Stability and equation of state of the post-perovskite phase in MgGeO$_3$ to 2 Mbar

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[1] The stability and equation of state of the post-perovskite phase in MgGeO$_3$ were investigated to 2 Mbar by in situ x-ray diffraction experiments using the laser-heated diamond cell as well as by theoretical calculations using density functional theory. The stability of the phase was demonstrated at 92-201 GPa during laser heating. By using the Birch-Murnaghan equation of state, we obtained a zero-pressure volume ($V_0$) of $179.2 \pm 0.7 \text{Å}^3$, bulk modulus ($K_0$) of $207 \pm 5 \text{GPa}$ with a pressure derivative ($K'_0$) of 4.4 from experiments at room temperatures, and $V_0 = 178.02 \text{Å}^3$, $K_0 = 201.9 \text{GPa}$, $K'_0 = 4.34$ from theoretical calculations at 0 K. The relative axial compressibilities of the silicate and germanate post-perovskite phases are similar although MgSiO$_3$ is more anisotropic than MgGeO$_3$.


1. Introduction

[2] Since the discovery of the post-perovskite phase (pPv) in MgSiO$_3$ by Murakami et al. [2004], numerous studies of this phase have been carried out by theory and experiment [e.g., Tsuchiya et al., 2004; Oganov and Ono, 2004; Shim et al., 2004; Mao et al., 2004; Stockhouse et al., 2005]. There has also been strong interest in understanding the occurrence and properties of the pPv phase in other systems [e.g., Caracas and Cohen, 2005; Tateno et al., 2006].

[3] Over the last 40 years, the crystal structures of germanates have been extensively examined as a low-pressure model for silicate structures [e.g., Ringwood and Seabrook, 1963]. Germanates have also been used as silicate analogs in studies of phase equilibria and thermodynamics [Ross and Navrotsky, 1988; Akaogi et al., 2005], equation of state [Sato et al., 1977], and elasticity [Liebermann, 1975]. In recent years, there has been emphasis on the use of germanates as analogs for the study of phase transformation mechanisms and kinetics, rheology, and microstructure development, especially in the Mg$_2$SiO$_4$ system [e.g., Riggs and Green, 2005]. Recently, Hirose et al. [2005] demonstrated that the pPv phase could be synthesized in MgGeO$_3$ composition at ~50 GPa lower than the transition pressure for MgSiO$_3$, suggesting that germanate could be a useful analog to study the physical properties of silicate pPv phase. Also, the first study of deformation behavior of MgGeO$_3$ pPv was recently reported [Merkel et al., 2006]. Here we report experimental and theoretical results on stability, equation of state, and axial compressibilities of MgGeO$_3$ pPv phase to 2 Mbar. Our results expand upon earlier measurements [Hirose et al., 2005] due to extended pressure range, use of soft pressure-transmitting media, and combination with first-principles calculations.

2. Experiment

[4] MgGeO$_3$ orthoenstatite was synthesized from a mixture of MgO (periclase) + GeO$_2$ (quartz) by heating in air at 1000 °C for 40 hours. Powder x-ray diffraction showed orthoenstatite with minor amounts of excess GeO$_2$. The sample was mixed with Pt (weight ratio of 8:2) which served as both a pressure standard and laser absorber.

[5] A symmetric diamond cell with Re gasket was used to generate high pressure. Three experimental runs were conducted. For run 1, the sample was insulated by Ar. In run 2, NaCl served as an insulating medium while for the third run MgGeO$_3$ unmixed with Pt was used as insulation.

[6] High-pressure x-ray diffraction experiments were carried out at 13-ID-D of the GSECARS sector at the Advanced Photon Source (APS). A monochromatic x-ray beam of 0.3344-Å wavelength was focused to a size of ~6 × 6 mm$^2$. An angle dispersive geometry with an image plate or CCD detector was employed. The detector was calibrated using CeO$_2$. We heated the samples from both sides using a TEM00 Nd:YLF laser. Temperature was measured by spectro-radiometry. A complete description of the diamond cell high-pressure research facility at GSECARS can be found elsewhere [Shen et al., 2005].

[7] Two-dimensional x-ray images were converted to one-dimensional diffraction patterns using Fit2d [Hammersley et al., 1996]. Pressure was determined based on the equation of state of Pt by Holmes et al. [1989], which is known to give the highest pressure value relative to the other pressure scales for Pt and Au [Akahama et al., 2002]. Lattice parameters of the pPv phase were calculated from the 002, 002, 110, and 112 diffraction lines. Pressure-volume ($P-V$) data were fit using a third-order Birch-
Murnaghan equation of state to obtain the bulk modulus ($K_0$), its pressure derivative ($K'_0$), and zero-pressure unit cell volume ($V_0$). Linear compressibilities were determined from a modified Birch-Murnaghan equation [Xia et al., 1998].

[8] Rietveld refinement was performed using GSAS [Larson and Von Dreele, 1994]. We refined lattice parameters, peak shape parameters, phase fractions, atomic positions, averaged displacement parameters, and spherical-harmonic terms in preferred orientation function.

[9] We also carried out first-principle calculations based on density functional theory (DFT) [Hohenberg and Kohn, 1964] using VASP [Kresse and Hafner, 1993; Kresse and Furthmüller, 1996] with the projector-augmented-wave method [Kresse and Joubert, 1999]. Electronic correlations were treated within the local density approximation (LDA). Converged solutions to the Kohn-Sham equations were obtained with energy-cutoff of 600 eV and a 6x4x6 k-point grid. Total energies were converged to better than 2.3 meV/atom and Pulay stresses were less than 0.6 GPa.

3. Results and Discussion

[10] Samples were initially compressed at room temperature to high pressures, where only weak and broad diffraction peaks were observed (Figure 1). In run 1, the sample at ~83 GPa was initially heated up to 1900 ± 300 K for ~4 minutes. After quenching, strong diffraction peaks of pPv phase (CaIrO$_3$-type structure, Cmcm) were observed. The sample was then compressed to ~95 GPa and heated to ~1700 K for 5 minutes, and further compressed up to 107 GPa and then decompressed in steps (see auxiliary material). During decompression, the sample was not heated to avoid back transformation to low-pressure phases.

[11] In run 2, the sample was heated to ~1750 K for ~10 minutes at 92-95 GPa. Diffraction patterns obtained during and after heating are shown in Figures 1b and 1c. In this run, we obtained smooth Debye rings of pPv suitable for Rietveld method. The sample was decompressed to room pressure in steps without heating. Significant weakening and broadening of pPv peaks were observed beginning at 48 GPa. Diffraction peaks of the pPv phase were observed at 7 GPa but disappeared at room pressure.

[12] In run 3, we heated the sample to ~1600 K at 170 GPa for 5 minutes. Crystallization of the pPv phase was confirmed during heating, and the phase was quenched to 300 K at 159 GPa (Figure 1d). The sample was further compressed to 196 GPa, and diffraction peaks from the pPv phase were still observed during heating at ~1600 K at ~201 GPa for ~1 minute. Further measurements were not possible due to catastrophic failure of a diamond anvil.

[13] Rietveld refinement showed that the crystal structure of the pPv phase at 88 GPa is reasonably refined by the structure model of CaIrO$_3$-type (space group Cmcm) (Figure 2 and Table 1) in agreement with Hirose et al. [2005]. Table 1 also lists results obtained from DFT calculations. Atomic positions and lattice parameters are in good agreement with the Rietveld refinement.

[14] From the calculated enthalpy difference between Pv and pPv phases as a function of pressure, we predict that the Ppv phase transition occurs at 45 GPa at 0 K without taking zero-point motion into account. This transition pressure is in agreement with that predicted by linear extrapolation of the phase boundary reported by Hirose et al. [2005] to 0 K.

[15] Analysis of deviatoric stress in Pt based on Singh’s [1993] method showed that the differential stress was 1–2 GPa during compression and 0–2 GPa during decompression. In this case, because of axial x-ray diffraction geometry employed in this study, pressures determined from diffraction lines of Pt are always underestimated. To reduce this systematic error, we used only 111 reflection of Pt to determine pressure since Pt has positive elastic anisotropy [Kavner and Duffy, 2003].

Table 1. Structural Parameters of MgGeO$_3$ pPv Phase From Rietveld Refinement and DFT Calculation

<table>
<thead>
<tr>
<th>Method</th>
<th>Rietveld</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$, GPa</td>
<td>87.8</td>
<td>86.3</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>2.596(4)</td>
<td>2.5943</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>8.4113(9)</td>
<td>8.3856</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>6.4059(6)</td>
<td>6.3853</td>
</tr>
<tr>
<td>Mg</td>
<td>0, 0.248(1), 0.25</td>
<td>0, 0.252, 0.25</td>
</tr>
<tr>
<td>Ge</td>
<td>0, 0, 0</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>O1</td>
<td>0, 0.928(2), 0.25</td>
<td>0, 0.915, 0.25</td>
</tr>
<tr>
<td>O2</td>
<td>0, 0.646(1), 0.440(2)</td>
<td>0, 0.642, 0.436</td>
</tr>
</tbody>
</table>

Figure 3. Pressure-volume data of MgGeO$_3$ and MgSiO$_3$ pPv phases. Compression curve is based on experimental results (see text). Inset shows variation of axial ratios versus pressure. Diamond symbols are after Murakami et al. [2004].

[16] Figure 3 shows our P-V data from experiments and DFT calculations together with previous results for MgGeO$_3$ and MgSiO$_3$. Average of the estimated standard deviation ($\sigma$) in the experimentally-determined lattice parameters of the pPv phase is 0.11%. Experimental data obtained in three different runs above 47 GPa form a smooth trend, but data below 45 GPa tend to lie above this trend. As noted above, these lower pressure data exhibit broader peak widths and lower peak intensities. Such changes may reflect metastability of pPv phase and/or accumulation of deviatoric stress, both of which could yield larger unit cell volume. Therefore, we did not use data below 47 GPa for the equation of state analysis. Volumes obtained from DFT calculations are similar to but slightly lower than those from experiment which is typical for LDA calculations (Figure 3).

[17] Due to lack of data at low pressures (<47 GPa), it is difficult to simultaneously constrain $V_0$ and $K_0$ from our data set. We therefore added a constraint from semi-empirical elasticity systematics ($K-V$ const. for a given crystal structure) [Anderson and Anderson, 1970]. As reference values, we used $K_0$ and $V_0$ of MgSiO$_3$ pPv at 0 K by theory and experiment (Table 2). By this method, we constrained equation of state parameters of MgGeO$_3$ pPv phase as $K_0 = 207 \pm 5$ GPa, $V_0 = 179.2 \pm 0.7 \text{Å}^3$ with fixed $K'_0$ of 4.4 (solid line in Figure 3). Our DFT calculations at 0 K yielded $V_0 = 178.02 \text{Å}^3$, $K_0 = 201.9$ GPa, and $K'_0 = 4.34$ for the pPv phase (Table 2). Our P-V data agree well with those reported by Hirose et al. [2005], but because they included the lower pressure data in the fitting, they obtained a larger $V_0$ and smaller $K_0$ (Table 2). If $K'_0 = 4$, we obtain $K_0 = 245 \pm 5$ GPa and $V_0 = 175.9 \pm 0.6 \text{Å}^3$, showing significant trade-off between $K_0$ and $K'_0$ due to lack of data at low pressures.

[18] The Figure 3 inset shows axial ratios of the pPv phase. Average of the estimated standard deviation ($\sigma$) in the experimentally-obtained axial ratios of the pPv phase is 0.09 % for $b/a$ and 0.07 % for $c/a$. Although the $b/a$ ratio decreases strongly with pressure at less than ~60 GPa, it becomes markedly less pressure dependent above 60 GPa. The $b/a$ ratio becomes nearly constant at 70–110 GPa and decreases strongly with pressure at less than ~45 GPa, showing a smooth trend, but data below 45 GPa tend to lie above this trend. As noted above, these lower pressure data exhibit broader peak widths and lower peak intensities. Such changes may reflect metastability of pPv phase and/or accumulation of deviatoric stress, both of which could yield larger unit cell volume. Therefore, we did not use data below 47 GPa for the equation of state analysis. Volumes obtained from DFT calculations are similar to but slightly lower than those from experiment which is typical for LDA calculations (Figure 3).

[19] Individual lattice parameters were fit using a modified form of the Birch-Murnaghan equation [Xia et al., 1998]:

$$P = 3/2 \cdot K_0 \left(\frac{b_0}{l_0}\right)^7 - \left(\frac{l_0}{b_0}\right)^5 \cdot \left\{1 + 3/4 \cdot \left(\frac{K'_0}{K_0}\right) - 4\right\} \cdot \left[\left(\frac{l_0}{b_0}\right)^3 - 1\right],$$

(1)

Figure 3 inset shows variation of axial ratios versus pressure (see text). Inset shows variation of axial ratios versus pressure. Diamond symbols are after Murakami et al. [2004].

The calculated linear compressibilities are shown in Figure 4, demonstrating good agreement between experiments and theory. Also shown are results for MgSiO$_3$ from Oganov and Ono [2004] and Stackhouse et al. [2005], indicating similar behavior in axial compressibility between germanate and silicate pPv phases. However, MgGeO$_3$ pPv at 60–120 GPa is 10–15 % less anisotropic than MgSiO$_3$ pPv at 120 GPa in terms of $\beta_{1,3}$, implying that anisotropy of MgGeO$_3$ pPv in various physical properties may be less than that of MgSiO$_3$ pPv.

Table 2. Equation of State Parameters of pPv Phases

<table>
<thead>
<tr>
<th>Formula</th>
<th>$V_0$, Å$^3$</th>
<th>$K_0$, GPa</th>
<th>$K'_0$</th>
<th>Method$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgGeO$_3$</td>
<td>179.2(7)</td>
<td>207 (5)</td>
<td>4.4</td>
<td>EXP, 1</td>
</tr>
<tr>
<td>MgGeO$_3$</td>
<td>183.1(8)</td>
<td>192 (5)</td>
<td>4.0</td>
<td>EXP, 2</td>
</tr>
<tr>
<td>MgGeO$_3$</td>
<td>178.02</td>
<td>201.9</td>
<td>4.34</td>
<td>DFT, 1</td>
</tr>
<tr>
<td>MgSiO$_3$</td>
<td>163.81(5)</td>
<td>222 (1)</td>
<td>4.2(1)</td>
<td>DFT, 3</td>
</tr>
<tr>
<td>MgSiO$_3$</td>
<td>162.86</td>
<td>231.9</td>
<td>4.43</td>
<td>DFT, 4</td>
</tr>
<tr>
<td>(Mg,Fe)SiO$_3$</td>
<td>164.9(6)</td>
<td>219 (5)</td>
<td>4.0</td>
<td>EXP, 5</td>
</tr>
<tr>
<td>MgSiO$_3$</td>
<td>162.86</td>
<td>225–249</td>
<td>4.0</td>
<td>EXP, 6</td>
</tr>
</tbody>
</table>

$^a$EXP: experiment; DFT: first principles calculation; 1, This study; 2, Hirose et al. [2005]; 3, Tsuchiya et al. [2004]; 4, Oganov and Ono [2004]; 5, Shi et al. [2006]; 6, Ono et al. [2006].

Figure 4. Linear compressibility of pPv phases. Open symbols at 0 K and 4000 K are by Oganov and Ono [2004] and Stackhouse et al. [2005], respectively.
Based on the above results, we conclude that germa-
nate could behave as a useful analog to silicate pPV phase
because of lower transition pressure, stronger diffraction
intensities, consistency in elasticity systematics, and gener-
ally similar behavior in axial compressibilities. We infer
that the pPV phase in MgSiO$_3$ should be stable to a few
megabars from the results of stability of MgGeO$_3$ pPV
phase to 2 Mbar and pPV transition pressure in MgGeO$_3$
[Hirose et al., 2005] that is ~60 GPa lower than that in
MgSiO$_3$ [e.g., Murakami et al., 2004].

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