

Synthesis and crystal chemistry of Fe³⁺-bearing (Mg,Fe³⁺)(Si,Fe³⁺)O₃ perovskite

DANIEL R. HUMMER* AND YINGWEI FEI

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, U.S.A.

ABSTRACT

We have synthesized magnesium-iron silicate perovskites with the general formula Mg_{1-x}Fe_{x+y}³⁺Si_{1-y}O₃, in which the iron cation is exclusively trivalent. To investigate the crystal chemistry of Fe³⁺-bearing perovskite, six samples (both with and without Al) were analyzed using scanning electron microscopy, electron microprobe, X-ray diffraction, and Mössbauer spectroscopy. Results indicate that Fe³⁺ substitutes significantly into both the octahedral and dodecahedral sites in the orthorhombic perovskite structure, but prefers the octahedral site at Fe³⁺ concentrations between 0.04 and 0.05 Fe per formula unit, and the dodecahedral site at higher Fe³⁺ concentrations. We propose a model in which Fe³⁺ in the A/B site (in excess of that produced by charge coupled substitution) is accommodated by Mg/O vacancies. Hyperfine parameters refined from the Mössbauer spectra also indicate that a portion of dodecahedral sites undergo significant structural distortion. The presence of Fe³⁺ in the perovskite structure increases the unit-cell volume substantially compared to either the Mg end-member, or Fe²⁺-bearing perovskite, and the addition of Al did not significantly alter the volume. Implications for increased compressibility and a partially suppressed spin transition of Fe³⁺ in lower mantle perovskite are also discussed.

Keywords: Perovskite, ferric iron, lower mantle, oxidation state, diffraction, Mössbauer, crystal chemistry