-Bm sample $Mg_{0.868}Fe_{0.087}Si_{0.944}Al_{0.101}O_{2.994}$ were recorded from 65 to 300 K at 1 bar. The temperature dependence of the center shift was fitted by the Debye model and yielded the Debye temperatures of 305 ± 3 K for Fe^{2+} and 361 ± 22 K for Fe^{3+}. These values are lower than those of Al-free bridgmanite by 17 and 24%, respectively, indicating that the presence of Fe and Al increases the average Fe-O bond length and weakens the bond strength. At 300 K, the calculated recoil-free fractions of Fe^{2+} (0.637 ± 0.006) and Fe^{3+} (0.72 ± 0.02) are similar and therefore the molar fractions of Fe^{2+} and Fe^{3+} are nearly the same as the area fractions of the corresponding Mössbauer doublets. At 900 K, the calculated recoil-free fractions of Fe^{3+} is 46% higher than that of Fe^{2+}, implying that the molar fraction of Fe^{3+} is only 41% for a measured spectral area fraction of 50%, and that the area fractions of iron sites may change with temperature without any changes in the valence state or spin state of iron. We infer that Fe^{3+} accounts for 46 ± 2% of the iron in the Al-Bm and it enters the A site along with Al^{3+} in the B site through the coupled-substitution mechanism. An Fe^{2+} component with large quadrupole splitting (~4.0 mm/s) was observed at cryogenic conditions and interpreted as a high-spin distorted iron site.

Keywords: Mössbauer spectroscopy, aluminous bridgmanite, ferric iron, recoil-free fraction, Debye temperature, crystallographic site, lower mantle