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$_6$ octahedron is 1.9 times larger than that for the MgO$_6$ octahedron. 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; Itatka 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; Shib 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; Kobo 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$_3$ (Santillán 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 pres-
sure (e.g., Kubo et al. 2006). Due to the complementary nature of these two methods, use of both Rietveld and theory is desirable to obtain robust structure parameters at very high pressures.

So far, the Rietveld method has been applied to the pPv phase in MgGeO₃ (Hirose et al. 2005, Kubo et al. 2006), Fe₂O₃ (Ono and Ohishi 2005), MnGeO₃ (Tateno et al. 2006), Mn₃O₇ (Santillán et al. 2006), and NaMgF₂ (Martin et al. 2006a) mainly to confirm that diffraction data are consistent with the CaIrO₃-type structure. An important goal of our study is to provide a test of the reliability of Rietveld refinement methods at megabar pressures where effects such as poor crystal statistics, limited 2D range, preferred orientation, and differential stress may limit refinement quality. Here we examine pressure and temperature dependencies of structure parameters of the pPv phase in MgGeO₃ by conducting both Rietveld refinements and first-principles calculations. The results are compared with structure parameters predicted for MgSiO₃ pPv at 120 GPa, NaMgF₂ pPv at 30 GPa, and experimentally determined for CaIrO₃ pPv at ambient conditions. This study presents further analysis of data reported by Kubo et al. (2006).

**METHODS**

**High-pressure experiments**

The pPv phase was synthesized from MgGeO₃ orthopyroxene using laser-heated diamond cells. Powder X-ray diffraction of the starting material showed orthoenstatite with minor amounts of excess GeO₂, as reported in Kubo et al. (2006). Unit-cell parameters of the orthopyroxene at ambient conditions were determined to be \( a = 18.8088(9) \) Å, \( b = 8.9490(4) \) Å, and \( c = 5.3431(2) \) Å from Le Bail refinement. These unit-cell parameters are in very good agreement with Ozima and Akimoto (1983). This starting material was mixed with 20 wt% Pt powder that served as both a pressure standard and laser absorber. Experiments were conducted using either Ar (run 1) or NaCl (run 2) as pressure media and thermal insulation. The sample was heated using a Nd:YLF laser (TEM₀₀₀ mode) with double-sided heating (Shen et al. 2001).

Angle dispersive X-ray diffraction experiments were conducted at beamline 13-ID-D of the GSECARS sector at the Advanced Photon Source (APS) (Shen et al. 2005). The incident monochromatic X-ray beam of 0.3344 Å wavelength was focused to a size of \( \sim 6 \times 6 \) μm². An angle dispersive geometry with an image plate (Mar 345) was used. The detector was calibrated using GeO₂. Pressure was determined from the equation of state of platinum (Holmes et al. 1989). Further details can be found in Kubo et al. (2006).

In run 1, the pPv phase was synthesized by heating the starting material to 1600–1900 K at 83–87 GPa for 10 min. We then compressed the sample to 99 GPa at room temperature and heated to \( \sim 1600 \) K. After quenching to room temperature, we further compressed the sample to 109 GPa at room temperature, but diffraction peaks of Pt and Ar completely overlapped at this pressure. The sample was then decompressed without further heating. Diffraction data were collected at room temperature at various pressures during both compression and decompression. In run 2, MgGeO₃ pPv phase was synthesized during laser heating at 92–94 GPa and 1400–1700 K. Diffraction data were also collected in situ during laser heating. Subsequently, the sample was decompressed without heating, and diffraction data were obtained at various pressures.

**Rietveld refinements**

Two-dimensional (2D) diffraction images obtained after laser heating contained continuous Debye rings from all phases in the diamond cell, and few diffraction spots were present (Fig. 2). These two factors are essential to conduct reliable Rietveld refinement (cf. McCusker et al. 1999). To reduce the intensity of some strong diffraction spots originating from diamond in run 2, we tilted the diamond cell 1° away from the normal. For this reason, the outermost Debye rings were only partially recorded. To obtain one-dimensional (1D) data with the maximum 20 range and reliable intensities, we restricted the region of integration to a \( \sim 60\)° slice where the outermost Debye ring was recorded (Fig. 2). Most of the observable diffraction spots in this region were masked, and then using Fit2d (Hammersley et al. 1996), the 2D data were integrated to obtain 1D diffraction patterns that were used for the Rietveld refinements.

We estimated the standard deviation (\( \sigma \)) of diffraction intensity at each 20 based on the equation (Von Dreele, unpubl.): \( \sigma = (F/V)\tan 2\theta \), where \( F \) is the parameter that represents intrinsic noise level of each diffraction datum and \( I \) is the diffraction intensity including background. \( F \) was assumed to be constant across the 20 range for each pattern. To determine \( F \), we sampled the noise level (\( \sigma \)) and background intensity \( I \) at \( 20 = 5.2 \pm 0.4° \) where no diffraction peaks were observed.

Prior to Rietveld refinements, we conducted Le Bail refinements using GSAS/EXPGUI (Larson and von Dreele 2004; Toby 2001) to refine lattice parameters and peak shape parameters (profile terms “GW” and “LX” in the constant wavelength profile function 2 in GSAS) to be used as initial values in Rietveld refinement. Here GW and LX are the basic profile terms that define pseudo-Voigt peak shape. It is known empirically that Le Bail refinement yields the best fitting results (with best reliability factor) achievable in Rietveld refinement. This in turn means that the diffraction data that cannot be well fitted by Le Bail refinement are unlikely to be successfully refined by Rietveld refinement.

After successful Le Bail refinement, we conducted Rietveld refinement using GSAS/EXPGUI by the following three steps. For each step, parameters for the pPv phase, Pt, and either Ar or NaCl were separately refined initially, but eventually refined simultaneously. Before starting the refinement, a background was manually defined using a Chebyshev polynomial (typically 10 terms). In the first step, we refined only phase fractions and atomic positions assuming no preferred orientation, with lattice parameters and profile terms being fixed. Subsequently, we fixed all the parameters refined in the first step, and then refined only spherical harmonic terms for preferred orientation correction. We assumed cylindrical
sample symmetry (fiber texture). The spherical harmonic order used for refinements was 2 (run 1) or 4 (run 2) for the pPv phase, and 6 for Pt, NaCl, and Ar. In the third step, we refined all the parameters including lattice parameters and profile terms simultaneously to complete the refinement and to obtain correct estimated standard deviations (McCusker et al. 1999). For data obtained at 105 and 109 GPa in run 1, we ignored the presence of Ar in the diffraction data because peak overlap between Pt and Ar was nearly complete and diffraction peaks from Ar seemed weak and broad.

It is very challenging to refine isotropic displacement parameters $U_{iso}$ (where $B$ is Debye parameter) from diffraction data obtained under pressure with a limited 20 range. We concluded that our diffraction data do not have enough quality to refine displacement parameters because negative displacement parameters that are physically meaningless were typically obtained. Sugahara et al. (2006) demonstrated in a single-crystal X-ray diffraction study up to 15 GPa that equivalent isotropic displacement parameters $B_{iso}$ for perovskite-type MgSiO$_3$ do not change strongly as a function of pressure at room temperature. Therefore, we fixed $U_{iso}$ to the following values: 0.005 Å$^2$ for all atoms in the pPv phase, 0.004 Å$^2$ for Pt, 0.04 Å$^2$ for Ar, and 0.02 Å$^2$ for all atoms in B2 phase of NaCl. These $U_{iso}$ values are based on equivalent isotropic displacement parameters of MgSiO$_3$, perovskite (Sugahara et al. 2006) and Debye parameters listed in International Tables for X-ray Crystallography (Ibers et al. 1968) for Pt (293 K), krypton (93 K), and B1 phase of NaCl (293 K), respectively.

We tried to reduce the number of refined parameters as much as possible to avoid mathematically better but physically meaningless fitting (“overfitting”). For this purpose, we did not refine the background and $U_{iso}$, and we limited the number of peak shape parameters and spherical harmonic order for the preferred orientation correction to be as small as possible. In fact, Kubo et al. (2006) presented atomic positions for MgGeO$_3$ pPv phase with some differences from those reported here because more parameters were refined for each phase including $U_{iso}$ and one more Gaussian-related peak shape parameter in that study. The atomic positions reported by Kubo et al. (2006) are superseded by those obtained here.

**Theoretical calculations**

We carried out first-principles calculations based on density functional theory (Hohenberg and Kohn 1964) to calculate atomic positions and lattice parameters of the pPv phase as a function of pressure at 0 K as described in Kubo et al. (2006). These calculations were carried out with the software package VASP (Kresse and Hafner 1993, 1994; Kresse and Furthmüller 1996) using the projector-augmented-wave (PAW) method (Blochl 1994; Kresse and Joubert 1999). Electronic correlations were treated within the local density approximation (LDA) in the parameterization of Perdew and Zunger (1981). The reliability of the predicted structure was verified by alternate calculations within the general gradient approximation (GGA) in the parameterization by Perdew-Burke-Anderson and Ernzerhof (PBE, Perdew et al. 1996). We used PAW-PBE potentials with core region cut-off radii of 1.20 a.u. for Mg (valence configuration 2p$^6$), 1.9 a.u. for Ge (valence configuration 3d$^1$4s$^2$4p$^2$), and 1.52 a.u. for O (valence configuration 2s$^2$2p$^4$). The core cut-off radii and valence configurations in the PAW-PBE calculations were the same with the exception of the cut-off radius for Ge that was 2.3 a.u. Tests showed that converged solutions to the Kohn-Sham equations (Kohn and Sham 1965) could be obtained with an energy-cutoff of 600 eV and a $6 \times 4 \times 6$ k-point grid. Total energies are converged to better than 2.3 meV/atom, and stresses due to the incompleteness of the basis-set are $<0.5$ GPa and 0.6 GPa in the LDA and GGA calculations, respectively.

We optimized the lattice parameters and atomic positions in the CaIrO$_3$-type structure for volumes between 108 and 180 Å$^3$ by LDA and between 110 and 195 Å$^3$ by GGA to determine the groundstate of MgGeO$_3$ at these volumes. The pressure and all structural parameters of MgGeO$_3$ pPv were obtained from the relaxed configurations for eleven volumes in the pressure range of $\sim$2 to 298 GPa by LDA and twelve volumes between 4 and 298 GPa by GGA. It is noted that the pPv phase is metastable below 47 GPa at 0 K according to the pPv phase transition boundary determined by Hirose et al. (2005), and Kubo et al. (2006) have confirmed the stability of the pPv phase up to 2 Mbar at $\sim$1600 K. The results are shown in Table 1.

**RESULTS AND DISCUSSION**

Using the CaIrO$_3$-type structure model, we could successfully conduct Rietveld refinements for three diffraction spectra in run 1 in the pressure range of 100–109 GPa and seven diffraction patterns including two data at high temperatures in run 2 at 78–94 GPa. Although we had diffraction data in a wide pressure range down to 7 GPa, we could not successfully refine lower pressure data probably due to higher differential stresses and metastability of the pPv phase at pressures $<\sim$45 GPa (Kubo et al. 2006). Peak widths for diffraction data below 45 GPa are much broader than higher pressure data. Figure 3 shows a selected Rietveld refinement result (see online supplementary materials for complete Rietveld results). It is clear from Figure 3 that diffraction peaks of the pPv phase are well fitted. Together with the reasonable atomic positions and lattice parameters listed in Table 2, this observation validates the CaIrO$_3$-type structure model for the pPv phase in MgGeO$_3$ at 78–109 GPa. However, misfit can be

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1. Deposit item AM-08-032, Supplementary Table 1 and Supplementary Figures 1 and 2 (complete Rietveld results). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
seen for the most intense diffraction peak of Pt 200 and peaks from B2 phase of NaCl due to differential stress in the sample chamber, as discussed later. To evaluate the effect of misfit of Pt on refined atomic positions of the pPv phase, we conducted another set of Rietveld refinements using the diffraction data with the Pt 200 peak manually subtracted. In these refinements, the atomic positions were mostly reproduced within 1σ deviation from original results, implying that effects of differential stress in Pt are not significant within 1σ. However, for patterns A038 and A042 (Table 2 and online supplementary items), atomic positions were not reproducible within 3σ. Therefore, despite better R-factor in run 1 than in run 2 (Table 2), Rietveld results from run 2 appear to be more reliable than those from run 1, which is supported by the larger 2θ range, weaker Pt intensity, and less peak overlap of Pt with pressure medium in run 2 (cf. Toby 2006). Note that the uncertainty shown in Table 2 and all the figures in this paper are 1σ obtained from least squares calculations in Rietveld refinements, and this represents the precision of the recovered parameters.

**Lattice parameters, axial ratios, and unit-cell volumes**

Lattice parameters, axial ratios, and unit-cell volume of the post-perovskite phase at 0 K predicted by theoretical calculations using local density approximation (LDA) and generalized gradient approximation (GGA) are presented in Table 1. These results are also shown in Figure 4 together with Rietveld figures in this paper are 1σ obtained from least squares calculations in Rietveld refinements, and this represents the precision of the recovered parameters.

**Table 1.** Lattice parameters and atomic positions for MgGeO₃ post-perovskite phase at 0 K predicted by theoretical calculations using local density approximation (LDA) and generalized gradient approximation (GGA)

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>-2.0</th>
<th>-0.1</th>
<th>3.6</th>
<th>27.5</th>
<th>46.5</th>
<th>68.1</th>
<th>86.3</th>
<th>108.5</th>
<th>148.6</th>
<th>196.9</th>
<th>297.9</th>
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<tr>
<td>a (Å)</td>
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<td>2.7960</td>
<td>2.7815</td>
<td>2.7060</td>
<td>2.6652</td>
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<td>2.4760</td>
<td>2.4082</td>
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<tr>
<td>Mg y</td>
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<td>0.2590</td>
<td>0.2580</td>
<td>0.2547</td>
<td>0.2534</td>
<td>0.2525</td>
<td>0.2519</td>
<td>0.2514</td>
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<td>0.2502</td>
<td>0.2494</td>
</tr>
<tr>
<td>O1 y</td>
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<td>0.9161</td>
<td>0.9159</td>
<td>0.9155</td>
<td>0.9153</td>
<td>0.9152</td>
<td>0.9151</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
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<tr>
<td>O2 y</td>
<td>0.6322</td>
<td>0.6326</td>
<td>0.6333</td>
<td>0.6368</td>
<td>0.6387</td>
<td>0.6404</td>
<td>0.6416</td>
<td>0.6428</td>
<td>0.6445</td>
<td>0.6461</td>
<td>0.6487</td>
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<tr>
<td>O2 z</td>
<td>0.4401</td>
<td>0.4399</td>
<td>0.4394</td>
<td>0.4379</td>
<td>0.4372</td>
<td>0.4366</td>
<td>0.4362</td>
<td>0.4358</td>
<td>0.4353</td>
<td>0.4348</td>
<td>0.4340</td>
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</table>

**Table 2.** Lattice parameters and atomic positions for MgGeO₃ pPv phase determined by Rietveld refinements

<table>
<thead>
<tr>
<th>Rietveld data</th>
<th>A036</th>
<th>A038</th>
<th>A042</th>
<th>B017</th>
<th>B018</th>
<th>B019</th>
<th>B020</th>
<th>B038</th>
<th>B040</th>
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<tr>
<td>P (GPa)</td>
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<td>109.3</td>
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<td>92.1</td>
<td>93.6</td>
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<td>89.5</td>
<td>85.0</td>
<td>79.2</td>
<td>78.2</td>
</tr>
<tr>
<td>T (K)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>174</td>
<td>174</td>
<td>120</td>
<td>160</td>
<td>140</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>a (Å)</td>
<td>2.5718(8)</td>
<td>2.5677(7)</td>
<td>2.5811(5)</td>
<td>2.6001(3)</td>
<td>2.5987(4)</td>
<td>2.5971(4)</td>
<td>2.5949(3)</td>
<td>2.6018(4)</td>
<td>2.6014(3)</td>
<td>2.6134(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.3274(21)</td>
<td>8.3132(19)</td>
<td>8.3628(14)</td>
<td>8.4123(9)</td>
<td>8.4107(11)</td>
<td>8.4089(9)</td>
<td>8.4090(9)</td>
<td>8.4259(11)</td>
<td>8.4602(12)</td>
<td>8.4674(12)</td>
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<tr>
<td>c (Å)</td>
<td>6.3536(11)</td>
<td>6.3453(15)</td>
<td>6.3730(10)</td>
<td>6.4097(7)</td>
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<td>6.4064(7)</td>
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<tr>
<td>Mg (Å)</td>
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<td>0.2614(13)</td>
<td>0.2590(14)</td>
<td>0.2533(10)</td>
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<td>0.2555(12)</td>
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<tr>
<td>O1 (Å)</td>
<td>0.9160(34)</td>
<td>0.9171(34)</td>
<td>0.9081(25)</td>
<td>0.9101(29)</td>
<td>0.9083(34)</td>
<td>0.9176(24)</td>
<td>0.9138(25)</td>
<td>0.9127(27)</td>
<td>0.9121(27)</td>
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</tr>
<tr>
<td>O2 (Å)</td>
<td>0.6404(23)</td>
<td>0.6410(21)</td>
<td>0.6383(16)</td>
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<td>0.6412(15)</td>
<td>0.6400(12)</td>
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<td>0.6398(13)</td>
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<tr>
<td>O2 z (Å)</td>
<td>0.4365(35)</td>
<td>0.4365(35)</td>
<td>0.4319(24)</td>
<td>0.4417(18)</td>
<td>0.4365(20)</td>
<td>0.4395(17)</td>
<td>0.4375(17)</td>
<td>0.4370(17)</td>
<td>0.4377(18)</td>
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</table>

Note: Rwp shows the quality of the least squares refinement after background subtraction based on following residual function: \( R_{wp} = \frac{1}{\sigma} \sqrt{\sum w_i (I_{obs} - I_{calc})^2} \), where \( w \), \( \sigma \), and \( I \) are weight, observed intensity, and calculated intensity, respectively (Larson and Von Dreele 2004).

**Figure 3.** An example of Rietveld refinement result at 88 GPa and room temperature from run 2. The crosses represent observed intensities (Iobs). The solid line is the calculated intensities (Icalc). The tick marks show the positions of calculated diffraction lines: upper ticks = NaCl (B2-phase); middle ticks = Pt; lower ticks = pPv. The line below the tick marks is the intensity difference curve (Icalc - Iobs).
results by Hirose et al. (2005) for MgGeO$_3$ pPv at 78 GPa and room temperature, theoretical predictions for MgSiO$_3$ pPv at 120 GPa and 0 K by Tsuchiya et al. (2004) and NaMgF$_3$ pPv at 30 GPa and 0 K by Umemoto et al. (2006), and single-crystal X-ray diffraction results for CaIrO$_3$ at ambient conditions by Rodi and Babel (1965). Note that theoretical results for MgSiO$_3$ pPv by Tsuchiya et al. (2004) using LDA are similar to within 0.2% for atomic positions and 0.3% for lattice parameters, and the differences between theoretical results by GGA (Oganov and Ono 2004) and LDA (Tsuchiya et al. 2004; Iitaka et al. 2004) are within 0.2% for atomic positions and 0.9% for lattice parameters. Although Rietveld results are available for both MgSiO$_3$ pPv (Ono et al. 2006b) and NaMgF$_3$ pPv (Martin et al. 2006a), we use theoretical results for these phases because, unlike for MgGeO$_3$, theory and experiment are not currently in good agreement in terms of atomic positions. In this and subsequent figures, open symbols refer to data at room temperature (Rietveld) or 0 K (theory), and filled symbols indicate data at high temperature from the present study. Data from other studies are triangle = Rietveld refinement by Hirose et al. (2006) for MgGeO$_3$ pPv at 78 GPa and 300 K; plus sign (+) = theoretical calculation by Tsuchiya et al. (2004) for MgSiO$_3$ pPv at 120 GPa and 0 K (LDA); asterisk (*) = theoretical calculation by Umemoto et al. (2006) for NaMgF$_3$ pPv at 30 GPa and 0 K (LDA); cross (×) = single-crystal X-ray diffraction by Rodi and Babel (1965) for CaIrO$_3$ pPv at ambient conditions. Dashed and dotted lines represent LDA and GGA results, respectively.

Almost all the data points at room temperature in Figure 4a determined here by Rietveld refinement fall on the compression curves previously reported by Kubo et al. (2006) that were based on individual peak fitting using five diffraction peaks of the pPv phase, indicating that peak fitting can yield lattice parameters that are as reliable as those determined by Rietveld method. Lattice parameters predicted by LDA (GGA) are slightly smaller (larger) than those observed in our experiments, which are typical for these calculations.

Figure 4b shows ratios of unit-cell axes. Pressure dependence of $b/a$ ratio shows that the $b$-axis is more compressible than the $a$- and $c$-axes whose axial compressibilities are similar as manifested by less pressure dependence of $c/a$ ratio. This finding is consistent with experimental observations for the MgGeO$_3$ pPv phase (Hirose et al. 2005; Merkel et al. 2006; Kubo et al. 2006) and the MgSiO$_3$ pPv phase (e.g., Murakami et al. 2004). While theory predicts a comparatively strong pressure dependence of $b/a$, experimental results show a small pressure dependence at 80–110 GPa, which is also reported in Kubo et al. (2006). On the other hand, $c/a$ at 80–110 GPa shows a mild increase with pressure, in excellent agreement between experiments and theory. At 1700 K, both $b/a$ and $c/a$ become slightly smaller. The $b/a$ ratio of MgSiO$_3$ pPv is expected to be 0.8, 4.2, and 4.2% larger than...
Preferred orientation and differential stress

Figure 5a shows values of texture indices from the Rietveld refinements, parameters that indicate the magnitude of preferred orientation, with \( J = 1 \) if there is no preferred orientation, otherwise \( J > 1 \) and \( J = \infty \) for a single crystal (Von Dreele 1997). All materials in the sample chamber exhibit evidence for preferred orientation. In all diffraction patterns, the relative intensity of pPv diffraction peaks 020 and 110 are stronger and weaker than expected from the ideal intensity relationship, respectively. All the spherical harmonic coefficients for the pPv phase are shown in Supplementary Table 1, from which one can obtain pole figures. Our pole figure analysis showed that the \( b \)-axis tends to align perpendicular to the compression direction of the diamond cell while \( \{100\} \), \( \{110\} \), \( \{101\} \), and \( \{111\} \) tend to align almost parallel to the compression axis. These observations are consistent with preferred orientation of MgGeO\(_3\) pPv observed by Merkel et al. (2006) and theoretical predictions by Oganov et al. (2005) for MgSiO\(_3\) pPv. Similar experimental observations have been reported for both MgSiO\(_3\) and MnO\(_3\) pPv by Murakami et al. (2004) and Santillán et al. (2006), respectively.

We estimated differential stress in Pt from \( d \)-values of Pt111 and Pt200 based on Singh’s (1993) method, assuming an axially symmetric stress field in the sample, iso-stress model (Reuss limit), and elastic anisotropy of Pt (Kavner and Duffy 2003). Details of our calculations can be found in Runge et al. (2006). The results, shown in Figure 5b, indicate that the magnitude of differential stress in our samples (MgGeO\(_3\) mixed with Pt) is \(-0.3\)–\(1.0 \) GPa. There is no discernible correlation between the magnitude of differential stress and type of pressure medium (Ar or NaCl). At high temperature, differential stress tends to be somewhat reduced.

Atomic positions

There are four variable atomic positions (fractional coordinates) in the CaIrO\(_3\)-type structure (Fig. 1). In the present study, we represent atomic positions of the ABX\(_3\) pPv phase as follows: A (0, \( y \), 1/4), B (0, 0, 0), X1 (0, \( y \), 1/4), X2 (0, \( y \), \( z \)), where X1 and X2 correspond to corner and edge shared anions of the BX\(_x\) octahedron (Fig. 1), respectively. Note that Rodi and Babel (1965) contains typographical errors in the table of atomic positions for CaIrO\(_3\).

Atomic positions from this study are shown in Tables 1–2, and Figure 6. Results by LDA and GGA calculations are in good agreement. Rietveld results are consistent with theoretical results within 3\(\sigma\), although both considerable data scatter and the limited pressure range make it difficult to constrain the pressure dependence of atomic positions solely from Rietveld results. Our theoretical calculations predict small changes of the atomic positions at pressures between \(\sim50\) and 300 GPa, implying no change in compression mechanism of the pPv phase at this pressure range. However, Mg\( y \) and O2\( y \) positions change much more between \(0\) and \(\sim50\) GPa, implying different compression behavior in the low-pressure metastable region. Within an uncertainty of 3\(\sigma\), we do not find any consistent temperature dependence of the atomic positions from Rietveld results, and thermal effects may be below our level of resolution.

Hirose et al. (2005) reported Rietveld refinement from a single diffraction spectrum of MgGeO\(_3\) pPv at 78 GPa and 300 K. Hirose et al.’s results for Mg\( y \) and O2\( z \) are consistent with our results, but their results for O1\( y \) and O2\( y \) are quite inconsistent beyond 3\(\sigma\). The diffraction data obtained by Hirose et al. (2005) exhibits a markedly different intensity relationship compared with our data in Figure 3. According to our Rietveld refinement, the texture index of the pPv phase is always \(<1.5\) (Fig. 5a), showing that preferred orientation of our samples is minimal. Also, our observed diffraction intensities are similar to expected intensities based on the structure. Therefore, we infer
and averaged Ge-O distances in MgSiO$_3$. Also shown are Rietveld results of averaged Mg-O distance in room pressure (Sasaki et al. 1983) determined by single-crystal GPa (Ross and Hazen 1990) and Ge-O in CaGeO$_3$.

Averaged distances of Mg-O in MgSiO$_3$ bonds in AX$_8$ octahedra. Figure 7a shows averaged lengths of A-X and B-X pyramid caps to form a layer that separates the sheets of BX$_8$ octahedra. X$_1$ and X$_2$ are corner- and edge-shared anions in BX$_8$ octahedra, respectively. Figure 7b shows individual bond lengths in the pPv phase. The average Mg-O bond length in MgSiO$_3$ pPv is 0.9% smaller than that in MgGeO$_3$ pPv at 120 GPa. Ratio of average bond lengths A-X/B-X in ABX$_3$ pPv is 1.13 for MgGeO$_3$, 1.17 for MgSiO$_3$, 1.16 for NaMgF$_3$, and 1.21 for CaIrO$_3$.

Figure 7b shows individual bond lengths in the pPv phase. Our Rietveld results from run 1 and run 2 are consistent within uncertainty, and they are also consistent with our theoretical results. Theory predicts enhanced compressibility of Mg-O2 (x4) bond between 0 and ~50 GPa, which is closely related to rapid change of Mg y and O2 positions predicted between 0 and ~50 GPa (Fig. 6a). This implies a change of the compression behavior in MgO$_3$ hendecahedral layer around 50 GPa, which might induce both unusual volume expansion below ~45 GPa and breakdown of the pPv phase below 7 GPa during decompression reported by Kubo et al. (2006). At high temperatures, it is likely that both Ge-O1 and Ge-O2 expand in the GeO$_3$ octahedron, while Mg-O2(4) is the only bond in MgO$_3$ hendecahedron that shows evidence for thermal expansion. In MgSiO$_3$, MgGeO$_3$, NaMgF$_3$, and CaIrO$_3$ pPv phases, bond lengths relationships are always B-X < B-X and A-X < A-X (x4) < A-X (x2).

Distances of seven different neighboring X-X anions in ABX$_3$ pPv phases are shown in Supplementary Figure 2.1. Rietveld results, which are generally consistent with theoretical predictions, show that compressibilities of O-O pairs in MgO$_3$ hendecahedron are generally greater than those in GeO$_3$ octahedron. The most incompressible O-O pair locates in octahedron (X2-X2 o in Supplementary Fig. 2), while the most compressible pair locates in hendecahedron (both X2-X2 h2 and X1-X2 h in Supplementary Fig. 2). Theoretical calculations showed that compressibilities of O-O pairs in hendecahedron are significantly different from each other compared with those in octahedron. The O2-O2 pair that aligns in the c-direction (X2-X2 h1 in Supplementary Fig. 2) is one of the closest O-O pairs, while the O2-O2 pair that aligns in the a-direction (X2-X2 o h in Supplementary Fig. 2) is one of the longest O-O pairs in both MgGeO$_3$ and MgSiO$_3$ pPv. These facts may explain the reason for the less axial compressibility of the c-axis than the a-axis in both MgGeO$_3$ and MgSiO$_3$ pPv (Kubo et al. 2006; Guignot et al. 2007) due to expected higher O-O repulsion in c-direction.

**Polyhedral volumes**

Figure 8a shows the volume change of GeO$_3$ octahedron and MgO$_3$ hendecahedron as a function of pressure and temperature. Polyhedral volumes can be calculated from unit-cell volume $V_{cell}$ and the atomic positions using the following equations: $V_{GeO3} = (8 \times O2 z \times O1 y - 8 \times O2 z - 4 \times O1 y + 2 \times O2 y + 3)$.
KUBO ET AL.: RIETVELD REFINEMENT OF MgGeO₃, POST-PEROVSKITE TO 1 MBAR

Following parameters at room temperature based on second-order Birch-Murnaghan equation of state fitting using Rietveld results are shown with dotted lines in a. See Figure 4 for references.

Theory predicts the following polyhedral compression parameters at 0 K based on third-order Birch-Murnaghan equation of state: polyhedral bulk modulus of 161 GPa for MgO₈ and 301 GPa for GeO₆, pressure derivative of 3.94 for MgO₈ and 4.91 for GeO₆, and zero-pressure polyhedral volume of 18.919 Å³ for MgO₈ and 9.069 Å³ for GeO₆. Rietveld results yield the following parameters at room temperature based on second-order Birch-Murnaghan equation of state fitting using Rietveld results are shown with dotted lines in a. See Figure 4 for references.

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2.02 for NaMgF₃, and 2.34 for CaIrO₃. Volume occupancy of the void space is insensitive to pressure, and is similar among the pPv phases.

**Octahedral tilting and distortion**

The pPv phase has fewer degrees of freedom than the perovskite phase in terms of both tilting and distortion of the octahedra. Because the octahedra in the perovskite phase share corners along all directions, both tilting and symmetrical distortion of octahedra are allowed in all the directions. On the other hand, since the octahedra in the pPv phase share X₂-X₂ edges along the a-axis and share corners in c-direction (Fig. 1), tilting of octahedra is allowed only around the a-axis, and the X₂-X₂-X₂-X₂ plane in an octahedron must have a square or rectangular shape (Fig. 1). Therefore, the shape of octahedral layer in ABX₃, pPv phase can be fully described by specifying both tilting of octahedra around the a-axis (B-X₁-B angle in b-c plane) and the distortion of an octahedron that can be fully described by following three variables: X₂-B-X₂ vector that represents the deviation of the X₂-X₂-X₂-X₂ plane from square to rectangular shape, the angle between X₂-X₂-X₂-X₂ plane normal and the B-X₁ vector in the b-c plane (angle q), and B-X₁/B-X₂ lengths ratio (Fig. 1). For an ideal octahedron these three variables are 90°, 0°, and 1°, respectively.

As shown below, Rietveld results at 78–109 GPa are consistent with theoretical predictions within 3σ, but considerable data scatter and the limited pressure and temperature range make it difficult to constrain the pressure and temperature dependencies of octahedral tilting and distortion solely from Rietveld results. Therefore, we use theoretical results to compare octahedral tilting and distortion in MgGeO₃, MgSiO₃, NaMgF₃, and CaIrO₃ pPv phases.

**Tilting of octahedra.** Figure 9 shows B-X₁-B angle in the b-c plane. Theoretical results show a subtle monotonic increase of this angle from 131.3 to 132.7° at 0–300 GPa, indicating that octahedral tilting is insensitive to pressure. Octahedral tilting is ~132° for MgGeO₃, ~138° for MgSiO₃, and ~140° for both NaMgF₃ and CaIrO₃, indicating a greater degree of bending in the connection of octahedra in MgGeO₃ than the other pPv. The order of octahedral tilting among these pPv can be qualitatively understood by polyhedral volume ratio $V_{AO6}/V_{BO6}$: A larger (smaller) octahedral tilting makes the length of octahedral layer in c-direction shorter (longer). Since MgGeO₃ (CaIrO₃) has the smallest (largest) $V_{AO6}/V_{BO6}$ among these pPv, octahedra in MgGeO₃ (CaIrO₃) need to be more (less) bent than the other pPv to share the a-c plane with the relatively small (large) hexahedral layer.

**Octahedral distortion.** At first, we survey the overall octahedral distortion using angular variance (Fig. 10a), which has been used to show variations in bond angle in an octahedron (Robinson et al. 1971). A regular octahedron has a value of 0°. Theoretical results show a mild decrease of angular variance from 12 to 6° by compression from 50 to 300 GPa, predicting that basic evolution of angular variance with pressure is to decrease distortion over a wide pressure range. However, the pressure change of angular variance is somewhat larger below 50 GPa (from 12 to 18° by decompression to 0 GPa), consistent with different compression behavior below 50 GPa. Angular variance of the pPv phase is greater than that of MgSiO₃ perovskite phase (1.7° at ambient conditions by Ross and Hazen 1990; 2.4° at 79.7 GPa, 1681 K by Fiquet et al. 2000), and is ~11° for MgGeO₃, ~7° for both MgSiO₃ and NaMgF₃, and ~38° for CaIrO₃, showing that MgSiO₃, MgGeO₃, and NaMgF₃ are similarly less distorted than CaIrO₃.

Figure 10b shows X₂-B-X₂ angle in a BX₆ octahedron. We define this angle so that the X₂-X₂ vector is parallel to the a-direction. Theoretical calculations predict a modest decrease of this angle with pressure, which contributes to decrease of octahedral distortion with pressure. Results from Rietveld refinements are consistent with theory within 3σ, but Rietveld results also imply that this angle may change more than predicted (~92° at 90 GPa to ~94° at 80 GPa during decompression). Since faster increase of this angle during decompression can result in rapid expansion of a-axis, we speculate that the greater change of this angle with pressure may explain the anomaly in b/a ratio reported by Kubo et al. (2006). This angle is 92.1° in MgGeO₃, 93.4° in MgSiO₃, 94.4° in NaMgF₃, and 99.2° in CaIrO₃, showing significant distortion of CaIrO₃. The order of this angle among these pPv can be qualitatively understood by considering the $V_{AO6}/V_{BO6}$ polyhedral volume ratio following the same logic put forward in the discussion of the octahedral tilting among these pPv.

Figure 10c shows pressure dependence of the angle between X₂-X₂-X₂-X₂ plane normal and B-X₁ vector in the b-c plane (angle q). Theory predicts slight monotonic decrease of this angle by compression, which also contributes to decrease of octahedral distortion with pressure. This angle is ~3° in MgSiO₃, ~1° in NaMgF₃, and ~5° in both MgGeO₃ pPv and CaIrO₃, showing that NaMgF₃ is least distorted.

Figure 10d shows the ratio of B-X₁ and B-X₂ lengths. Theory predicts deviation of this ratio from 1 with pressure with relatively rapid change below 50 GPa and relatively mild change above 50 GPa, contributing to an increase of octahedral distortion with pressure. This ratio is 0.971 in MgGeO₃, 0.967 in both MgSiO₃ and NaMgF₃, and 0.939 in CaIrO₃, showing that MgSiO₃, NaMgF₃, and MgGeO₃ are similarly less distorted than CaIrO₃.

**Figure 9.** Tilting angle of octahedra around the a-axis (= B-X₁-B angle between two octahedra in the b-c plane) in ABX₃ pPv phase. See Figure 4 for references.
Comparison of MgGeO$_3$, MgSiO$_3$, NaMgF$_3$, and CaIrO$_3$, pPv

There are some similarities between MgSiO$_3$ and MgGeO$_3$ pPv represented by axial ratios, averaged Mg-O distance, MgO$_8$ polyhedral volume, and degree of octahedral distortion as well as consistency in elastic systematics and generally similar behavior in axial compressibilities reported by Kubo et al. (2006). On the other hand, NaMgF$_3$ pPv phase shows more similarities in structural parameters with MgSiO$_3$ pPv than MgGeO$_3$ pPv, while the similarity between MgSiO$_3$ and CaIrO$_3$ pPv is limited to octahedral tilt angle. Therefore, we infer that NaMgF$_3$ may be a good analog material to MgSiO$_3$ pPv, and among oxide pPv, MgGeO$_3$ is a better analog than CaIrO$_3$. It is noted that Lindsay-Scott et al. (2007) have also inferred that CaIrO$_3$ may not be a good analog for MgSiO$_3$ pPv based on comparison of elastic incompressibilities ratios for CaIrO$_3$ and MgGeO$_3$ pPv. It should also be noted that MgGeO$_3$ and CaIrO$_3$ pPv phases tend to show qualitatively opposite character with the relationship to MgSiO$_3$ pPv phase, such as axial ratios, atomic positions, ratio of average bond lengths (A-O/B-O), variation of bond lengths in AO$_8$ and BO$_6$ polyhedra (Fig. 7b), polyhedral volume ratio, and octahedral tilting angle. This implies that physical properties of MgSiO$_3$ pPv (such as elasticity and rheology) might be intermediate between the properties of the two analog materials.

Reliability of Rietveld refinements to Mbar pressures

Many previous high-pressure studies report only a single optimum Rietveld refinement and this leaves open significant questions about the robustness of the reported results. In addition, there is a large disagreement between the Rietveld results reported here and that of Hirose et al. (2005) on the same material at similar conditions. The existence of such discrepancies, despite each providing an overall reasonable fit to the diffraction data, could raise questions about the reliability of the Rietveld method at extreme conditions.

The present results show that we can obtain consistent Rietveld refinements for experiments involving separate samples with different pressure transmitting media that cover a similar pressure range. Furthermore, these refinement results are in good agreement with our independent first-principles calculations. Consistent results are also obtained for individual and averaged bond lengths between theory and experiment. Finally, the averaged Mg-O and Ge-O bond lengths found here are consistent with previous experimental studies (single-crystal and polycrystalline) of other materials with similar structural elements at high pressures. These consistencies all suggest that Rietveld refinement can provide reasonable structural parameters at pressures approaching 1 Mbar.

ACKNOWLEDGMENTS

This work was supported by NSF and the Carnegie-DOE Alliance Center. A.K. benefited greatly from the powder X-ray diffraction workshop held at National Synchrotron Light Source in January 2005 organized by John Parise, Peter Stephens, and Patrick Woodward. We thank Robert J. Cava for his help with sample synthesis and Sean R. Shieh for experimental assistance. Preliminary experiments were conducted at HPCAT, APS, Argonne National Laboratory with the help of Yue Meng. Comments by Leonid Dubrovinsky and anonymous reviewers improved the manuscript. Discussions with Haozhe Liu and Przemyslaw Dera were also helpful. This work was performed at GSECARS, APS, Argonne National...
KUBO ET AL.: RIETVELD REFINEMENT OF MgGeO$_3$ POST-PEROVSKITE TO 1 MBAR

975

Laboratory. GSECARS is supported by the NSF. Earth Sciences (EAR-0622171) and DOE-Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source is supported by DOE Office of Basic Energy Sciences under contract no. DE-AC02-06CH11357.

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