Investigation into high-pressure behavior of MnTiO₃: X-ray diffraction and Raman spectroscopy with diamond anvil cells

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Lithium niobate;
Perovskite;
Phase transition;
Equation of state

Abstract The structural stability of manganese titanate MnTiO₃ at high pressure was investigated by X-ray diffraction and Raman spectroscopy with diamond anvil cells. Ilmenite-type MnTiO₃ is stable at least to 26.6 GPa, and lithium niobate type MnTiO₃ reversibly transforms at room temperature to perovskite at 2.0 GPa. Bulk moduli (K₃₀₀) of ilmenite, lithium niobate and perovskite are 174(4) GPa, 179 (8) GPa, and 208(5) GPa, respectively (at fixed first pressure derivative K' = 4). The Grüneisen parameter γ has been estimated to be 1.28 for ilmenite and 1.75 for perovskite. In ilmenite phase, TiO₆ octahedra become more regular with increasing pressure. In perovskite phase structural distortion increases with pressure increase.

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1. Introduction

Ilmenite (R₃ and Z = 6) and perovskite (Pbnm and Z = 4) structures are common phases for ABO₃-type compounds where such compounds have a relatively larger A-site cation and a small B-site cation. At various temperatures, pressures and compositions, an ilmenite-type ABO₃ compound can transform to perovskite structure. Some high-pressure ABO₃ perovskites are unquenchable on decompression to ambient conditions. For example, perovskite-type CaSiO₃ becomes amorphous at atmospheric pressure (Liu and Ringwood, 1975; Mao et al., 1989); perovskite-type MgSiO₃ is metastable at zero pressure and becomes amorphous on heating as low as 150 °C (Durben and Wolf, 1992); perovskite-type MgGeO₃ and FeTiO₃ transform on decompression to the lithium niobate phase (Ln: R₃c and Z = 6) (Leinenweber et al., 1991, 1994).
Previous investigations have shown that Ln-type ABO$_3$ compounds quenched from perovskite-type phases are metastable (Mehta et al., 1994; Navrotsky, 1998; Ming et al., 2006), which can be used as an important indicator of mineralogical or petrological processes, such as a geo-barometer. Recently, a natural mineral Ln-type FeTiO$_3$ consisting of polysynthetic twin components has been discovered observed by optical microscopy in shocked gneiss from the Ries crater, southern Germany, which indicates that this impact structure suffered at least 20 GPa shock pressure (Dubrovinsky et al., 2009). Therefore, the relationship of ilmenite, Ln and perovskite for ABO$_3$ compounds is of fundamental interest in high-pressure crystal chemistry and of significance in Earth science.

MnTiO$_3$ crystallizes into ilmenite structure at ambient conditions. Forty years ago, a new high-pressure polymorph of MnTiO$_3$ with 1.5% higher density at room temperature was observed in the quenched product from high temperature and high-pressure experiments (Syono et al., 1969). It was determined to be Ln-type phase by single crystal X-ray diffraction (XRD) (Ko and Prewitt, 1988). Prime phase equilibrium and calorimetric studies showed that Ln-type MnTiO$_3$ was a stable phase with its stability field in P–T space (Ko et al., 1989). Subsequently a denser phase of MnTiO$_3$ with perovskite structure was observed by in situ XRD with a diamond anvil cell (DAC) (Ross et al., 1989) at 2–3 GPa and room temperature when Ln-type MnTiO$_3$ was used as the starting material. In addition, this phase transition between Ln and perovskite is reversible. The phase-transition pressure between Ln and perovskite is lower than that of the ilmenite-Ln transition observed in multianvil quenchable experiments. Thus, one concern has been whether Ln-type MnTiO$_3$ is stable or metastable. Now it is generally accepted that the Ln phase is metastable and formed by a diffusionless transition on pressure release (Navrotsky, 1998).

Since the discovery of the MgSiO$_3$ post-perovskite phase with a CaIrO$_3$ structure ($Cmcm$ and $Z = 4$) under conditions approaching those of the lowermost mantle (Murakami et al., 2004; Oganov and Ono, 2004), which can explain some of the observed phenomena in the D$^+$ layer, interest toward this novel phase has grown quickly. By now, perovskite to post-perovskite transformations have been observed experimentally in several ABO$_3$-type compounds and sesquioxides (M$_2$O$_3$, M = metal element) with lower transition pressures, such as MgGeO$_3$ at 60–70 GPa (Hirose et al., 2005), Mn$_2$O$_3$ at 28–30 GPa (Santillán et al., 2006). Some ABO$_3$-type perovskites are predicted by theoretical simulation or semi-empirical methods to be within the post-perovskite phase at high pressure, such as CaTiO$_3$ (Wu et al., 2005) and MnSnO$_3$ (Kojitani et al., 2007). Up to the present, there are no structural data for perovskite-type MnTiO$_3$ above 5 GPa. Also, no available information is reported about the possibility of the phase transition from perovskite to post-perovskite for MnTiO$_3$ compound. Therefore, as reported here, in order to know better the high-pressure behavior of MnTiO$_3$, we carried out an in situ high-pressure experiment up to 26.6 GPa using XRD and Raman spectroscopy.

2. Methods

A polycrystalline sample of MnTiO$_3$ was synthesized using a standard solidstate reaction. Stoichiometric amounts of MnCO$_3$ (99.9%) and TiO$_2$ (99.998%) were mixed and ground under ethanol in an agate mortar. The mixtures were compressed into a pellet with a diameter of 3 mm. The pellet was then heated in an open platinum capsule at 1200 °C for 24 h in CO–CO$_2$ gas mixtures corresponding to oxygen fugacity ($f$O$_2 = 10^{-11}$). The product was drop quenched, and then examined by XRD with a Co target and a JEOL JXA-8200 electron microprobe with an accelerating voltage of 15 kV and a beam current of 15 nA. A chemical composition analysis showed that the product is stoichiometric with a Mn/Ti ratio of one. XRD results confirmed a single-phase (ilmenite-type) product with no impurities. The lattice constants are $a = 5.13936(8)$ Å, $c = 14.2832(2)$ Å and the $c/a$ ratio is 2.78.

The Ln-type MnTiO$_3$ sample was synthesized from the above product (ilmenite-type MnTiO$_3$) at 15 GPa by heating at 1200 °C for 2 h using a Kawai-type high-pressure and high-temperature apparatus (Sumitomo Press 1200 T) at the Bayerisches Geoinstitut (BGI), University of Bayreuth. The starting material was loaded into an MgO capsule (inner diameter 1.2 mm and 2 mm in depth)

![Figure 1 Selected X-ray diffraction patterns of ilmenite-type MnTiO$_3$ at high pressure with the background subtracted. Vertical bars at the bottom represent the positions of diffraction peaks from ilmenite phase at 2.0 GPa. Star symbol represents the diffraction peak from cubic Ne.](image1)

![Figure 2 Selected X-ray diffraction patterns of Ln-type MnTiO$_3$ as the starting material during compression (a–d) and decompression (e–g). Backgrounds were subtracted from the original data. Vertical bars at the bottom represent the positions of diffraction peaks from Ln-type MnTiO$_3$ at ambient condition; vertical bars in the middle show those from the perovskite phase. At 2.0 GPa, some peaks from perovskite appear, such as the upward arrow (b) indicates, at the same time typical double peaks (15°–16° of 2θ) from the Ln phase disappear. Star symbol shows positions of the diffraction peak from cubic Ne.](image2)
that was then inserted into a cylinder made of LaCrO₃ as the heater. ZrO₂ was applied as the thermo-insulator. All parts were assembled in a Cr-doped MgO octahedron of 10-mm edge-length, which then was compressed within tungsten carbide cubes with truncated 5-mm edge-lengths. The recovered sample was also characterized using XRD. The product has a Ln-type structured MnTiO₃ (a = 5.1981(8) Å, c = 13.679(4) Å and the c/a ratio = 2.63).

During the in situ high-pressure experiments, a four-pin modified Merrill-Bassett type DAC was applied; the culets are 400 μm in diameter; 200-μm diameter holes were drilled in the rhenium gasket with an initial thickness of 260 μm, which were pre-indentated to 40–50 μm in thickness. Ne was used as the pressure-transmitting medium. Two small ruby spheres were loaded for pressure calibration, which was determined according to its R₂ fluorescence peak position (Mao et al., 1986). One ruby was at the center and the other was close to the edge of the sample chamber in order to monitor pressure gradients. In this study, the pressure error was small, and did not exceed 0.8 GPa.

In situ XRD measurements up to 26.6 GPa were carried out at BGI using a system consisting of a high-brilliance FRD rotating anode generator and a Bruker APEX charge-coupled device area detector. An accelerating voltage of 55 kV and a beam current of 60 mA were applied. Mo Kα radiation (λ = 0.7108 Å) was focused on the sample in a spot less than ~50 μm in diameter. Collection time for each pattern was 15 min. All collected images were integrated using the Fit2D program in order to obtain conventional one-dimensional diffraction spectra. The XRD patterns were analyzed using the GSAS software (Toby, 2001).

Raman spectra of samples were recorded using a LabRam (Horiba Scientific Inc.) spectrometer in a back-scattering geometry. A 632.8 nm He–Ne laser was used for excitation. The incident laser beam was focused on the sample using a 50× long-distance working objective. Collecting time for each spectrum was 10 min.

### 3. Results

#### 3.1. X-ray powder diffraction

XRD data for ilmenite-type MnTiO₃ as the starting material were recorded at room temperature up to 26.6(8) GPa; several selected patterns are plotted in Fig. 1. Above 10 GPa, the reflection peak from Ne (111) was observed, labeled with a star symbol in Fig. 1b–d. The remaining peaks are from ilmenite and they shift to high angles on compression and to low angles on decompression. No phase transition of ilmenite-type MnTiO₃ occurs in the examined pressure range.

In an experiment using Ln-type MnTiO₃ as the starting sample, XRD data were collected up to 23.9(1) GPa at room temperature. An obvious phase transition was observed from Ln-type phase to high angles on compression and to low angles on decompression. In situ XRD measurements up to 26.6(8) GPa were carried out at BGI using a system consisting of a high-brilliance FRD rotating anode generator and a Bruker APEX charge-coupled device area detector. An accelerating voltage of 55 kV and a beam current of 60 mA were applied. Mo Kα radiation (λ = 0.7108 Å) was focused on the sample in a spot less than ~50 μm in diameter. Collection time for each pattern was 15 min. All collected images were integrated using the Fit2D program in order to obtain conventional one-dimensional diffraction spectra. The XRD patterns were analyzed using the GSAS software (Toby, 2001).

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#### Table 1. Unit-cell parameters and volume of ilmenite-type MnTiO₃ at various pressures. The numbers in parentheses are estimated deviations in the units of the last digit.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>5.1981(8)</td>
<td>13.679(4)</td>
<td>320.1(1)</td>
</tr>
<tr>
<td>2.0(1)</td>
<td>5.185(4)</td>
<td>13.579(12)</td>
<td>316.1(3)</td>
</tr>
<tr>
<td>3.7(1)</td>
<td>5.1792(9)</td>
<td>14.507(3)</td>
<td>313.8(1)</td>
</tr>
<tr>
<td>0.6</td>
<td>5.195(1)</td>
<td>13.644(6)</td>
<td>318.8(1)</td>
</tr>
<tr>
<td>0.0001</td>
<td>5.198(1)</td>
<td>13.666(4)</td>
<td>319.8(1)</td>
</tr>
</tbody>
</table>

 axial ratios of ilmenite and the Ln phase are plotted as a function of pressure in Fig. 3. Here the c/a values of ilmenite are larger than those of the Ln-type phase, consistent with the criterion to distinguish ilmenite and lithium niobate proposed by previous investigations (Ming et al., 2006; Wu et al., 2010). The decrease in c/a ratios with increasing pressure demonstrates the distinctive anisotropy of axial compressibility in both phases, i.e., the c axis is more compressible than the a axis. Perovskite lattice parameters reduced to those of a pseudo-cubic sub-cell show a divergent tendency with increasing pressure (Fig. 4), which indicates that the distortion from ideal cubic perovskite becomes greater.

The isothermal equation of state (EOS) for each polymorph of MnTiO₃ was fitted to the third-order Birch–Murnaghan EOS (Fig. 5). In the fitting process, the pressure derivative Kᵣ was constrained at 4. The parameters of EOS obtained are follows: V₀ = 54.27(1) Å³, K₀ = 176(4) GPa for ilmenite; V₀ = 53.32(2) Å³, K₀ = 179(8) GPa for the Ln phase; and V₀ = 51.22(6) Å³.

#### Table 2. Unit-cell parameters and volume of Ln-type MnTiO₃ at various pressures.

<table>
<thead>
<tr>
<th>P (GPa)</th>
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$K_0 = 208(5)$ GPa for perovskite, where $V_0$ is the volume of per formula unit and $K_0$ is the bulk modulus at ambient pressure. All results agree well with previous results obtained from high-pressure single crystal data (Ross et al., 1989). The bulk modulus of ilmenite MnTiO$_3$ is very close to that of Ln-type and smaller than that of perovskite, the behavior of which is similar to that of FeTiO$_3$ (Wu et al., 2010).

### 3.2. Raman spectroscopy

Group theoretical calculations yield 10 Raman active phonon modes $\Gamma = 5A_g + 5E_g$ (where $E_g = E_{1g} + E_{2g}$) for the ilmenite-type structure (Fateley et al., 1971), 13 Raman modes $\Gamma = 4A_1 + 9E$ for the Ln-type phase (Schaufele and Weber, 1966), and 24 Raman modes $\Gamma = 7A_g + 5E_{1g} + 7B_{2g} + 5B_{3g}$ for orthorhombic perovskite-type structure in the first-order Raman scattering (Qin et al., 2002).

In the present in situ high-pressure Raman experiments, all spectra were recorded after the XRD measurements at the same pressure. In ilmenite-type MnTiO$_3$, ten Raman active bands labeled $v_i$ ($i = 1-10$) were all observed, the frequency shifts of which at ambient conditions are 166, 203, 237, 264, 335, 359, 467, 474, 601, and 685 cm$^{-1}$, respectively, in agreement with previously reported nine peaks (168, 202, 235, 264, 335, 360, 468, 599, and 682 cm$^{-1}$) with just 1–2 wave numbers differences (Ko et al., 1989). Selected Raman spectra at various pressures are plotted in Fig. 6. Each band shifts to a higher frequency with increasing pressure, and to a lower with decreasing pressure, where no peaks merge and no new peaks appear. This result shows that the ilmenite phase is stable at least to 26.6 GPa at room temperature, consistent with the above XRD results.

Thirteen clear Raman bands (180, 196, 236, 280, 303, 337, 381, 452, 480, 565, 736, 774 and 859 cm$^{-1}$) were observed in Ln-type MnTiO$_3$ at ambient conditions (Fig. 7a). However, in a previous report, only ten Raman bands were observed (179, 196, 237, 274, 309, 362, 456, 467, 562 and 774 cm$^{-1}$) (Ko et al., 1989). At 2.0 GPa, the peak around 253 cm$^{-1}$ splits into two and the highest frequency peak (859 cm$^{-1}$) disappears (Fig. 7b), meaning that a phase transition occurs from Ln-type to perovskite. At 3.7 GPa, many new and very clear Raman bands from perovskite appear in the spectrum, as indicated by a star symbol, and at 5.3 GPa all peaks from the Ln-type disappear. Here only 15 clear Raman bands of a total 24 Raman active phonon modes for perovskite were observed, labeled $v_i$ ($i = 1-15$) in Fig. 7d. With increasing pressure, all the bands of perovskite shift toward a higher frequency, and broaden and weaken in intensity, as seen for example in Fig. 7d–e. On decompression to zero pressure, MnTiO$_3$ crystallizes into the Ln-type structure again (Fig. 7g). The pressure range of the two coexisting phases (Ln and perovskite) is 2.0–3.7 GPa, in agreement with the above XRD results and a previous result (Ross et al., 1989).

The evolution of Raman frequency shifts as a function of pressure for the ilmenite and perovskite phases is shown in Fig. 8.
The shifts were fitted linearly using 
\[ \omega = \omega_0 + \alpha P \]
where \( \omega_0 \) is the frequency at 0 GPa, \( \alpha \) is the linear pressure coefficient and \( P \) is the pressure. Thus the Grüneisen parameter (\( \gamma \)) is obtained by

\[ \gamma = \frac{-\partial \ln \omega / \partial \ln V}{B_0 \times \alpha / \omega_0}, \]

where \( B_0 \) is the bulk modulus at zero pressure. All results are summarized in Table 4; the mean \( \gamma \) parameter of ilmenite is 0.96 and that of perovskite is 1.31. Thus, the \( \gamma \) parameter increases by 36% across the ilmenite-to-perovskite transition. In fact, the mean \( \gamma \) parameter obtained by the above method is lower than the true \( \gamma \) of 25% (Hofmeister and Mao, 2002). Therefore, the true \( \gamma \) parameter should be close to 1.28 for ilmenite and 1.75 for perovskite. The relevant information of Ln-type MnTiO\(_3\) was not obtained because of lack of data.

4. Discussion

The ilmenite structure is based on a hexagonal close-packed oxygen lattice with metal atoms occupying two-thirds of the available octahedral sites. Each octahedron shares three edges with octahedra inside the layer, a face with an octahedron of the second type of cation in the adjacent layer, and the opposite face with a vacant octahedral site. Behavior of ilmenite-type crystal structures of MgBO\(_3\) (B=Si, Ge and Ti; Yamanaka et al., 2005) and ATiO\(_3\) (A = Fe, Mn; Wechsler and Prewitt, 1984; Ross et al., 1989; Yamanaka and Komatsu, 2007) has been discussed based on in situ high-pressure single crystal XRD data. One can use refined lattice parameters and atomic positions to obtain accurate bond lengths, bond angles and octahedral volumes at various pressures, to further describe the deformation of the octahedra. For example, in ilmenite-type FeTiO\(_3\), the deformation of FeO\(_6\) and TiO\(_6\) octahedra from the ideal octahedron is gradually decreased at high pressure, i.e., the regularity of the octahedron is enhanced (Yamanaka and Komatsu, 2007). However, the pressure range of single crystal experiments is usually limited by about 10 GPa and structural changes are relatively small. Powder X-ray diffraction experiments can be easily extended to higher pressures, but it is hard to refine and get reliable values of atomic positions, especially using in-house diffractometer. Thus, we cannot satisfactorily describe crystal chemical behavior of ilmenite-structured phase above 10 GPa, and can only make extrapolation from lower-pressure data.

Raman spectroscopy is another useful technique in determining the mechanism of structural change for ilmenite compounds at high pressure.

Figure 4  Pseudo-cubic perovskite sub-cell parameters as a function of pressure. \( a_p = a \sqrt{3} \), \( b_p = b \sqrt{2} \) and \( c_p = c / 2 \) where \( a \), \( b \), \( c \) are the lattice parameters in Table 3. Solid square symbols are the data on compression, and open symbols are those on decompression.

Figure 5  Volume compression of MnTiO\(_3\) phases as a function of pressure. The solid curves are the fit of the experimental data in this work using the third-order Birch–Murnaghan equation of state; single crystal data at high pressure from Ross et al. (1989) are plotted for comparison. Solid square symbols are the data on compression, and open symbols are those on decompression.

Figure 6  Selected Raman spectra of ilmenite-type MnTiO\(_3\) at various pressures. Backgrounds were subtracted from the original data.

Figure 7  Selected Raman spectra of Ln-type MnTiO\(_3\) as the starting material during compression (a–e) and decompression (f–g). Backgrounds were subtracted from the original data. At 3.7 GPa (c), some new peaks from perovskite are denoted by star symbols.
and $E_{g5}$ ($v_2)$ to translations of the Mn$^{2+}$ cation against the oxygen framework (Hofmeister, 1993). In a simple harmonic oscillator model, the vibrational frequency of the stretching band ($v$) equates to $(1/2\pi)\sqrt{\kappa/\mu}$ where $\mu$ is the reduced mass of the two-mass system and $\kappa \propto (e_i e_j r_0^2)^{1/4}$ ($r_0$ is the cation-anion bond length and “$e$” is the electronegativity). The Ti–O bond distance (shared face) in the TiO$_6$ octahedron is longer than that of the unshared face. Thus, $A_g(1)$ ($v_{10}$) is assigned to the shorter Ti–O bond (unshared face) and $E_g(1)$ ($v_9$) is related to the longer Ti–O bond (shared face) according to the above simple harmonic oscillator model. However, $\alpha(v_9)$ is greater than $\alpha(v_{10})$ (Table 4 and Fig. 8a), meaning that the difference between the shorter and longer Ti–O bonds decreases with increasing pressure, i.e., the regularity of the TiO$_6$ octahedron is enhanced. This behavior of MnTiO$_3$ is similar to those of FeTiO$_3$ and MgTiO$_3$, but in contrast to those of MgSiO$_3$ and MgGeO$_3$ (Okada et al., 2008). The most possible reason is that Ti is a 3d transition metal unlike Si and Ge.

For orthorhombic GdFeO$_3$-type structural distortion from ideal cubic perovskite can be described by tilting of the octahedral framework, the tolerance factor, and the ratio of polyhedral volume. In general, if the degree of distortion of GdFeO$_3$-type perovskite enhances with increasing pressure, it tends to transform to post-perovskite at high enough pressure (Wu et al., 2005). One the other hand, GdFeO$_3$-type perovskite could transform to high-symmetry structures like tetragonal and cubic phase if the distortion degree decreases at high pressure (Wu et al., 2006). Here, we did not obtain atomic positions of MnTiO$_3$ perovskite, thus we cannot further calculate the tolerance factor or the ratio of polyhedral volume at various pressures to describe the structural distortion. Recently, the tilting angle $\Phi$, representing rotation of the octahedron about pseudo-cubic axes of [111], has been proposed to predict the high-pressure behavior of perovskite, i.e., those perovskites with $\Phi > 16^\circ$ tend to transform to post-perovskite (Kojitani et al., 2007). Assuming all the octahedra remain regular, the tilt angle $\Phi$ is expressed by $\cos^{-1}(\sqrt{2}a^2/bc)$, where $a$, $b$ and $c$ are lattice parameters of GdFeO$_3$-type perovskite (space group Pbnm) (Zhao et al., 1993). The tilt angle $\Phi$ of perovskite MnTiO$_3$ can be plotted as a function of pressure (Fig. 9). $\Phi$ increases with increasing pressure, which means that structural distortion deviation from ideal cubic perovskite is enhanced, i.e., perovskite MnTiO$_3$ will tend to transform to post-perovskite at

| Table 4 | Results of linear regressions ($\omega$ and $\alpha$) and calculated mode for Gruneisen parameter $\gamma$ using experimental $B_0$ (176 GPa for ilmenite and 208 GPa for perovskite). |
|---------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Ilmenite | $\omega_0$ (cm$^{-1}$) | $\alpha$ (cm$^{-1}$/GPa) | $\gamma$ | Perovskite | $\omega_0$ (cm$^{-1}$) | $\alpha$ (cm$^{-1}$/GPa) | $\gamma$ |
| v$_1$ $A_g(5)$ | 171 | 0.851 | 0.88 | v$_1$ | 147 | 1.175 | 1.66 |
| v$_2$ $A_g(5)$ | 207 | 0.953 | 0.81 | v$_2$ | 166 | 0.814 | 1.02 |
| v$_3$ $E_g(4)$ | 240 | 0.898 | 0.66 | v$_3$ | 171 | 1.671 | 2.03 |
| v$_4$ $A_g(4)$ | 266 | 1.607 | 1.06 | v$_4$ | 196 | 1.077 | 1.14 |
| v$_5$ $A_g(3)$ | 339 | 2.148 | 1.12 | v$_5$ | 201 | 1.778 | 1.84 |
| v$_6$ $E_g(3)$ | 360 | 2.109 | 1.03 | v$_6$ | 256 | 1.562 | 1.27 |
| v$_7$ $A_g(2)$ | 468 | 2.557 | 0.96 | v$_7$ | 308 | 1.607 | 1.09 |
| v$_8$ $E_g(2)$ | 477 | 3.132 | 1.16 | v$_8$ | 361 | 2.818 | 1.62 |
| v$_9$ $A_g(1)$ | 603 | 4.371 | 1.28 | v$_9$ | 419 | 3.116 | 1.55 |
| v$_{10}$ $A_g(1)$ | 689 | 2.665 | 0.68 | v$_{10}$ | 476 | 2.387 | 1.04 |
| v$_{11}$ | | | | v$_{11}$ | 501 | 3.931 | 1.63 |
| v$_{12}$ | | | | v$_{12}$ | 529 | 3.787 | 1.49 |
| v$_{13}$ | | | | v$_{13}$ | 631 | 3.902 | 1.29 |
| v$_{14}$ | | | | v$_{14}$ | 748 | 1.168 | 0.32 |
| v$_{15}$ | | | | v$_{15}$ | 771 | 2.632 | 0.71 |

Figure 8 Variation of Raman frequency as a function of pressure. (A): ilmenite phase; (B): perovskite phase. Solid square symbols are the data on compression, and open symbols are those on decompression. The solid lines are obtained using a linear fit.
higher pressure. This high-pressure behavior is consistent with the semi-empirical prediction (Kojitani et al., 2007). However, recently we have observed in situ the breakdown of FeTiO₃ perovskite into an (Fe₁₋ₓ,Tiₓ)O + Fe₁₋ₓ,TiₓO assemblage rather than the post-perovskite beyond 53 GPa and 2000 K (Wu et al., 2009b). Crystal chemistry properties of both perovskite FeTiO₃ and perovskite MnTiO₃ are very similar, thus it is possible for MnTiO₃ to exhibit the same high-pressure behavior as FeTiO₃. Further exploration of this variation at higher pressure is needed to provide a more realistic answer.

The mechanism of structural change from ilmenite/Ln to perovskite has been discussed previously (Megaw, 1968; Ross et al., 1989; Yusa et al., 2006; Wu et al., 2010). The transformation from Ln to perovskite is much simpler than that from ilmenite to perovskite, because the structural change between Ln and perovskite requires only a small rotation of the TiO₆ octahedron whereas that between ilmenite and perovskite involves the bonds breaking and atomic rearrangement. At room temperature ilmenite FeTiO₃ starts to transform to perovskite at 20 GPa (Wu et al., 2009a) whereas ilmenite MnTiO₃ was found to remain stable up to 26.6 GPa in the present study, which indicates that the binding energy of ilmenite FeTiO₃ is less than that of ilmenite MnTiO₃. At room temperature Ln-type FeTiO₃ transforms to perovskite at 16 GPa (Leinenweber et al., 1991; Mehta et al., 1994; Wu et al., 2010) whereas Ln-type Mn TiO₃ transforms to perovskite at a lower pressure of 2.0 GPa. At a phase-transition pressure of 2 GPa, the calculated tilting angle $\phi$ of Ln-type MnTiO₃ is 20.8° and that of perovskite is 19.8°. In the FeTiO₃ compound, the $\phi$ of Ln-type phase is 21.5° and that of perovskite is 17.1° at a phase-transition pressure of 16 GPa (Leinenweber et al., 1991). The rotation angle (1°) of the TiO₆ octahedron in the Ln-to-perovskite transition of MnTiO₃ is obviously smaller than that of FeTiO₃ (4.4°), which explains well why Ln-type MnTiO₃ has a lower phase-transition pressure.

5. Conclusions

We have carried out in situ high-pressure XRD and Raman spectroscopy experiments on MnTiO₃ up to 26.6(8) GPa at room temperature. Our results show that ilmenite MnTiO₃ is still stable at 26.6 GPa, and lithium niobate MnTiO₃ reversibly transforms to perovskite at 2.0 GPa. The results of compression for the three polymorphs are well presented by the third-order Birch–Murnaghan equation of state with $V₀ = 54.27(1) \text{Å}³$, $K₀ = 176$ (4) GPa for ilmenite; $V₀ = 53.32(2) \text{Å}³$, $K₀ = 179(8)$ GPa for Ln phase; and $V₀ = 51.22(6) \text{Å}³$, $K₀ = 208(5)$ GPa for orthorhombic perovskite. The axial compressibility shows an obvious anisotropy in both ilmenite and lithium niobate phases, i.e., the c axis is more compressible than the a axis. Raman data further demonstrate that the regularity of TiO₆ octahedron is enhanced in the ilmenite phase at high pressure. The unit-cell parameters of perovskite MnTiO₃ and its TiO₆ octahedral tilting angle $\phi$ as a function of pressure show that structural distortion deviation from the ideal cubic perovskite is enhanced, meaning that perovskite MnTiO₃ will tend to transform to the post-perovskite at higher pressure. However, we did not observe any sign of post-perovskite phase of MnTiO₃ in this study.

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