Ferric iron content in (Mg,Fe)SiO₃ perovskite and post-perovskite at deep lower mantle conditions

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ABSTRACT

We have determined the Fe³⁺/ΣFe ratio of Al-free (Mg,Fe)SiO₃ perovskite, post-perovskite, and (Mg,Fe)O ferropericlase synthesized at 99 to 187 GPa and 1830 to 3500 K based on the electron energy-loss near-edge structure (ELNES) spectroscopy. The results demonstrate that post-perovskite includes minor amounts of ferric iron with Fe³⁺/ΣFe ratios of 0.11 to 0.21. These values are substantially lower than those of Al-rich post-perovskite (Fe³⁺/ΣFe = 0.59 to 0.69) reported in a previous study, suggesting that the Fe³⁺-Al⁴⁺ coupled substitution is important in post-perovskite, as in the case of perovskite. The Al-bearing post-perovskite in a pyrolitic mantle composition likely contains a considerable amount of ferric iron, which affects various physical properties in the lowermost mantle.

Keywords: Post-perovskite, perovskite, ferric iron, lower mantle, D* layer

INTRODUCTION

MgSiO₃ perovskite is a main constituent mineral in the Earth’s lower mantle and undergoes a phase transition to post-perovskite in its lower several hundred kilometers (e.g., Murakami et al. 2004). Iron is the most important chemical impurity, and is included as Fe²⁺ and Fe³⁺ in both perovskite and post-perovskite (e.g., McCammon et al. 1992; Sinmyo et al. 2006). The valence state of iron in perovskite has been extensively studied under uppermost lower mantle conditions using a multi-anvil apparatus combined with Mössbauer and ELNES spectroscopy measurements on recovered samples (Lauterbach et al. 2000; Frost et al. 2004). Ferric iron content in perovskite was examined also by synchrotron Mössbauer and X-ray emission spectroscopy measurements at room temperature with increasing pressure up to 120 GPa in a diamond-anvil cell (DAC) (Jackson et al. 2005; Li et al. 2006). The Fe³⁺/ΣFe ratio in perovskite increases with increasing Al content, and the Al-bearing perovskite in a pyrolitic lower mantle contains a substantial amount of ferric iron (Lauterbach et al. 2000; Frost and Langenhorst 2002). The concentration of ferric iron strongly affects the various physical properties of perovskite such as electrical conductivity (Xu and McCammon 2002), elasticity (Andrault et al. 2001), and Mg-Fe partitioning (Frost and Langenhorst 2002; McCammon et al. 2004).

In contrast, little is known about the valence state of iron in post-perovskite. Sinmyo et al. (2006) first demonstrated that Al-enriched post-perovskite that was formed in a MORB bulk composition included high concentration of ferric iron, with Fe³⁺/ΣFe = 0.59 to 0.69. In addition, the Fe³⁺/ΣFe ratio in perovskite synthesized in deep lower mantle conditions remains uncertain. Theory predicts that both Al-free and Al-rich perovskite and post-perovskite favor Fe³⁺ rather than Fe²⁺ at all lower mantle conditions, as a result of the valence disproportionation reaction 3Fe²⁺ → 2Fe³⁺ + Fe⁶⁺ (Zhang and Oganov 2006).

In this study we synthesized both Al-free (Mg,Fe)SiO₃ post-perovskite and post-perovskite in a laser-heated DAC at 99 to 187 GPa and 1830 to 3500 K. The Fe³⁺/ΣFe ratios were determined from ELNES spectra on recovered samples. The results show small amounts of ferric iron (Fe³⁺/ΣFe of ~0.1 to 0.2) in these Al-free perovskite and post-perovskite.

EXPERIMENTAL METHODS

The perovskite and post-perovskite samples were synthesized in three separate runs at high pressure and temperature (P-T) using the laser-heated DAC techniques at BL10XU of SPring-8. Starting materials were prepared originally as gels with chemical compositions of (Mg₀.₉₋ₓFeₓ)₂SiO₄ and (Mg₀.₈₋ₓFeₓ)₂SiO₄. The gel powder was dehydrated by heating to 1273 K for 1 h in a H₂O gas-mixing furnace, in which oxygen fugacity was controlled to be slightly above the iron-wüstite (IW) buffer (3 log units below the QFM buffer). The Fe³⁺/ΣFe ratio of the starting material was not directly measured but could be about 0.2 according to Ohta et al. (2008), in which (Mg₀.₉₋ₓFeₓ)₂SiO₄ gel was dehydrated at high temperature using the same procedures.

Two runs (OL99 and OL128) were conducted using (Mg₀.₉₋ₓFeₓ)₂SiO₄ as staring material (Table 1). The sample was mixed with a fine powder of gold (about 9:1 by weight), which served as a pressure internal standard and a laser absorber. It was loaded into a 50 µm hole drilled in a preindented rhenium gasket together with insulation layers of NaCl. After compression by diamond anvils to high pressure at room temperature, the sample was heated by a focused TEM mode Nd:YLF laser to 2170 K at 99 GPa for 72 min in run OL99 and to 1830 K at 128 GPa for 45 min in run OL128. The angle-dispersive X-ray diffraction (XRD) spectra obtained in situ at high P-T showed that the sample consisted of perovskite + ferropericlase and post-perovskite + ferropericlase in the former and latter experiments, respectively. A representative XRD pattern is shown in Figure 1. Pressure was determined from the unit-cell volume of gold obtained by XRD measurement and the P-V-T equation of state of gold (Hirose et al. 2008).

The run FOL187 was conducted on (Mg₀.₉₋ₓFeₓ)₂SiO₄. The sample powder was mixed with metallic iron (9:1 by weight). A pure (Mg₀.₉₋ₓFeₓ)₂SiO₄ powder was used for thermal insulation. Heating was done at 3500 K at 187 GPa for 1 min. Pressure was determined from the Raman spectrum of diamond (Akahama and Kawamura...