High-temperature structural evolution of hexagonal multiferroic YMnO₃ and YbMnO₃

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Neutron powder diffraction studies on the structural evolution of hexagonal multiferroic YMnO₃ and YbMnO₃ from 1000 K to 1400 K, and from 1000 K to 1350 K, respectively, are presented. The temperature evolution of diffraction patterns suggests that YMnO₃ undergoes a phase transition to a non-polar structure above 1200 K, while YbMnO₃ remains ferroelectric up to 1350 K. Detailed structural parameters were obtained as a function of temperature from Rietveld refinements. Based on this result, the distinct differences in temperature behaviour between YMnO₃ and YbMnO₃, and the origin of the ferroelectricity in these hexagonal multiferroics are discussed.

1. Introduction

Multiferroic rare earth manganites have attracted resurging interest since the recent observation of the coexistence of ferromagnetism and ferroelectricity as well as the giant coupling between them (Kimura et al., 2003; Hur et al., 2004). From a technological point of view, this magnetoelectric effect (Fiebig, 2005; Prellier et al., 2005; Spaldin & Fiebig, 2005; Eerenstein et al., 2006; Cheong & Mostovoy, 2007; Ramesh & Spaldin, 2007) allows mutual control of a material’s electric and magnetic properties, opening new possibilities in device design.

Several mechanisms for the ferroelectricity have been proposed for different kinds of multiferroic materials. In orthorhombic TbMnO₃, the ferroelectric state appears below the Neel temperature, with strong dependence on the applied magnetic field. Thus, it has been suggested that an ordering of magnetic structure induces a structural modulation which results in electric polarization (Kimura et al., 2003; Katsura et al., 2005). In addition, a new mechanism has been proposed in which the coexistence of site-centered and bond-centered charge order can break inversion symmetry in doped manganites, Rₓ―₀.₅CaₓMnO₃ (R = La, Pr) (Efremov et al., 2004).

The ferroelectric mechanism in hexagonal RMnO₃ (R = Ho–Lu, or Y and Sc), however, is rather controversial. According to van Aken et al. (2004), the electric polarization in YMnO₃ originates from a geometric effect of a tilting of MnO₅ bipyramids and a buckling of rare earth ions (Fig. 1), rather than the usual changes in chemical bonding due to the off-centerings of ions at ferroelectric phase transitions in perovskite oxides. This new mechanism, however, is contrary to the earlier conclusion that the ferroelectric polarization arises from an off-center distortion of the Mn ion in hexagonal LuMnO₃ (Yakel et al., 1963). Furthermore, recent synchrotron X-ray powder diffraction studies on hexagonal RMnO₃ (R = Sc, Lu, Y) at 300 and 1000 K suggest both temperature and ionic size dependence of Mn off-centering (Katsufuji et al., 2002). Thus, it is still questionable whether the geometric effect is the origin of the electric polarization or whether the off-centering of Mn ions also contributes to the polarization.

In addition, a transition from a low-temperature ferroelectric to a high-temperature non-polar phase in hexagonal RMnO₃ is still a matter of debate. Based on the measurement of pyroelectric current, Ismailzade & Kizhaev (1965) proposed

![Figure 1](image-url)
that an intermediate phase exists between the high- and low-temperature phases. A couple of recent diffraction studies combined with group theoretical calculations also suggest the existence of this intermediate phase, but disagree on the nature of the phase (Lonkai et al., 2004; Nenert et al., 2005). In contrast, earlier synchrotron X-ray diffraction studies up to 1000 K (Katsufuji et al., 2002) as well as first-principles density-functional calculations (Fennie & Rabe, 2005) found no evidence for the intermediate phase.

To address the issues related to the origin of the ferroelectricity and structural phase transition in hexagonal RMnO₃, we studied the high-temperature structural evolution of YMnO₃ (1000 < T < 1400 K) and YbMnO₃ (1000 < T < 1350 K). Since neutron diffraction has much larger scattering contrast between manganese (b = 3.37 fm) and oxygen (b = 5.8 fm) ions than the case of X-ray diffraction, we expect to determine the positions of oxygen and manganese ions more reliably. Therefore, our results will help to elucidate the off-centering of the Mn ion with temperature as well as the high-temperature structural phase transition in hexagonal rare earth manganites.

2. Experiments

Polycrystalline YMnO₃ and YbMnO₃ were prepared through conventional solid-state reaction in air. Stoichiometric quantities of Y₂O₃(Yb₂O₃) and MnO₂ were heated at 1573 K for two days with intermediate grindings. High-temperature time-of-flight neutron powder diffraction measurements were performed on the NPDF instrument at Lujan Neutron Scattering Center, Los Alamos National Laboratory. YMnO₃ and YbMnO₃ were loaded into a vanadium sample can under He environment. Powder diffraction patterns of each sample were collected as a function of temperature using a vanadium furnace from 1000 to 1400 K for YMnO₃ and from 1000 to 1350 K for YbMnO₃. For YMnO₃ we observed small extra peaks due to slight sample decomposition (not shown here) when the temperature increases above 1200 K. The temperature dependence of the structural parameters was obtained through Rietveld refinements using the EXPGUI (Toby, 2001) and GSAS (Larson & Von Dreele, 1986) programs.

3. Results and discussion

Fig. 2(a) shows the temperature evolution of a part of the YMnO₃ diffraction pattern from 1000 to 1400 K. The arrow indicates that the intensity of the Bragg peak decreases as the temperature increases up to 1200 K and disappears at and above 1250 K. This Bragg peak appears due to a trimer distortion and the disappearance of the Bragg peak signals a phase transition to high-temperature P6₃/mmc space group (Lukaszewicz & Karut-Kalicinska, 1974). In contrast, YbMnO₃, which is isostructural with YMnO₃, shows rather different temperature dependence. As shown in Fig. 2(b), the Bragg peak with the arrow on it persists up to 1350 K. This result suggests that the ferroelectric phase in YbMnO₃ is stable up to 1350 K. We expect that this distinct temperature evolution between YbMnO₃ and YMnO₃ is related to the difference in the ionic size between rare earth Yb (0.985 Å) and Y (1.019 Å) ions, as we discuss later.

We performed Rietveld refinements on both YMnO₃ and YbMnO₃. For YMnO₃, the ferroelectric P6₃cm space group was used for the refinements up to 1200 K. Above 1200 K, the

Figure 2

(a) Temperature evolution of a part of the YMnO₃ diffraction patterns, with increasing temperature from 1000 to 1400 K (top to bottom). The arrow indicates a Bragg peak due to a trimer distortion (Katsufuji et al., 2002). The intensity of the Bragg peak decreases with increasing temperature and disappears at 1250 K, indicating a phase transition. (b) For YbMnO₃, the Bragg peak does not disappear up to T = 1350 K. Only the position of the Bragg peak shifts toward high d spacing. For clarity, the diffraction patterns are shifted vertically from one another.

Figure 3

(a) Neutron powder diffraction pattern of YMnO₃ (open circles) at (a) 1000 K and (b) 1400 K with the corresponding Rietveld refinements (solid lines) using ferroelectric P6₃cm and P6₃/mmc space groups, respectively. Tick marks indicate the positions of the Bragg reflections. Difference curves are also shown. Each inset shows a part of the diffraction pattern for 1.875 < d < 2.024 Å.
Atomic positions of ions are \(R1\) at \((0, 0, z)\), \(R2\) at \((1/3, 2/3, z)\), \(\text{Mn at } (x, 0, 0)\), \(O1\) and \(O2\) at \((x, 0, z)\), \(O3\) at \((0, 0, z)\), and \(O4\) at \((1/3, 2/3, z)\).

<table>
<thead>
<tr>
<th>Atomic positions</th>
<th>Mn—O4</th>
<th>Mn—O3</th>
<th>Mn—O2</th>
<th>Mn—O1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>2.032 (6)</td>
<td>2.067 (6)</td>
<td>2.022 (2)</td>
<td>2.021 (5)</td>
</tr>
<tr>
<td>(R2)</td>
<td>0.238 (5)</td>
<td>0.238 (5)</td>
<td>0.238 (3)</td>
<td>0.239 (5)</td>
</tr>
<tr>
<td>(\text{Mn at } (x, 0, 0))</td>
<td>0.3516 (9)</td>
<td>0.3525 (9)</td>
<td>0.3576 (7)</td>
<td>0.3584 (8)</td>
</tr>
<tr>
<td>(O1)</td>
<td>0.3127 (7)</td>
<td>0.3164 (8)</td>
<td>0.3196 (8)</td>
<td>0.3232 (9)</td>
</tr>
<tr>
<td>(O2)</td>
<td>0.1647 (6)</td>
<td>0.1651 (6)</td>
<td>0.1653 (4)</td>
<td>0.1654 (7)</td>
</tr>
<tr>
<td>(O3)</td>
<td>0.3367 (6)</td>
<td>0.3370 (6)</td>
<td>0.3373 (4)</td>
<td>0.3378 (7)</td>
</tr>
<tr>
<td>(O4)</td>
<td>0.4974 (8)</td>
<td>0.5015 (8)</td>
<td>0.5038 (8)</td>
<td>0.5071 (9)</td>
</tr>
</tbody>
</table>

Bond lengths (Å):

- \(O4\) to \(O3\): 3.194 (5) to 3.163 (5) to 3.279 (4) to 3.263 (6)
- \(O3\) to \(O2\): 2.4971 (5) to 2.488 (5) to 2.495 (5) to 2.515 (5)
- \(O2\) to \(O1\): 2.291 (3) to 2.284 (3) to 2.288 (3) to 2.280 (4)
- \(O1\) to \(O4\): 0.0197 (5) to 0.0196 (6) to 0.0191 (4) to 0.0180 (7)

Reactivity factors (%):

- \(R_{wp}\): 2.60 to 2.63
- \(R_g\): 2.02 to 2.05

In Fig. 4, we compare the temperature evolution of the \(a\)-axis (in-plane) and \(c\)-axis (out-of-plane) lattice parameters for \(\text{YMnO}_3\) and \(\text{YbMnO}_3\). For \(\text{YMnO}_3\), the open square symbols denote that the diffraction patterns were refined using the centrosymmetric \(P6_3/mmc\) space group. In this case, \(3/2\) to 2.05

Figure 4: Temperature evolution of lattice parameters of \(\text{YMnO}_3\) (squares) and \(\text{YbMnO}_3\) (triangles). For \(\text{YMnO}_3\), the open square symbols denote that the diffraction patterns were refined using the centrosymmetric \(P6_3/mmc\) space group. In this case, \(3/2\) to 2.05

Table 1: Atomic parameters and selected bond lengths for \(\text{YMnO}_3\) and \(\text{YbMnO}_3\) in the ferroelectric phase, \(P6_3/mmc\).

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMnO(_3)</td>
<td>6.22215 (8)</td>
<td>11.3707 (2)</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>YbMnO(_3)</td>
<td>6.23609 (9)</td>
<td>11.3641 (2)</td>
<td>90°</td>
<td>90°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic displacement parameters (Å(^2))</th>
<th>(R1)</th>
<th>(R2)</th>
<th>(\text{Mn at } (x, 0, 0))</th>
<th>(O1)</th>
<th>(O2)</th>
<th>(O3)</th>
<th>(O4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0107 (0)</td>
<td>0.0223 (6)</td>
<td>0.0147 (7)</td>
<td>0.0227 (8)</td>
<td>0.0207 (6)</td>
<td>0.0380 (26)</td>
<td>0.0186 (7)</td>
</tr>
<tr>
<td></td>
<td>0.0190 (8)</td>
<td>0.0244 (7)</td>
<td>0.0156 (7)</td>
<td>0.0251 (9)</td>
<td>0.0234 (7)</td>
<td>0.0365 (24)</td>
<td>0.0226 (8)</td>
</tr>
<tr>
<td></td>
<td>0.0206 (7)</td>
<td>0.0251 (5)</td>
<td>0.0157 (6)</td>
<td>0.0259 (7)</td>
<td>0.0256 (6)</td>
<td>0.0355 (24)</td>
<td>0.0247 (7)</td>
</tr>
</tbody>
</table>

The space group. In this case, 31 is plotted for the a-axis lattice parameter.

\(P6_3/mmc\) space group was used. For \(\text{YbMnO}_3\), all patterns were refined using the ferroelectric \(P6_3/cm\) space group. Fig. 3 shows neutron powder diffraction patterns of \(\text{YMnO}_3\) at 1000 and 1400 K, with the corresponding Rietveld refinements. High quality of the fittings suggests that \(\text{YMnO}_3\) maintains the ferroelectric phase at 1000 K and the non-polar phase at 1400 K. Table 1 summarizes the atomic parameters and selected bond lengths for \(\text{YMnO}_3\) and \(\text{YbMnO}_3\) as a function of temperature.

For \(\text{YbMnO}_3\), all patterns were refined using the ferroelectric \(P6_3/cm\) space group. In this case, 31 is plotted for the a-axis lattice parameter.
temperatures also resulted in similar temperature behavior. For YbMnO₃, the c-axis lattice parameter monotonically increases with increasing temperature. Similarly, Katsufuji et al. observed that the c-axis lattice parameter of RMnO₃ (R = Sc, Lu, Y) exhibits an upward slope, is almost flat, and exhibits a downward slope with increasing temperature from 300 to 1000 K as the rare earth (R) ionic size increases from 0.87 Å (Sc), to 0.976 Å (Lu), and to 1.019 Å (Y), respectively. This size dependence of the evolution of the c-axis lattice parameter is closely related to the R-ionic-size-dependent tilting of MnO₅ bipyramids. According to Katsufuji et al. (2002), the tilting of the MnO₅ bipyramids pushes R ions vertically up (R1) and down (R2), thus causing buckling of the R plane, which expands the lattice along the c axis. Therefore, if the magnitude of the R-plane buckling decreases with increasing temperature, the temperature dependence of the c-axis parameter can exhibit upward, flat and downward slopes depending on the rate of the buckling decrease.

Fig. 5(a) shows the temperature dependence of the R-plane buckling. With increasing temperature, the buckling of the Y plane decreases much faster than that of the Yb plane. As we discussed above, this difference in the buckling behavior due to the size difference is responsible for the distinct temperature evolution of the c-axis lattice parameter for YMnO₃ and YbMnO₃. Figs. 5(b) and 5(c) show the tilting behavior of in-plane O atoms (O3—O4) and apical O atoms (O1—O2) for YMnO₃ and YbMnO₃. The in-plane tilting angle (Opl) is measured between the O3—O4 bond and the ab plane, and the apical tilting angle (Oap) is measured between the O1—O2 bond and the c axis. Similar to the buckling behavior, the magnitude of the tilting decreases much faster in YMnO₃ than in YbMnO₃. The dashed lines are fits to the Opl and Oap tilting angles of YMnO₃ using a power-law function $y = y_0|t - t_0|^p$. From the fitting, we could estimate that the tilting will disappear around $T = 1250$ K, consistent with the temperature evolution of the powder diffraction pattern for YMnO₃.

Using the atomic positions of ions in Table 1, we determined Mn—O and R—O bond lengths (refer to Fig. 1) as a function of temperature. Fig. 6 shows Mn—O1, Mn—O2 and R1—O3 short and long bonds. The Mn—O1 and Mn—O2 bond lengths exhibit little temperature dependence and the difference between two bonds is about 0.04 Å and 0.03 Å for YMnO₃ and YbMnO₃, respectively. These values are much smaller than the differences of 0.15 Å (YMnO₃), 0.20 Å (LuMnO₃) and 0.08 Å (ScMnO₃) reported from synchrotron X-ray powder diffraction studies at 1000 K by Katsufuji et al. (2002). For R1—O3 short and long bonds of YMnO₃, the difference is about 0.57 Å at 1000 K and decreases to 0.24 Å at 1200 K. Similar behavior was observed for YbMnO₃, where the difference decreases from 0.61 to 0.39 Å as the temperature decreases from 1000 to 1350 K. Overall, the off-centering of the R ion along the c axis is much larger than that of the Mn ion. We roughly estimated the respective polarization due to the off-centering of the Mn ion and the displacement of Y ions at 1000 K. For the calculation we used the Born effective charges of Y (+3.6) and Mn (+3.3) ions reported by van Aken et al. (2004), and displacements of Y1 (−0.286 Å), Y2 (0.408 Å) and Mn (0.087 Å) along the c axis relative to the O₅ pyramid calculated using the atomic coordinates reported in Table 1. Simple calculation using these numbers gave a polarization of about 9.2 μC cm⁻². This value agrees reasonably with the reported value of 5.5 μC cm⁻² (Fujimura et al., 1996). The estimated polarization due to the Y and Mn off-centering is about 87% and 13%, respectively. These

![Figure 5](image1)

**Figure 5**

(a) The magnitude of the buckling, $R1z - R2z$, of rare earth ions in YMnO₃ and YbMnO₃. (b) Tilting in-plane oxygen, O3—O4. The tilting angle is between the O3—O4 bond and the ab plane. (c) Tilting of apical oxygen, O1—O2. The tilting angle is between the O1—O2 bond and the c axis. The dashed lines are fits using a power-law function $y = y_0|t - t_0|^p$.

![Figure 6](image2)

**Figure 6**

Temperature dependence of Mn—O1, Mn—O2, Mn—O3, Mn—O4 and R1—O3 long and short bonds in YMnO₃ and YbMnO₃.
results suggest that the ferroelectricity in (Y,Yb)MnO₃ mainly arises from the displacement of the rare earth ions with a minor contribution from the off-centering of the Mn ion. Finally, we would like to note that Figs. 5 and 6 show that tilting of the bipyramid, which appears below \( T \lesssim 1250 \) K, accompanies the off-centering of rare earth ions as well as the Mn ion. Therefore, our results do not agree with the claim that the ferroelectric distortion occurs in two steps, where MnO₅ bipyramids tilt first and then a ferroelectric distortion follows at about a few hundred degrees below (Lonkai et al., 2004; Nenert et al., 2005).

4. Summary
In summary, we have studied the high-temperature crystal structure of hexagonal multiferroic YMnO₃ and YbMnO₃ above 1000 K up to 1400 K. We found that YMnO₃ undergoes a phase transition to a centrosymmetric \( P\bar{6}_3/mmc \) structure above 1200 K, while YbMnO₃ retains a ferroelectric \( P\bar{6}_3cm \) structure up to 1350 K. This difference is due to the different \( R \)-size dependencies of the MnO₅ tilting behavior between two materials. In addition, we found no evidence for the presence of the intermediate phase between the high-temperature non-polar and the low-temperature ferroelectric phases. Finally, we showed that the displacement of rare earth ions is much larger than the off-centering of the Mn ion at all temperatures, supporting the idea that ferroelectricity in hexagonal (Y, Yb)MnO₃ mainly arises from the buckling of the rare earth ions caused by the tilting of MnO bipyramids.

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