Crystal chemistry of NaMgF₃ perovskite at high pressure and temperature

JIUHUA CHEN,* HAOZHE LIU,† C. DAVID MARTIN, JOHN B. PARISE, AND DONALD J. WEIDNER

Mineral Physics Institute, State University of New York at Stony Brook, Stony Brook, New York 11794-2100, U.S.A.

ABSTRACT

The crystal structure of NaMgF₃ perovskite (neighborite) has been studied at 4 GPa and temperatures up to 1000 °C using the Rietveld structure-refinement method. In situ synchrotron X-ray powder diffraction data was collected using monochromatic radiation. The orthorhombic (Pbnm) to cubic (Pm3m) transition was observed when the temperature increased from 900 to 1000 °C. Structure refinements show that the ratio of polyhedral volumes of the A and B sites (Vₐ/Vₕ) of the orthorhombic phase increases with temperature, approaching the ideal value (5) for the cubic structure. However, this ratio becomes smaller at 4 GPa compared to the result from previous studies at the same temperature but ambient pressure, indicating that pressure makes it more difficult to transform from the orthorhombic phase to the cubic phase in this kind of perovskite.

INTRODUCTION

Geophysical interest in the perovskite family of materials dates from Ringwood’s proposing that Earth’s lower mantle is dominated by iron-bearing MgSiO₃ perovskite (Ringwood 1962). Until now, however, knowledge about the crystal chemistry of this mineral at lower mantle pressure and temperature conditions is very limited. MgSiO₃ perovskite is stable only at pressures beyond about 23 GPa (Ito and Yamada 1982), and high quality diffraction data are very difficult to obtain at such high pressures due to several limitations on experimental techniques. Several provocative proposals of decomposition and phase transitions in Ca- and MgSiO₃-related materials have far-reaching implications for the composition and structure of the lower mantle (Saxena et al. 1996, 1998; Shim et al. 2001, 2002). Although a transmission electron microscopy (TEM) study showed a hint of an orthorhombic-cubic phase transition in the iron-bearing MgSiO₃ perovskite system (Wang et al. 1992), more detailed investigations on the effect of pressure, temperature, and composition on lattice parameters and the density of iron-bearing MgSiO₃ perovskite indicated a trend of more structural distortion with increasing pressure (Mao et al. 1991). A recent study indicates that MgSiO₃ perovskite transforms to a new high-pressure phase at 125 GPa (Murakami et al. 2004). This pressure corresponds to the depth near the base of the mantle. Therefore the perovskite phase still dominates the Earth’s lower mantle. A fundamental understanding of the behavior of selected representatives of the perovskite family of structures to high-pressure/high-temperature conditions is valuable for establishing possible behaviors for this family in general. We have chosen to study NaMgF₃ perovskite (neighborite) and its solid solution with KMgF₃ as it has gained significant attention as an analogue material of MgSiO₃ perovskite (Chakhmouradian et al. 2001; O’Keefe and Bovin 1979; O’Keefe et al. 1979; Rönnebro et al. 2000; Street et al. 1997; Zhao et al. 1994a, 1994b, 1993a, 1993b; Zhou et al. 1997). Neighborite is isoelectronic with MgSiO₃, and they are isostructural, possessing the same type of distortion from the ideal cubic perovskite structure to crystallize in space group Pm3m.

NaMgF₃ perovskite was first synthesized (Ludekens and Welch 1952) before natural NaMgF₃ was discovered (Chao et al. 1961). The mineral was initially found in an oil shale of the Utah Green River formation (named neighborite after geologist Frank Neighbor), and was crystallographically described by Chao et al. (1961). Although O’Keefe et al. (O’Keefe and Bovin 1979; O’Keefe et al. 1979) pointed out the structural similarity between NaMgF₃ and MgSiO₃ in the late 1970s, systematic studies of the NaMgF₃ structure did not start until a decade ago. Following an extensive study of the NaMgF₃ structure and its temperature-induced phase transition by Zhao et al. (Zhao et al. 1994a, 1994b, 1993a, 1993b), several experimental and theoretical studies have been reported (Chakhmouradian et al. 2001; Rönnebro et al. 2000; Street et al. 1997; Zhou et al. 1997). Using the “macroscopic” relation between the structural distortion and unit-cell dimensions described by O’Keefe and Hyde (1977), Zhao et al. (1994b) investigated the pressure and temperature dependence of the structural distortion, and demonstrated two decoupled mechanisms for thermal expansion and compression, i.e., thermal expansion is mostly accommodated by octahedral tilting and compression is dominated by changes in the octahedral bond lengths. However, no structure refinement had been done for a sample maintained simultaneously at high pressure and temperature to study the pressure effect on the structure distortion from a microstructural point of view. Derivation of the microscopic atomic parameters from cell parameters alone, as was proposed by O’Keefe and Hyde (1977) and Zhao et al. (1994b), is only accurate when the assumption of rigid octahedra is valid. This does not appear to be the case at high pressure (Zhao et al. 1994a). In this paper, we present crystal chemistry data derived from structure refinements based on X-ray diffraction data collected at high pressure and high temperature.