Rietveld structure refinement of perovskite and post-perovskite phases of NaMgF₃ (Neighborite) at high pressures

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ABSTRACT

Neighborite (NaMgF₃) with the perovskite structure, transforms to a post-perovskite (ppv) phase between 27 and 30 GPa. The ppv phase is observed to the highest pressures achieved (56 GPa) at room temperature and transforms to an as yet unknown phase upon heating. Rietveld structure refinement using monochromatic synchrotron X-ray diffraction data provide models for the perovskite and post-perovskite structures at high pressure. The refined models at 27(1) GPa indicate some inter-octahedral F-F distances rival the average intra-octahedral distance, which may cause instability in the perovskite structure and drive the transformation to the post-perovskite phase. The ratio of A-site to B-site volume (Vₐ/Vₖ) in perovskite structured NaMgF₃ (ABX₃), spans from 5 in the zero-pressure high-temperature cubic perovskite phase to 4 in this high-pressure perovskite phase at 27(1) GPa, matching the Vₐ/Vₖ value in post-perovskite NaMgF₃. Using Rietveld refinement on post-perovskite structure models, we observe discrepancies in pattern fitting, which may be described in terms of development of sample texture in the diamond-anvil cell, recrystallization, or a change of space group to Cmc₂₁, a non-isomorphic subgroup of Cmcm—the space group describing the structure of CaIrO₃.

Keywords: Perovskite, post-perovskite, pressure, diamond anvil cell, X-ray diffraction, Rietveld modeling, structure

INTRODUCTION

At the lowermost region of Earth’s mantle, the D'' layer (Dziewonski and Anderson 1981) is the medium through which heat and chemistry from the core may contact the mantle above. As a result, D'' is a complex boundary region (Lay et al. 2004), laterally variable and marked by seismic anomalies. Researchers have long sought to understand the origin and dynamics of this distinct layer (Karato and Karki 2001; Lay et al. 1998). Many high-pressure experiments have investigated MgSiO₃ perovskite for explanations to anomalous seismic phenomena observed in D'' and recent experiments have uncovered a post-perovskite structure of MgSiO₃ at pressures and temperatures thought to exist at D'' (Murakami et al. 2004; Oganov and Ono 2004).

A perovskite (pv) post-perovskite (ppv) transformation is reported to occur in several ABX₃ materials: MgGeO₃ (Hirose et al. 2005), CaIrO₃ (Hirose and Fujita 2005), and others (Tateno et al. 2006). In addition, the ppv structure is reportedly adopted in A₂X₃ materials Fe₂O₃ (Ono and Ohishi 2005), and Mn₂O₃ (San-tillan and Shim 2005). The ppv structure is based on the CaIrO₃ model, which is orthorhombic (Cmcm, Z = 4), and rarely adopted among oxides and sulfides at room pressure. The CaIrO₃ structure (Rodí and Babel 1965) may be summarized as alternating layers of BX₆ octahedra and A-site cations normal to the b axis within a C-centered lattice (Fig. 1a). Octahedra share edges along the a axis and corners along the c axis. The significant anisotropy of a CaIrO₃-type MgSiO₃ structure may explain the zones of strong seismic anisotropy observed within the D'' layer (Garnero 2004; Murakami et al. 2004; Tsuchiya et al. 2004).

The post-perovskite structure is now under intense study (Caracas and Cohen 2005; Mao et al. 2006; Murakami et al. 2005; Shieh et al. 2006) and debate. However, Rietveld structure modeling of ppv-MgSiO₃ is not yet documented. Powder statistics of X-ray diffraction data collected from samples in excess of 120 GPa are often compromised due to small scattering volumes present during experiments. Rietveld refinement of ppv structure will confirm the accuracy of the CaIrO₃ (Cmcm) model and the study of analog materials at extreme conditions is an alternative route to this goal. Analogs, such as MgGeO₃ (Duffy et al. 2005; Hirose and Fujita 2005), transform at lower pressures, increasing sample size, peak-to-background discrimination, and overall data quality.

The structure of neighborite (NaMgF₃) (Chao et al. 1961) was recently studied as an analog material for pv MgSiO₃ (O’Keeffe et al. 1979) using Rietveld structure modeling (Martin et al. 2005; Zhao et al. 1993). Previous work (Liu et al. 2005; Martin et al. 2006) finds a pv-ppv phase transition in NaMgF₃ between 28 and 30 GPa, in agreement with enthalpy calculations (Parise et al. 2004).

Previously we have reported the high-pressure phase transformations of NaMgF₃ (Martin et al. 2006). In the following letter, we report results of Rietveld refinement, detailing the high-pressure perovskite and post-perovskite structures of NaMgF₃.