Rietveld structure refinement of MgGeO$_3$ post-perovskite phase to 1 Mbar

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Abstract

Using the CaIrO$_3$-type structure model (space group Cmcm), lattice parameters and atomic positions of the MgGeO$_3$ post-perovskite (pPv) phase were determined based on Rietveld refinements at 78–109 GPa and first-principles calculations based on density functional theory. The reproducibility of structural parameters obtained for different samples, consistency with theoretical calculations, and good agreement with expected bond lengths based on structurally similar materials all provide evidence for both validity of CaIrO$_3$-type structure model for the pPv phase in MgGeO$_3$ exceeding 1 Mbar and reliability of structural parameters obtained by Rietveld refinements approaching 1 Mbar. The MgGeO$_3$ pPv phase exhibits strong anisotropy in axial compressibility, with the b-axis being most compressible. The polyhedral bulk modulus for the GeO$_3$ octahedron is 1.9x larger than that for the MgO$_3$ hendecahedron. Examination of neighboring O-O distances shows that the O-O distance aligned along the a direction is one of the longest and that aligned along c is one of the shortest, and these may be related to the lower compressibility along c compared with a. Comparison of structural features of MgGeO$_3$ pPv with those for MgSiO$_3$, NaMgF$_3$, and CaIrO$_3$ pPv show that MgSiO$_3$ pPv has more similarity with NaMgF$_3$ and MgGeO$_3$ pPv than with CaIrO$_3$ pPv in such parameters as degree of octahedral distortion, implying that both NaMgF$_3$ and MgGeO$_3$ pPv are better analogs to MgSiO$_3$ pPv than CaIrO$_3$ pPv.

Keywords: Post-perovskite, MgGeO$_3$, Rietveld refinement, high-pressure experiment, first-principles calculation, laser-heated diamond anvil cell, density functional theory, polycrystalline X-ray diffraction

Introduction

The post-perovskite (pPv) phase, with CaIrO$_3$-type structure (space group Cmcm) (Rodi and Babel 1965) (Fig. 1) discovered in MgSiO$_3$ at 125 GPa and 2500 K (Murakami et al. 2004; Oganov and Ono 2004; Itikata et al. 2004), has been extensively studied due to its geophysical importance (e.g., Ono and Oganov 2006; Hirose 2006; Merkel et al. 2007). Due to the experimental difficulties in the synthesis of silicate pPv phase at >1 Mbar and high temperature (e.g., Shim et al. 2004; Mao et al. 2004; Shieh et al. 2006), theoretical calculations have played an important role in predicting stability and physical properties of the pPv phase (e.g., Oganov and Ono 2004; Tsuchiya et al. 2004; Oganov et al. 2005; Wentzcovitch et al. 2006). Experimental studies have also focused on the CaIrO$_3$-type pPv phase in analog materials to silicates such as MgGeO$_3$ (Hirose et al. 2005; Kubo et al. 2006), MnGeO$_3$ (Tateno et al. 2006), and NaMgF$_3$ (Liu et al. 2005; Martin et al. 2006a). For example, MgGeO$_3$ pPv phase can be synthesized as low as ~70 GPa at 2000 K (Hirose et al. 2005; Runge et al. 2006), and the pPv phase of CaIrO$_3$ is stable at ambient conditions up to ~1650 K (Hirose and Fujita 2005; Kojitani et al. 2007). By using these analog materials, predictions for the behavior of the silicate pPv phase can be obtained experimentally (e.g., Merkel et al. 2006; Miyagi et al. 2008; Shim et al. 2007; Walte et al. 2007). It should also be noted that the CaIrO$_3$-type phase also has been discovered in several sesquioxide compounds at high pressures: Al$_2$O$_3$ (Ono et al. 2006a), Fe$_2$O$_3$ (Ono and Ohishi 2005), and Mn$_2$O$_3$ (Santilán et al. 2006).

At high pressures where single-crystal diffraction is not accessible, the Rietveld method has been applied to examine detailed structures of polycrystalline materials (e.g., Fiquet et al. 2002). As pressure increases, the use of this technique becomes more challenging because diffraction data may suffer from effects of differential stress, preferred orientation, and poorer crystal statistics. Although differential stress in the sample can be reduced by annealing (e.g., Fiquet et al. 2002), it is generally difficult to eliminate preferred orientation in the sample. If preferred orientation exists in the sample, refined parameters that depend on diffraction intensities such as atomic positions could be affected (Martin et al. 2006b), even if lattice parameters can be reliably refined. Theoretical calculations based on density functional theory also can predict structure parameters as a function of pressure.