High-pressure phase transition in Mn$_2$O$_3$: Application for the crystal structure and preferred orientation of the CaIrO$_3$ type

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[1] Our X-ray diffraction measurements reveal that Mn$_2$O$_3$ undergoes a phase transition to the CaIrO$_3$ type, which is proposed for the post-perovskite in MgSiO$_3$, at 27–38 GPa and 300 K, bypassing the other phase transitions observed in sesquioxides. Small distortions in the polyhedra after the transition indicate that the Jahn-Teller effect, which is strong at ambient conditions, is suppressed during the transition. The CaIrO$_3$-type phase exhibits strong preferred orientation of the (010) plane perpendicular to the loading axis before annealing whereas preferred orientation of the (100) and (110) planes was observed after annealing. The pre-annealing texture may result from either the deformation under strong differential stresses or the phase transition. The post-annealing texture may be related to either lower differential stresses or thermal annealing. Our result shows that the texture of the CaIrO$_3$ type can be sensitive to phase transition and annealing as well as differential stresses.


1. Introduction

[2] Phase transitions in sesquioxide minerals (e.g., corundum, hematite, and escolite) have long been the subject of interest due to the relevance of their high-pressure (P) structures to mantle minerals [e.g., Reid and Ringwood, 1969]. From experiments [e.g., Funamori and Jeanloz, 1997; Shim et al., 2004b; Ono et al., 2004; Lin et al., 2004] and first-principles calculations [e.g., Thomson et al., 1996], a general sequence of phase transitions has been established for sesquioxides at high P: corundum-type → Rh$_2$O$_3$-II or perovskite-type. A sequence of phase transition for MgSiO$_3$ with pressure is: pyroxene → ilmenite or garnet (depending on temperature) → perovskite. It is notable that the ilmenite type has essentially a cation-ordered corundum structure. More recent works have shown that hematite and corundum further transform to the CaIrO$_3$-type (Cmcm) phases at 60 and 160 GPa at high temperatures, respectively [Ono and Ohishi, 2005; Oganov and Ono, 2005]. This is geophysically important because MgSiO$_3$ perovskite, the dominant lower-mantle mineral, also transforms to a CaIrO$_3$-type phase at 120 GPa [Murakami et al., 2004].

[3] Bixbyite, (Mn$_{1-x}$Fe$_x$)$_2$O$_3$, is unique among sesquioxide minerals in that it has the C-type rare earth structure instead of the corundum-type structure at ambient conditions [Geller, 1971]. In Mn endmember (α-Mn$_2$O$_3$), Mn$^{3+}$ exists in five different crystallographic sites, each surrounded by a highly distorted octahedron of O atoms. This distortion, known as the Jahn-Teller (JT) distortion, is due to the loss of degeneracy in the 3d-orbitals when Mn$^{3+}$ is coordinated by six O atoms. It has been predicted that suppression of the JT effect with compression would make bixbyite transform to a corundum-type phase [Prewitt et al., 1969] and then follow the sequence of high-P transitions observed in other sesquioxide minerals. Prewitt et al. [1969] found that Mn$_2$O$_3$ transitions to a distorted C-type structure at 1573 K and 6.5 GPa. Syono et al. [1985] reported a phase transition at 29 GPa. Yamanaka et al. [2005] confirmed the transition and tentatively assigned a monoclinic unit cell to the high-P phase. However, the crystal structure of the high-P phase is not known.

[4] Here we report that Mn$_2$O$_3$ transforms directly to the CaIrO$_3$ type. We focus on distortions in the crystal structure, phase transition, and lattice preferred orientation of the CaIrO$_3$-type phase, which provides insights on properties of the post-perovskite phase in MgSiO$_3$.

2. Experimental Techniques

[5] Pure synthetic Mn$_2$O$_3$ powder was placed in a hole of a pre-indented Re gasket with ruby grains near the edge of the hole to serve as a pressure calibrant [Mao et al., 1986]. Diamond-anvil cells (DACs) were prepared with 500-μm culet anvils. The piston diamond was epoxied onto a cubic BN seat to allow for diffraction measurement up to 23° 20. Argon was loaded as a pressure medium.

[6] X-ray diffraction patterns were collected up to 40.4 GPa at the OSECARS sector of the Advanced Photon Source. At 40.4 GPa, in order to anneal differential stresses, the edge of the sample was laser heated to less than 1000 K. We did not scan laser beams at the center of the sample where post-annealing diffraction patterns were obtained. Thus, the temperature of the X-rayed area should not exceed a few hundred kelvins during annealing. Diffraction images were collected using an imaging plate. Images were processed using the FIT2D application [Hammersley, 1997]. The sample-to-detector distance and tilt of the imaging plate were corrected by measuring the diffraction patterns of CeO$_2$. We corrected for the attenuation of diffracted X-ray beams through a cBN seat. Cell parameters were refined using the UNITCELL program [Holland and
Redfern, 1997]. Rietveld refinements of diffraction patterns were carried out using the GSAS package [Larson and Von Dreele, 1988]. A spherical harmonics function [Bunge, 1983] for the cylindrical sample symmetry was used for fitting the preferred orientation effect.

3. Results

Mn$_2$O$_3$ diffraction lines broaden with an increase of pressure even with the soft Ar pressure medium, while the Ar peaks remain sharp (Figures 1a and 1b). At 27.7 GPa, several new peaks appear (Figure 1c). However, the 211 peak, diagnostic of the low-$P$ phase, remains to 38.0 GPa, at which the phase transition completes (Figure 1d). This is consistent with Yamanaka et al. [2005].

At 40.4 GPa, we laser annealed the sample resulting in a pronounced sharpening of all the peaks, but not in the appearance of additional new peaks (Figure 2). This suggests that no phase separation or temperature-induced phase transition occurs during annealing. In addition, the diffraction rings in the 2D image remain continuous and do not become spotty, indicating little or no crystal growth is induced during the annealing. The pressure slightly drops after annealing (0.2 GPa). At least 25 peaks are clearly resolved after annealing (Figure 2) and they are indexed well with an orthorhombic unit cell. Yamanaka et al. [2005] tentatively assigned a monoclinic unit cell for the high-$P$ phase. No angles deviate significantly from 90° in our monoclinic unit-cell fitting. In Yamanaka et al. [2005]’s study, diffraction lines are significantly broader and only 11 diffraction lines were used for unit-cell determination. The observed diffraction pattern of the high-$P$ phase agrees well with that of the CaIrO$_3$ type (Figure 2), which has been proposed for the crystal structure of the post-perovskite phase in MgSiO$_3$ [Murakami et al., 2004]. We perform Rietveld refinements on diffraction patterns by taking the CaIrO$_3$ type as a starting model (Figure 2). We observe a pronounced preferred orientation effect in the pre-annealing patterns that becomes smaller in the post-annealing patterns. The background-subtracted residual value ranges from 0.055 to 0.085. Upon decompression, the diffraction patterns indicate that a mixed phase region exists between 30 and 4.5 GPa. All the diffraction lines observed for the recovered sample can be explained by $\alpha$-Mn$_2$O$_3$, indicating that the high-$P$ phase is not quenchable.

The volume of Mn$_2$O$_3$ at high $P$. The circle and square symbols represent low-$P$ and CaIrO$_3$-type phases, respectively. Solid and open symbols represent data points from compression and decompression, respectively. The error bars are 1σ estimated uncertainties. The compressional curve reported by Yamanaka et al. [2005] is shown in a dashed line. The solid lines to guide the eye. The insets show the crystal structures of $\alpha$-Mn$_2$O$_3$ (a) and the CaIrO$_3$ type (b).

**Figure 1.** X-ray diffraction patterns of Mn$_2$O$_3$ at high $P$. The indexed lines in (a) and (d) are for the major diffraction lines of $\alpha$-Mn$_2$O$_3$ and CaIrO$_3$-type phases, respectively. The arrows in (c) indicate new diffraction lines observed during the phase transition. The asterisk in (f) indicates a spotty ring from a heating product.

**Figure 2.** Rietveld refinement result of the diffraction pattern measured after annealing at 40.4 GPa ($R_{wp} = 0.085$). The circles are the observed intensities and the line behind the circles is the calculated diffraction pattern. Differences between observed and calculated intensities are shown below the pattern. The bars represent peak positions for the CaIrO$_3$-type phase (top) and argon (bottom). Due to severe overlap of diffraction lines between Ar and Mn$_2$O$_3$, we do not include the data points at 11.6–12.0°2θ in the refinement.

**Figure 3.** Volume of Mn$_2$O$_3$ at high $P$. The circle and square symbols represent low-$P$ and CaIrO$_3$-type phases, respectively. Solid and open symbols represent data points from compression and decompression, respectively. The error bars are 1σ estimated uncertainties. The compressional curve reported by Yamanaka et al. [2005] is shown in a dashed line. The solid lines to guide the eye. The insets show the crystal structures of $\alpha$-Mn$_2$O$_3$ (a) and the CaIrO$_3$ type (b).
whereas Yamanaka et al. [2005] used a methanol-ethanol mixture which becomes non-hydrostatic above 10–15 GPa. The volume decreases by 8% across the phase transition between 25.1 GPa and 27.9 GPa.

4. Discussion

[10] The stability of the C-type structure in bixbyte at ambient conditions has been attributed to strong distortions in the MnO₂ octahedra resulting from the Jahn-Teller (JT) effect [Geller, 1971]. Therefore, if the JT effect is suppressed by compression, bixbyte would follow a sequence of the phase transitions found in other sesquioxide minerals without the JT distortion. Escolite [Shim et al., 2004b], hematite [Ono et al., 2004], and corundum [Lin et al., 2004] undergo a phase transition from the corundum-type to an orthorhombic (either Rh₂O₃-II or perovskite-type) phase at 30, 35, and 90 GPa, respectively. It has recently been reported that hematite and corundum further transform to the CaIrO₃ type at 60 GPa and 160 GPa, respectively [Ono and Ohishi, 2005; Oganov and Ono, 2005], which is proposed for the crystal structure of the post-perovskite phase in MgSiO₃.

[11] However, we find that Mn₂O₃ bypasses the phase transitions to the corundum- and perovskite- or Rh₂O₃-II-type phases. Instead, it directly transforms to the CaIrO₃ type, which appears after the perovskite type in MgSiO₃ [Murakami et al., 2004; Shim et al., 2004a; Oganov and Ono, 2004] and after an orthorhombic phase in Fe₂O₃ [Ono and Ohishi, 2005]. Another interesting observation is that the transition occurs without heating. So far, the phase transitions to the CaIrO₃ type have been observed after heating to at least 2000 K, such as MgSiO₃ [Murakami et al., 2004; Oganov and Ono, 2004; Shim et al., 2004b], Al₂O₃ [Oganov and Ono, 2005], and Fe₂O₃ [Ono and Ohishi, 2005]. This indicates a large kinetic energy barrier for the phase transition to the CaIrO₃ type except for Mn₂O₃.

[12] The crystal structure data for CaIrO₃-type Mn₂O₃ obtained from Rietveld refinements allow us to infer the existence of the JT effect through the distortions of the polyhedra. We calculate the quadratic elongation [Robinson et al., 1971] as shown in Table 1: the more the deviation of the quadratic elongation from 1, the larger the distortion. Compared to the octahedra in α-Mn₂O₃, the distortion of the octahedron in the CaIrO₃-type phase is negligible. Although the quadratic elongation of the MnO₈ bicapped trigonal prism deviates significantly from 1, this is mainly because of the difference in shape between a bicapped trigonal prism and an ideal 8-fold geometry, i.e., cubic. The degree of distortion in the bicapped trigonal prism in Mn₂O₃ is similar to those in other CaIrO₃-type materials without the JT distortion (Table 1).

[13] It is possible that the JT effect may be suppressed gradually with compression. However, a single crystal X-ray diffraction study for bixbyte with 40% Fe up to 9 GPa has shown no clear change in the quadratic elongation with P within the uncertainty [Yamanaka et al., 2005]. An alternative possibility is suppression of the JT distortion during the phase transition to the CaIrO₃ type. Although the JT effect is strong for octahedrally coordinated Mn³⁺ in the high-spin configuration, it should not exist in the low-spin configuration [Burns, 1993]. Thus, the observed absence of the JT distortion in the octahedra after the phase transition may result from a change in the spin configuration. Indeed, Fe⁴⁺ in hematite undergoes a change to a low-spin state at 60 GPa [Badro et al., 2002]. Furthermore, the bicapped trigonal prism configuration is not an efficient way to accommodate the JT effect compared with the octahedral coordination [Burns, 1993]. The charge disproportionation of 2Mn³⁺ to Mn³⁺ and Mn⁴⁺ can also result in the suppression of the JT effect. Because Mn⁴⁺ is smaller and Mn³⁺ receives zero crystal field splitting energy in octahedral coordination, Mn⁴⁺ would enter into the octahedral site. However, Mn⁴⁺ (3d⁵) in the octahedral site would not show any JT distortion, because no electrons enter in e_g orbitals [Burns, 1993]. However, the possible association of the phase transition to the CaIrO₃ type in Mn₂O₃ with either change in the spin configuration or the charge disproportionation remains to be examined using a more direct probe.

[14] Although the JT distortion is apparently suppressed, Mn₂O₃ does not follow the sequence of the phase transitions found in other sesquioxide minerals without the JT distortions. We recognize some similarities between the C-type and CaIrO₃-type structures (insets in Figure 3). Bixbyte is made up of alternating layers of the less distorted (Mn₁, Mn₂, and Mn₅) and the more distorted (Mn₃ and Mn₄) octahedra (Table 1). Although Mn⁵ has lower site symmetry, it shows slightly lower distortion than the other two lower symmetry octahedra (Mn₃ and Mn₄). On the other hand, the crystal structure of the CaIrO₃ type consists of alternating layers of the octahedra and the bicapped trigonal prisms. Thus, perhaps the most energetically favorable way is to reorganize the intra-layer structure while largely maintaining the 2D nature of the crystal structure during the phase transition. This may explain such a low kinetic barrier for the transition to the CaIrO₃ type in Mn₂O₃.

[15] Before annealing, the intensities of the 110 and 131 peaks for the CaIrO₃ type are larger and smaller than those expected for randomly oriented crystals, respectively. However, after annealing, the 110 peak intensity becomes smaller than expected, while the 131 peak intensity becomes comparable to an expected value. In Rietveld analysis, we refine the preferred orientation (Figure 4). The CaIrO₃ type shows strong preferred orientation of the (010) plane perpendicular to the loading axis of the DAC (or the plane normal aligning along the loading axis). However, after annealing, we found that 010 becomes
The pre-annealing texture observed for CaO-type MnO3 is consistent with the former proposal. This texture may be induced by deformation under higher differential stresses. However, it is also possible that the texture is related to the phase transition: if displacement along the (010) plane occurs during the phase transition as inferred from the structural similarities between low- and high-P phases, the grains may be aligned along the (010) plane during the phase transition. Our post-annealing texture is consistent with more recent proposals [Oganov et al., 2005; Merkel et al., 2006]. This may represent the texture developed under lower differential stress conditions. However, we do not rule out a possibility that this texture results from the thermal annealing process [Green, 1967], although the temperature of the X-rayed area should not exceed a few hundred kelvins and our diffraction patterns indicate no significant recrystallization during annealing. We note that one of the recent proposals is based on measurements for MgGeO3 post-perovskite after heating to 1600 K [Merkel et al., 2006]. Our observation demonstrates that the texture of the CaIrO3 type can be affected by phase transition and heating as well as differential stresses.

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References


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