Equation of state of NaMgF₃ postperovskite: Implication for the seismic velocity changes in the D'' region

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Recent first-principles calculations have proposed that bulk sound speed \( V_{qs} \) decreases at the perovskite (Pv) → postperovskite (PPv) transition. Yet some measurements suggest an increase in \( V_{qs} \) at the PPv transition in (Mg,Fe)SiO₃ and NaMgF₃. Our new measurements on NaMgF₃ up to 50 GPa under quasi-hydrostatic stress conditions reveal that the \( V_{qs} \) of PPv remains lower than that of Pv near the PPv transition, consistent with a first-principles study on NaMgF₃. Combined with similar observations in (Mg,Fe)SiO₃, MgGeO₃, and CaIrO₃, our result on NaMgF₃ suggests that the \( V_{qs} \) decrease is a robust trend in the PPv transition and is controlled more by crystal structure than by chemical composition. Our finding also strengthens the proposal that the elastic properties of PPv can explain the small \( P \)-wave increase across the D'' discontinuity and the anticorrelation between the \( V_{qs} \) and \( S \)-wave velocity anomalies in the D'' region.

1. Introduction

Many studies have related enigmatic seismic observations at the D'' region of the mantle to the physical properties of the postperovskite (PPv) phase (see Hirose [2006] and Shim [2008] for review). A decrease in bulk sound speed \( V_{qs} \) has been predicted across the perovskite (Pv) → postperovskite (PPv) transition. Together with a predicted increase in \( S \)-wave velocity \( V_{s} \), this change would provide explanations for the small \( P \)-wave velocity \( V_{p} \) increase observed at the D'' discontinuity and the anticorrelation between the \( V_{qs} \) and \( V_{s} \) anomalies at the D'' region. However, most of the predictions have been based on theoretical calculations [Itaaka et al., 2004; Oganov and Ono, 2004; Wentzczovitch et al., 2006] and existing equation of state (EOS) measurements on silicate PPv [Shieh et al., 2006; Mao et al., 2006] suffer from technical difficulties at the extreme \( P-T \) stability field of the PPv phase.

2. Experimental Techniques

NaMgF₃ was synthesized from NaF and MgF₂ following the method of Chao et al. [1961]. The quality and purity of the sample was confirmed with X-ray diffraction (XRD) at MIT. NaMgF₃ powder was mixed with 10 wt% Pt which serves as both a laser absorber and an internal pressure standard. The NaMgF₃+ Pt mixture was pressed to 10–15 kbar using a diamond-anvil cell (DAC) with Ar as a pressure transmitting medium. The samples were compressed with diamond anvils with either 200 or 300-μm diameter culets.

Angle-dispersive XRD measurements were conducted at the GSECARS sector of the Advanced Photon Source (APS) and beamline 12.2.2 of the Advanced Light Source (ALS). Diffraction images were collected using a MAR345 imaging plate and a MarCCD detector with monochromatic X-ray beams of 30 and 40 keV at ALS and APS, respectively. Double-sided laser heating was performed at GSECARS for the synthesis of PPv and stress annealing. Use of X-ray semi-transparent cubic BN seats in the DAC allows for diffraction measurements up to 2θ = 60°. XRD images are reduced to 1D patterns using the Fit2D software [Hammersley, 1997]. Unit-cell parameters are obtained by fitting 5–19 diffraction lines of Pv and PPv in the UnitCell software [Holland and Redfern, 1997].

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1997]. A total of 2–5 diffraction lines of Pt are used for calculating pressure from the EOS by Holmes et al. [1989].

3. Results

A total of three different samples were measured. The first sample was compressed from 13 to 37 GPa while a diffraction pattern was measured about every 4 GPa (Figure 1a). This sample was not thermally annealed. The diffraction lines are well explained by a NaMgF$_3$-Pv + Pt + Ar mixture.

The second sample was compressed from 22 to 49 GPa at room temperature. The diffraction lines of PPv appear between 37 and 42 GPa during compression and a Pv + PPv mixture was observed up to 49 GPa. The most intense PPv line, 022, has an intensity less than 5% of the most intense Pv line even at 49 GPa. This observation is in contrast with previous measurements in rigid media (which therefore should be more non-hydrostatic) where a complete transition to PPv was reported at much lower pressures, 13–30 GPa [Liu et al., 2005; Martin et al., 2006a, 2006b]. The difference in transition pressure in different media suggests that deviatoric stresses may help the system to overcome kinetic barriers at room temperature.

At 49 GPa this sample was heated to 1500 K for 15 min. The temperature-quenched diffraction pattern shows predominantly Pv with some amount of PPv, indicating an incomplete transition. Diffraction patterns of the Pv + PPv mixture were collected during decompression to 18 GPa. Before each diffraction measurement we annealed deviatoric stresses in the sample.

The third sample was directly compressed to 30 GPa and heated for 30 min at $T \leq 2000$ K. XRD patterns measured during and after heating indicate that nearly pure PPv was synthesized (Figures 1b and 1c). Some diffraction lines of Pv remain in the diffraction patterns. However, their intensities are significantly lower than those of PPv. Therefore, the transition to PPv is incomplete at these pressures.

**Figure 1.** XRD patterns of the (a) Pv and (b–d) PPv phases in NaMgF$_3$. The PPv and Pv lines are indicated with solid and open triangles, respectively. The backgrounds are subtracted. Pt: platinum pressure scale, Ar: argon pressure medium, Ar-H: diagnostic hcp-Ar lines, and question mark: unidentified line (consists of a few dots in the diffraction image).
Diffraction patterns of PPv in our study are in higher quality than previous studies due to the use of an Ar medium and thermal annealing; the width of PPv lines is a factor of 5 smaller than those presented by Martin et al. [2006a].

Diffraction patterns of PPv were measured while the sample was decompressed. Unlike (Mg,Fe)SiO$_3$ and MgGeO$_3$, the PPv phase in NaMgF$_3$ was quenched to ambient conditions (Figure 1d). In fact, the PPv peaks remain fairly sharp. Accurate determination of volume at reference state ($V_0$) improves the quality of EOS fit significantly.

Because of unknown $V_0$ of (Mg,Fe)SiO$_3$ [Shieh et al., 2006; Mao et al., 2006; Guignot et al., 2007; Shim et al., 2008], the EOS fit for silicate suffers a larger uncertainty.

A new phase ("N-phase") was reported in NaMgF$_3$ by Martin et al. [2006a] during and after laser heating at pressures higher than 30 GPa. In our measurements mentioned above, no evidence of the "N-phase" was detected. This discrepancy is perhaps due to low-temperature heating ($T/C20 2000 K) in our measurements compared with Martin et al. [2006a] who heated to 2000 K. In some of the runs which are not used for this work, we observe weak lines which can be assigned to those of the "N-phase" in some parts of the samples at 60 GPa after laser heating to 2000 K.

The measured $P$–$V$ relations of the PPv and Pv phases are fit to the third-order Birch-Murnaghan equation by fixing $V_0$ to the measured values at ambient conditions. We do not find any systematic differences among volumes from different runs with or without thermal annealing or during compression or decompression (Figure 2). Within the experimental uncertainties, our Pv EOS is in excellent agreement with previous X-ray results in a He medium [Liu et al., 2005], Brillouin measurements [Zhao et al., 1993], and theoretical calculations [Umemoto et al., 2006] (Table 1). However, our quasi-hydrostatic measurements yield a much smaller bulk modulus ($K_0$) of PPv than previously reported by Martin et al. [2006a]. Our fit also indicates that $K_0 = (dK/dP)_0$, of PPv should be significantly higher than that of Pv. Our PPv EOS is much more consistent with recent theoretical predictions by Umemoto et al. [2006] (Table 1).

### Table 1. The EOS Parameters of the PPv and Pv Phases in NaMgF$_3$

<table>
<thead>
<tr>
<th>Phases</th>
<th>$V_0$ (Å$^3$)</th>
<th>$K_0$ (GPa)</th>
<th>$K_0'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Postperovskite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>223.0 ± 0.1</td>
<td>54 ± 3</td>
<td>5.7 ± 0.4</td>
</tr>
<tr>
<td>Martin et al. [2006a]$^*$</td>
<td>200 ± 3</td>
<td>137 ± 18</td>
<td>4$^b$</td>
</tr>
<tr>
<td>Umemoto et al. [2006]$^c$</td>
<td>213</td>
<td>69</td>
<td>4.8</td>
</tr>
<tr>
<td>Perovskite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>225.13</td>
<td>81 ± 4</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>Liu et al. [2005]$^a$</td>
<td>225.13</td>
<td>76 ± 1</td>
<td>4$^b$</td>
</tr>
<tr>
<td>Umemoto et al. [2006]$^a$</td>
<td>218</td>
<td>80</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$^a$Experimental work.
$^b$Fixed parameter in EOS fitting.
$^c$First-principles calculation with the local density approximation at 300 K.

**4. Discussion**

Recent first-principles calculations have predicted that bulk sound speed ($V_F$) would decrease across the PPv transition in (Mg,Fe)SiO$_3$ [Iitaka et al., 2004; Oganov and Ono, 2004; Wentzcovitch et al., 2006]. This decrease across the PPv transition is surprising as other mantle transitions show $V_F$ increases across the boundaries according to laboratory measurements. For example, $V_F$ increases approximately 6% across the olivine-wadsleyite and post-spinel transitions [Ia and Stixrude, 1992; Duffy et al., 1995]. However, existing measurements on (Mg,Fe)SiO$_3$ are discrepant in the bulk modulus of PPv. A study by Shieh et al. [2006] is consistent with a small decrease in $V_F$ whereas a later study by Mao et al. [2006] indicates a large increase in $V_F$. A recent study by Shim et al. [2008] has identified a series of changes in the compressional behavior of PPv outside of its stability field. Using the data points...
measured only in the stability field they found that \( V_F \) decreases by 2.4±1.4% across the PPv transition in an Ar pressure medium.

[16] In the case of NaMgF\(_3\), a PPv EOS by Martin et al. [2006a] indicates a large increase in \( V_F \) across the PPv transition as shown in the inset of Figure 3. However, a first-principles study on NaMgF\(_3\) [Umemoto et al., 2006] has predicted a \( V_F \) decrease similar to what has been predicted for mantle silicate. Our measurements show that the \( V_F \) of PPv is smaller than that of Pv below 20 GPa (Figure 3).

[17] The PPv transition pressure at 300 K in NaMgF\(_3\) is reported to be 13–19 GPa [Liu et al., 2005; Martin et al., 2006b]. In our study with an Ar medium, room temperature transition was not observed until 38 GPa and the discrepancy with previous studies is perhaps because deviatoric stresses allow the system to overcome the kinetic barrier at room temperature. Therefore, these results cannot be used for the equilibrium phase boundary at 300 K. We observe synthesis of PPv from Pv at 30 GPa and 2000 K. Using the Clapeyron slope predicted for the PPv transition, 6–10 MPa/K [Oganov and Ono, 2004; Tsuchiya et al., 2004a; Umemoto et al., 2006], the transition pressure at 300 K is estimated to be 13–20 GPa, which is consistent with a first-principles study [Umemoto et al., 2006]. We note that our estimation of the transition pressure should be regarded as an upper bound because 30 GPa and 2000 K should be already within the stability field of PPv. Therefore, our measurements in quasi-hydrostatic conditions show that the \( V_F \) of PPv remains smaller than that of Pv near the PPv transition (Figure 3).

[18] The existing measurements on MgGeO\(_3\)-PPv and Pv [Kubo et al., 2006; Runge et al., 2006] also imply that the \( V_F \) of PPv should be smaller than that of Pv near the PPv transition (Figure 3). In addition, a recent EOS result for CaIrO\(_3\)-Pv and PPv is compatible with a 5% smaller \( V_F \) of PPv (the PPv transition occurs at high \( T \) and ambient \( P \) in CaIrO\(_3\)) [Ballaran et al., 2007].

[19] A decrease in \( V_F \) across the PPv transition can provide explanations for some intriguing seismic velocity changes observed in the D\(_00\) region as pointed out by previous first-principles studies [Iitaka et al., 2004; Oganov and Ono, 2004; Wentzcovitch et al., 2006]. It has been reported that \( P \)-wave velocity (\( V_P \)) shows a very small increase at the D\(_00\) discontinuity whereas the \( V_S \) increase is much more pronounced (see review by Wysession et al. [1998] and Lay et al. [2004]). The observed decrease in \( V_F \) across the PPv transition will result in a smaller change in \( V_P = \sqrt{V_F^2 + 4/3 V_S^2} \), whereas \( V_S \) will be unaffected.

[20] The anticorrelation between the \( V_F \) and \( V_S \) anomalies has been documented in the mid- to lowermost-mantle, although the depth where the anticorrelation begins is not well constrained, 1000-km depth by Su and Dziewonski [1997] and 2400-km depth by Masters et al. [2000]. Based on the observation of a \( V_F \) decrease together with a suggested \( V_S \) increase across the PPv transition [Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004b; Murakami et al., 2007], it is intriguing to explain the anticorrelation in terms of variations in mineral phases between Pv and PPv: a PPv-rich region will have a larger \( V_S \) but a smaller \( V_F \) than a Pv-rich region.
should exist below the PPv transition depth, which would be 2700 ± 100-km depth [Murakami et al., 2004]. The transition depth is not well constrained due to the pressure scale issues and experimental discrepancies (see Shim [2008] for review). Some studies suggest that the PPv transition can be elevated to as much as 2300-km depth in Fe-rich regions [Mao et al., 2004]. Another possibility is that the anticorrelation observed at the mid lower mantle might have different origin [Hernlund and Houser, 2008], such as changes in composition or spin state of Fe. This hypothesis needs to be further investigated.

[21] In summary, our improved measurements show that $V_0$ decreases across the PPv transition in NaMgF$_3$, unlike previous measurements. This decrease in $V_0$ has been found across the PPv transition in four different systems, NaMgF$_3$, CaIrO$_3$, MgGeO$_3$, and (Mg,Fe)SiO$_3$, which strongly suggests that a $V_0$ decrease is a robust trend in the PPv transitions and is controlled more by crystal structure than by chemical composition. The unusual decrease in $V_0$ may provide explanations for some intriguing seismic observations, such as the smaller $V_p$ increase at the D'' discontinuity and the anticorrelation between the $V_0$ and $V_S$ anomalies in the D'' region.

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