LETTER

Stability and equation of state of MgGeO$_3$ post-perovskite phase

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Abstract

A phase transition of MgGeO$_3$ perovskite was examined at high-pressure and -temperature using synchrotron X-ray diffraction measurements. The results demonstrate that it transforms to a CaIrO$_3$-type post-perovskite phase above 63 GPa at 1800 K. The density increase is 1.5% at the transition pressure. These observations confirm that MgGeO$_3$ is a low-pressure analogue to MgSiO$_3$, for which a similar phase transition was recently found above 125 GPa and 2500 K. The unit-cell parameters of MgGeO$_3$ post-perovskite phase obtained at 300 K during decompression from 79 to 6 GPa show that the b-axis is significantly more compressible than are the a- and c-axes, which could be due to the GeO$_6$-octahedral sheet stacking structure along b. The bulk modulus was determined to be $K'_0 = 192(\pm 5)$ GPa with a fixed pressure derivative of the bulk modulus, $K'$, of 4.

Introduction

Recently Murakami et al. (2004) discovered a novel phase transition from perovskite to post-perovskite phase with a CaIrO$_3$-type structure in MgSiO$_3$ above 125 GPa and 2500 K, corresponding to the lowermost mantle conditions. The stability and phase transitions of MgSiO$_3$ perovskite, however, have long been controversial (e.g., Saxena et al. 1996; Shim et al. 2001). It is known that germanates act as low-pressure analogues to silicates due to the larger size of the Ge cation and MgGeO$_3$ exhibits a similar phase transition was recently found above 125 GPa and 2500 K. The unit-cell parameters of MgGeO$_3$ post-perovskite phase obtained at 300 K during decompression from 79 to 6 GPa show that the b-axis is significantly more compressible than are the a- and c-axes, which could be due to the GeO$_6$-octahedral sheet stacking structure along b. The bulk modulus was determined to be $K'_0 = 192(\pm 5)$ GPa with a fixed pressure derivative of the bulk modulus, $K'$, of 4.

Experimental Procedures

High-pressure and high-temperature conditions were generated using LHDAC techniques. The starting material was a commercially available MgGeO$_3$ orthoenstatite powder. It was mixed with platinum black that served both as an internal pressure standard and a laser absorber. The sample mixture was embedded between layers of pure MgGeO$_3$ powder unmixed with platinum. They were compressed with a rhenium gasket and 300 µm culet diamond anvils. We heated the sample from both sides with a focused multimode continuous wave Nd:YAG laser. The temperature was measured from one side by the spectroradiometric method (Watanuki et al. 2001).

Angle-dispersive X-ray diffraction spectra were collected with an imaging plate at BL10XU of SPring-8. Exposure time was 1 to 3 min. A monochromatic incident X-ray beam with a wavelength of 0.4133 Å was collimated to 20 µm in diameter. The two-dimensional X-ray diffraction image was integrated as a function of 2θ using the FIT2D program (Hammersley 1996).

The uncertainty in temperature within the 20 µm area from which X-ray diffraction data was collected was about ±10% (e.g., Kurashina et al. 2004). Pressure was determined using the equation of state of platinum proposed by Holmes et al. (1989) using the (111), (200), or (220) lines, depending on the peak overlap. The uncertainty in pressure was less than ±0.6 GPa at room temperature and ±1.3 to 2.6 GPa at 1700–2230 K. The greater errors at high temperatures were due to large uncertainties in temperature in the application of the P-V-T equation of state. The diffraction patterns were repeatedly collected at high temperatures and at room temperature before and after heating.

Results

We conducted two separate sets of experiments. In the first one, the sample was compressed at room temperature to 39 GPa and subsequently heated for 11 minutes at 39–42 GPa and 1710–1850 K. The diffraction peaks of orthorhombic perovskite phase (space group Pbnm) appeared within 2 min and did not change with further heating. We then compressed this sample to 94 GPa at room temperature and reheated it for 41 min at 101–103 GPa and 2030–2230 K. New peaks appeared within 2 min during heating, while peaks from perovskite became weak with time. The pattern collected at room temperature after 41 min during heating, while peaks from perovskite became weak with time. The pattern collected at room temperature after 41 min heating consist predominantly of these new peaks and platinum with minor perovskite peaks [(002) and (112)] (Fig. 1). We calculated the atomic positions and interatomic distances by the Rietveld analysis using RIETAN-2000 program (Izumi and Ikeda 2000) and MD calculations (Murakami et al. 2004). The

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peak positions and intensities of these new peaks are consistent with those calculated for the CaIrO$_3$-type post-perovskite phase (space group Cmcm). The diffraction pattern from the Rietveld refinement with preferred orientation of the sample corresponds best with the observed pattern. The observed and calculated diffraction patterns for the post-perovskite phase are presented in Figure 1 and Table 1. The atomic coordinates and interatomic distances based on the Rietveld analysis and the MD calculations are given in Table 2.

In the second set of experiments, the pressure of the phase transition was precisely determined. Similarly to the first experiment, the perovskite phase was first synthesized by heating to 1700 K for 5 min at 60 GPa. The sample was quenched to room temperature at 52 GPa, and was then further compressed to 60 GPa. With heating to 1820–1960 K at 67–75 GPa, intermittently for a total of 45 min, peaks from the post-perovskite phase were again found in the diffraction patterns, coexisting with those from perovskite. The unit-cell volume of the post-perovskite phase is smaller by 1.5% than that of the coexisting perovskite phase at 61 GPa and 300 K. These observations suggest that such P-T conditions are within the stability of the post-perovskite phase but are close to the phase transition boundary. The stabilities of the perovskite and post-perovskite phases are summarized in Figure 2. The phase transition boundary is located at 63 GPa and 1800 K.

The equation of state for the MgGeO$_3$ post-perovskite phase was also determined at room temperature during decompression in the first set of experiments. The press load was decreased stepwise from 79 GPa. The entire sample was heated to 1500–1700 K at each pressure by scanning a laser beam for several minutes to reduce pressure gradient across the sample. Heating was not done at 6 GPa, since part of the sample transformed back to the perovskite phase during heating at 20 GPa. The post-perovskite phase disappeared upon decompression to

\[ \begin{array}{cccc}
\text{hkl} & d_{\text{obs}} (\text{Å}) & \Delta d_{\text{obs}} (\text{Å}) & I_{\text{obs}} \\
\hline
020 & 4.2384 & 0.0020 & 90 \\
002 & 3.2212 & 0.0000 & 20 \\
022 & 2.5645 & 0.0003 & 82 \\
110 & 2.4967 & 0.0000 & 96 \\
040 & 2.1187 & 0.0005 & 23 \\
041 & 2.0125 & 0.0003 & 3 \\
112 & 1.9744 & 0.0010 & 27 \\
130 & 1.9177 & 0.0002 & 100 \\
012 & 1.9177 & 0.0021 & 8 \\
131 & 1.8383 & 0.0001 & 13 \\
042 & 1.7700 & 0.0003 & 7 \\
113 & 1.6286 & 0.0004 & 8 \\
004 & 1.6098 & 0.0009 & 16 \\
033 & 1.5048 & 0.0008 & 5 \\
133 & 1.4302 & 0.0003 & 2 \\
150 & 1.4214 & 0.0003 & 16 \\
151 & 1.4120 & 0.0001 & 3 \\
152 & 1.3879 & 0.0004 & 5 \\
114 & 1.3535 & 0.0000 & 20 \\
152 & 1.3007 & 0.0000 & 38 \\
062 & 1.2932 & 0.0001 & 28 \\
044 & 1.2818 & 0.0003 & 11 \\
220 & 1.2479 & 0.0004 & 7 \\
134 & 1.2333 & 0.0001 & 9 \\
202 & 1.2110 & 0.0004 & 3 \\
222 & 1.1642 & 0.0002 & 16 \\
\end{array} \]

Notes: The refined XRD pattern is based on the orthorhombic unit cell: $a = 2.6127$, $b = 8.4728$, and $c = 6.4429$ Å ($Z = 4$).

* Peak overlapping with platinum.
the ambient pressure.

The unit-cell parameters and volumes of the MgGeO₃ post-perovskite phase were obtained in a pressure range from 79 to 6 GPa at 300 K (Table 3). The relative cell length along each axis is plotted as a function of pressure in Figure 3. As shown, MgGeO₃ post-perovskite phase is elastically anisotropic; the b-axis is approximately 30% to 50% more compressible than the a- and c-axes. To determine the elastic parameters, the P-V data were fitted to the Birch-Murnaghan equation of state (Birch 1947) (Fig. 4):

\[ P = 1.5 K_0(x^2 - x^3)[1 + 0.75(K_0' - 4)(x^2 - 1)] \]

where \( x = (V/V_0)^{1/3} \), and \( V_0 \), \( K_0 \), and \( K_0' \) are the volume, isothermal bulk modulus, and its first pressure derivative, respectively, at ambient conditions. The bulk modulus, \( K_0 \), was determined to be 210(±20) GPa with \( K_0' = 3.5(±0.5) \) and \( V_0 = 182.2(±1.1) \text{ Å}^3 \). When \( K_0' \) was fixed at 4, we obtained \( K_0 = 192(±5) \text{ GPa and } V_0 = 183.1(±0.8) \text{ Å}^3 \). This value of \( K_0 \) is greater than those for other MgGeO₃ polymorphs reported in the previous studies [\( K_0 = 187(±2) \text{ GPa for ilmenite-type phase} \)](Sato et al. 1977; Ashida et al. 1985).

**Figure 2.** Phase diagram for MgGeO₃. Open squares and closed circles indicate the stabilities of perovskite and post-perovskite phase, respectively. The Clapeyron slope of the phase transition boundary is estimated to be +8 MPa/K.

**Figure 3.** Relative cell length at 300 K as a function of pressure. Each unit-cell parameter was normalized to that at ambient condition (assumed: \( a_0 = 2.800, b_0 = 9.390, \) and \( c_0 = 6.965 \text{ Å} \)).

**Figure 4.** Pressure-volume data for MgGeO₃ post-perovskite phase fitted to the Birch-Murnaghan equation of state.

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**Table 2.** Atomic coordinates and interatomic distances in MgGeO₃ post-perovskite phase at 78 GPa and 300 K

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<tr>
<th>Atomic coordinates</th>
<th>Rietveld analysis</th>
<th>MD model</th>
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<tr>
<td>Mg</td>
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<td></td>
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<tr>
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<td>y</td>
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<td>z</td>
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<td>0.25</td>
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<td>Ge</td>
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<td></td>
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<tr>
<td>x</td>
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<tr>
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<tr>
<td>z</td>
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<td>0.4375</td>
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<tr>
<th>Interatomic distances (Å)</th>
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<tr>
<td>Mg-O₁</td>
<td>1.995 (x2)</td>
<td>1.924 (x2)</td>
</tr>
<tr>
<td>Mg-O₂</td>
<td>2.090 (x4)</td>
<td>2.077 (x4)</td>
</tr>
<tr>
<td>Mg-Ge</td>
<td>2.612</td>
<td>2.612</td>
</tr>
<tr>
<td>Ge-O₁</td>
<td>1.705 (x4)</td>
<td>1.739 (x2)</td>
</tr>
<tr>
<td>O₁-O₂</td>
<td>2.415 (x4)</td>
<td>2.435 (x4)</td>
</tr>
<tr>
<td>O₁-O₁</td>
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<td>2.612</td>
</tr>
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**Table 3.** Lattice parameters and volumes of post-perovskite phase

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
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<td>78.55 (21)</td>
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<td>8.490 (1)</td>
<td>6.456 (1)</td>
<td>143.47 (3)</td>
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<tr>
<td>72.27 (15)</td>
<td>2.628 (0)</td>
<td>8.533 (1)</td>
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<td>55.36 (23)</td>
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<td>8.646 (4)</td>
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<td>150.58 (11)</td>
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<tr>
<td>54.37 (17)</td>
<td>2.663 (2)</td>
<td>8.642 (6)</td>
<td>6.560 (3)</td>
<td>150.95 (18)</td>
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<tr>
<td>41.65 (32)</td>
<td>2.735 (2)</td>
<td>9.022 (6)</td>
<td>6.790 (6)</td>
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<td>6.25 (34)</td>
<td>2.775 (6)</td>
<td>9.261 (14)</td>
<td>6.905 (13)</td>
<td>177.45 (60)</td>
</tr>
</tbody>
</table>

Notes: The MD method and interatomic potential parameters are the same as those described in Murakami et al. (2004).
**DISCUSSION**

These results confirm that a GdFeO₃-type MgGeO₃ perovskite undergoes a pressure-induced phase transition to a CaIrO₃-type post-perovskite structure (space group Cmcm), in the same way as MgSiO₃ perovskite. The transition pressure of 63 GPa at 1800 K in MgGeO₃ is much lower than 125 GPa at 2500 K in Mg-SiO₃, which is consistent with the idea that germanates are the low-pressure analogues of silicates (Ross and Navrotsky 1988; Leinenweber et al. 1994).

Germanium is six-coordinated in both the perovskite and post-perovskite structures. Ono et al. (2003) demonstrated that α-PbO₂-type GeO₂ transforms to a pyrite (modified fluorite)-type phase above 80 GPa at 1500 K, with an increase in the coordination number of germanium from six to eight. Our present study shows that MgGeO₃ post-perovskite is stable to at least 103 GPa at 1500 K, with an increase in the coordination number of silicates (Ross and Navrotsky 1988; Leinenweber et al. 1994).

In the post-perovskite phase, the SiO₆ (or GeO₆)-octahedra share edges to make an octahedral chain like that of rutile-type structures (Murakami et al. 2004). These chains run parallel to a and are interconnected by apical O atoms in the c direction to form edge- and apex-shared octahedral sheets. The octahedral sheets are stacked along b-axis with interlayer Mg²⁺ ions. Murakami et al. (2004) showed on the basis of MD calculations that the b-axis is more compressible than are the a- and c-axes in the MgSiO₃ post-perovskite phase. Our experiments consistently demonstrated a greater compressibility along b in the MgGeO₃ post-perovskite phase, which could be due to the stacked sheet structure along b. The post-perovskite phase has a strong elastic anisotropy.

**ACKNOWLEDGMENTS**

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**REFERENCES CITED**


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