Effect of A-site cation radius on ordering of BX₆ octahedra in (K,Na)MgF₃ perovskite

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ABSTRACT

We present a structural model for (K,Na)MgF₃ perovskite using results from high-resolution synchrotron X-ray powder diffraction and nuclear magnetic resonance (NMR) spectroscopy. (K,Na)MgF₃ perovskite is found to transition from orthorhombic (Pbmm) to tetragonal (P4/mmb) to cubic (Pm3m) as potassium concentration is increased. These phase transitions are not accompanied by a discontinuity in pseudo-cubic unit-cell volume and occur close to compositions (K₀.₃N₀.₆₃)MgF₃ and (K₀.₄₇N₀.₅₃)MgF₃, respectively. ¹⁹F NMR spectra indicate that the Na⁺ and K⁺ cations do not occupy the A cation site at random and end-member local environments are favored for all compositions. Based on results from both X-ray diffraction and NMR, we propose that diffuse diffraction is the result of strain between coexisting regions of different octahedra (MgF₆) tilts brought about by the ionic radius mismatch of Na⁺ and K⁺ cations. We suggest A-site cations group with like cations as neighbors to reduce excess volume and total strain.

INTRODUCTION

Changes in seismic velocities marking discontinuities in Earth’s lower mantle (Dziewonski and Anderson 1981; Lay et al. 1998; Liu et al. 1998; Sidoren et al. 1999; Su and Dziewonski 1997; Vinnik et al. 2001) are only partially understood in a mineralogical context. Alternative to chemical stratification (Kellogg et al. 1999; van der Hilst and Karason 1999) and magnetic collapse (Cohen et al. 1997; Guo et al. 2002), these discontinuities may result from structural phase transitions in lower mantle minerals. With the transition of upper mantle garnet and spinel below 660 km (~22 GPa, 1700 °C), the Earth’s lower mantle is expected to be dominated by (Mg,Fe)O and (Mg,Ca,Fe,Al)(Al,Si)O₃ perovskite (Brodholt 2000; Liu 1976; Liu and Ringwood 1975; Zhang and Weidner 1999). Since this discovery, many studies have applied extreme conditions and/or molecular dynamics simulations to investigate the structure of silicate perovskite under lower mantle conditions (Hemley et al. 2000; Ito et al. 1984; Knittle and Jeanloz 1991; Knittle et al. 1986; Matsui and Price 1991; Shim et al. 2001, 2002; Wolf and Bukowinski 1987; Zhou et al. 1998). Yet the literature remains divided upon the controversy and large errors (Dubrovinsky et al. 1999) introduced when generating lower mantle conditions within the laboratory. One way to circumvent this difficulty, and that caused by the metastability of silicate perovskite (Knittle et al. 1986; Wang et al. 1990), is the study of materials with analogous structure and higher compressibility. Thus, analogs work as a proxy, providing an opportunity to examine structural modifications that are difficult to attain with (Mg,Fe)SiO₃ + Al₂O₃ perovskite (Redfern 1996; Ringwood and Major 1967; Wang et al. 1992; Zhao et al. 1993b) or post-perovskite.

Neighborite (NaMgF₃) is isostructural and isoelectronic to MgSiO₃ (Chao et al. 1961; O’Keeffe and Bovin 1979), making it an ideal analog. MgSiO₃ and NaMgF₃ contain ions with similar radius ratios (A > B > X) and a 1:2 electronic charge ratio for both anion and cations. The flexible bonding of fluoride perovskite permits simulation of the effects of ultra-high pressure and temperature conditions on silicate perovskites at much lower conditions.

In the perovskite structure, variables such as pressure, temperature, and partial ion substitution commonly drive structural changes (Brodholt 2000; Salje 1992; Woodward et al. 2000; Woodward et al. 1999, 1998; Zhang and Weidner 1999). Understanding how structural phase transitions affect acoustic waves and elastic moduli is of particular interest in understanding observations for the deep Earth. While the study of structural changes in (K,Na)MgF₃ provides a fundamental understanding of perovskite dynamics, the structural effects of substitution must be very well characterized prior to measurement of elastic properties. This paper addresses the topic of long vs. short range order in (Na,K)MgF₃ perovskite while adding extensions and caution to the results predicted or observed in other perovskite materials.

Structure

Simple stoichiometric compounds crystallizing with the perovskite structure have the composition ABX₃, where BX₆ octahedra form a framework by corner-sharing each X ion. The