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Ferroelectricity in single crystal InMnO₃

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Single crystal synthesis, structure, electric polarization, and heat capacity measurements on hexagonal InMnO₃ show that this small R ion in the RMnO₃ series is ferroelectric (space group P6₃cm). Structural analysis of this system reveals a high degree of order within the MnO₅ polyhedra but significant distortions in the R-O bond distributions compared to the previously studied materials. Point-charge estimates of the electric polarization yield an electrical polarization of ~7.8 μC/cm², 26% larger than the well-studied YMnO₃ system. This system with enhanced room temperature polarization values may serve as a possible replacement for YMnO₃ in device applications. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803171]

The hexagonal manganites are part of a class of materials which exhibit coupled ferromagnetism and ferroelectricity (multiferroic systems).¹ Hexagonal phase RMnO₃ is found for small radius ions (R = Ho, Er, Tm, Yb, Lu, and also Y and Sc, see Refs. 2–4). From an application’s perspective, these materials have attracted much attention as data storage media in nonvolatile random access memory.⁵ These devices have the advantage of low power consumption and decreased memory cell size over existing technology because the electric charge induced by the remnant polarization controls the conductivity of the Si substrate where they are deposited. Low dielectric constant materials such as the hexagonal RMnO₃ systems (YMnO₃, ε = 20) do not suffer from the problem of high electrical noise due to SiO₂ at the interface. The YMnO₃ system has been studied extensively and is currently being utilized in device applications.⁶

Tuning this RMnO₃ system by replacing the R ion with other species or multiple species serves as a possible path to enhance the ferroelectric properties of these materials. One system which is being studied is the R = In system. However, the room temperature structure and ferroelectric properties of InMnO₃ are still not well understood. InMnO₃ x-ray single crystal structural refinement by Giaquinta et al.³ yielded a non-polar space group of P6₃/mmc for samples prepared by the flux method similar to earlier work on single crystals. The group also reported neutron diffraction measurements for polycrystalline samples prepared by a nitrate decomposition technique and found a space group P6₃cm. Fabrèges et al.⁸ reported the space group P6₃cm based on neutron powder diffraction measurements on polycrystalline samples prepared by high pressure solid state synthesis. Kumagai et al.⁹ prepared polycrystalline samples of InMnO₃ and examined them by synchrotron x-ray powder diffraction methods. A significant impurity phase of In₂O₃ was observed. Equally good fits to the experimental powder diffraction patterns (very close Rwp values) for both the polar P6₃cm and non-polar P-3c structure were found. Combined refinements of x-ray powder diffraction data, piezoresponses, and density functional theory calculations of the electric polarization reveal an upper limit of 7.8 μC/cm² on the electrical polarization, which is 26% larger than that for YMnO₃.

InMnO₃ single crystals were grown by the flux method starting from In₂O₃ (99.99%, Stanford Materials) and MnO₂ (99.999%, Alfa Aesar) in a 1:2 molar ratio, with 1 part (molar) Bi₂O₃ added relative to In₂O₃. After the oxides were ground together and pelletized, the pellets were calcined at 830°C, single crystal samples were grown and the structure as well as the thermal and electronic properties was studied. Previous electrical measurements were conducted on polycrystalline and single crystal samples, and density functional theory calculations of the electric polarization reveal an upper limit of 7.8 μC/cm² on the electrical polarization, which is 26% larger than that for YMnO₃.

To fully understand the properties of the InMnO₃ system, single crystal samples were grown and the structure of the InMnO₃ single crystal for XRD measurements (b), and the crystal structure for InMnO₃ (c) are shown.

FIG. 1. Images of a typical synthesized crystal (a), a mounted InMnO₃ single crystal for XRD measurements (b), and the crystal structure for InMnO₃ (c) are shown.

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950 °C for 3 days in air in a platinum crucible and quenched to ambient temperature by taking the crucible out of the furnace at 950 °C. Black hexagonal plates [Fig. 1(a)] were visible on the surface of the pellet. The flux matrix was mechanically weakened and dissolved with concentrated nitric acid by soaking for 2 weeks and cleaned in an ultrasonicator with acetone.\(^{(7b)}\) The cleaned single crystals were examined by energy dispersive x-ray (EDX) and x-ray absorption fine-structure (XAFS) spectroscopy and surface traces of Bi were found but verified as amorphous by x-ray absorption spectroscopy. Single crystal x-ray diffraction measurements were conducted utilizing a Bruker APEX II diffractometer with 4 K CCD detector and Cu K\(\alpha\) radiation (see details below). A single crystal of dimensions \(\sim 0.214 \times 0.263 \times 0.025 \text{ mm}^3\) was used [Fig. 1(b)].

Polycrystalline samples of hexagonal RMnO\(_3\) (R = Sc, Y, and Lu) were prepared by the solid state reaction method. InMnO\(_3\) powder was obtained by grinding single crystals. X-ray absorption samples were prepared by brushing powder (500 mesh) onto Kapton tape and spectra were collected at beamline X19A, the National Synchrotron Light Source. A Mn foil reference was employed for energy calibration. The reduction of the XAFS data was performed using standard procedures.\(^{(12)}\)

To estimate the electrical polarization, the reference structure at high temperature was determined by full structural optimization with DFT in the projector augment wave approach\(^{(13)}\) holding the Mn and In ions at high symmetry positions (Mn at (1/3,0,0), In1 at (0,0,1/4), and In2 at (1/3,2/3,1/4)) following the methods used in Ref. 14.

Electrical polarization loops of an InMnO\(_3\) single crystal (thickness \(\sim 25 \mu\text{m}\), sample area \(0.26 \times 0.54 \text{ mm}^2\), and small electrode area \(\sim 8991 \mu\text{m}^2\)) were obtained using a Radiant Technology Multiferroic instrument with the remanent hysteresis method at room temperature. Silver paste was used to connect to the electrodes on both sides. We achieved similar results from other samples in the thickness range of 15 \(\mu\text{m}\) to 30 \(\mu\text{m}\) for frequencies of 500–2000 Hz. Heat capacity measurements of an InMnO\(_3\) single crystal from 300 K to 2 K were carried out with a Physical Property Measurement System (PPMS, Quantum Design).

Fig. 2(a) shows the near edge x-ray absorption spectra of a series of hexagonal RMnO\(_3\) systems (R = Sc, Y, and Lu) compared to InMnO\(_3\). Note the similarity in shape of all of the spectra indicating equivalent local structure and local symmetry. Compared to the other samples, no additional peaks appear in the R = In spectrum. However, the InMnO\(_3\) spectrum has lower amplitude and is broadened. This indicates a lower level of long-range order. Note the shift in the position of the main peak of the ScMnO\(_3\) to higher energy compared to the other samples. This shift shows that the Mn–O bond distance is shorter in this system than the others according to the “Natoli’s Rule,” \((E_p - E_0)R^2 = \text{const.}\), where \(E_p - E_0\) is the energy of the peak measured from \(E_0\), and \(R\) is the bond distance.\(^{(15)}\)

The Fourier transform of the full XAFS data is shown in Fig. 2(b). Note that the peak for Mn–O bond is the largest for ScMnO\(_3\) and InMnO\(_3\) indicating high structural order within the MnO\(_3\) polyhedra. The second peak (R \(\sim 3 \text{ Å}\)) corresponds to Mn–R and Mn–Mn (first neighbor) and depends on the R ions’ scattering power. The distant peak (R \(\sim 6.5 \text{ Å}\)) is dominated by Mn–Mn correlations and is significantly suppressed in the case InMnO\(_3\), indicating weak higher order Mn–Mn correlation. More structural details can be gained from the analysis of the single crystal x-ray diffraction data.

Single crystal structure solution was conducted using SHELXL\(^{(16)}\) after the data were corrected for absorption by face indexing.\(^{(17)}\) Refinements with respect to P-3c, P\(_{3}\)c1, and P\(_{6}\)cm space groups were conducted. Use of the non-polar space group P-3c yielded \(R_1 = 6.12\%\) and \(wR_2 = 15.6\%\) with ratio of number of \(F_0 > 4\sigma(F_0)\) values to free parameters of 199/21 = 9.5 while the polar space group P\(_{3}\)c1 yielded \(R_1 = 4.81\%\) and \(wR_2 = 12.8\%\) and ratio of number of \(F_0 > 4\sigma(F_0)\) values to free parameters of 371/40 = 9.3. Analysis of the coordinates revealed that this space group solution (P\(_{3}\)c1) corresponded to the higher space group P\(_{6}\)cm (Ref. 18). Refinement of the diffraction data in the polar space group P\(_{6}\)cm yielded \(R_1 = 5.07\%\) and \(wR_2 = 12.6\%\) with ratio of number of \(F_0 > 4\sigma(F_0)\) values to free parameters of 230/29 = 7.9. For this latter structure, racemic twinning was modeled by SHELXL yielding weights of 0.44 and 0.56 for the twin components (structure and its inverse). This is close to the 50% value expected for ferroelectric samples. Use of Cu \(K_\alpha\) radiation produced non-negligible anomalous scattering factors\(^{(19)}\) from the In (\(f' = 0.0822, f'' = 5.0449\)) and Mn (\(f' = -0.5299, f'' = 2.8052\)) ions making the Friedel pairs distinct thus stabilizing the refinement with respect to the twin structure. A Bayesian statistical analysis\(^{(20)}\) of the Friedel (Bijvoet) reflection pairs revealed a 99.9% probability of the 1:1 racemic twin model being correct and
negligible probability for either component of the pair being the correct solution. We note that racemic twinning was also found in the YMnO$_3$ and YbMnO$_3$ ferroelectric systems with P6$_3$cm space group.\textsuperscript{21} The existence of this twinning is expected for a ferroelectric system with no bulk polarization (not poled).

Details for the structural solution are given in Table I, and the bonding compared to the systems with R = Y, Sc, and Lu\textsuperscript{22} are given in Table II. Compared to ScMnO$_3$ ([Mn-O] = 1.932(3) Å), YMnO$_3$ ([Mn-O] = 1.984(14) Å), and LuMnO$_3$ ([Mn-O] = 1.966(8) Å), the coordination of Mn by O revealed by the bond distance is closest to ScMnO$_3$, consistent with the XAFS results. In addition, the distribution of Mn-O bonds ($\varepsilon$$_{Mn-O}$, Table II) is significantly more narrow (more ordered) for InMnO$_3$ than any of these other systems. We also note that the first neighbor Mn-Mn distribution ($\varepsilon$$_{Mn-Mn}$, Table II) is the smallest for InMnO$_3$. On the other hand, the distribution of R-O is much larger for R = In than for the other systems. Since the coordination of the R site which primarily drives the electrical polarization, it suggests a much higher polarization for InMnO$_3$. The structural data reveal that the system is polar with the same space group P6$_3$cm of R = Sc, Y, and Lu systems. To further confirm the assignment, electrical polarization measurements were conducted.

Polarization hysteresis loops were calculated by integrating the total transferred charge during application of a bipolar triangular voltage waveform, then dividing the remanent charge by the projected area as done in Ref. 23. We examined a large range of electric fields from 64 kV/cm to 216 kV/cm and displaying the P-E loops, which give a remanent polarization (Pr) of ~4.4 $\mu$C/cm$^2$ for the saturated loop at room temperature shown in Fig. 3. The remanent polarization exhibits negligible frequency dependence in the range 500 Hz to 2000 Hz. The polarization was estimated by the point-charge model with the experimental structure derived above and using DFT to estimate the reference paraelectric structure. The polarization amplitude of 7.8 $\mu$C/cm$^2$ on InMnO$_3$ single crystal was obtained indicating a theoretical upper limit ~26% larger than that for YMnO$_3$ (near 6.2 $\mu$C/cm$^2$).\textsuperscript{24} Our measurement gave a value of ~4.4 $\mu$C/cm$^2$ for the remanent TABLE II. Selected bond distances (Å).\textsuperscript{5}

<table>
<thead>
<tr>
<th>Bond type</th>
<th>InMnO$_3$</th>
<th>YMnO$_3$</th>
<th>ScMnO$_3$</th>
<th>LuMnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-O1</td>
<td>1.904(50)</td>
<td>1.850(15)</td>
<td>1.884(7)</td>
<td>1.882(7)</td>
</tr>
<tr>
<td>Mn-O2</td>
<td>1.907(40)</td>
<td>1.875(15)</td>
<td>1.876(7)</td>
<td>1.859(7)</td>
</tr>
<tr>
<td>Mn-O3</td>
<td>1.969(5)</td>
<td>1.996(11)</td>
<td>1.968(5)</td>
<td>2.050(5)</td>
</tr>
<tr>
<td>Mn-O4 x 2</td>
<td>1.982(10)</td>
<td>2.097(6)</td>
<td>1.967(5)</td>
<td>2.019(7)</td>
</tr>
<tr>
<td>(Mn-O)</td>
<td>1.949(2)</td>
<td>1.984(14)</td>
<td>1.932(3)</td>
<td>1.966(8)</td>
</tr>
<tr>
<td>$\varepsilon$$_{Mn-O}^{\text{max}}$</td>
<td>3.568</td>
<td>10.476</td>
<td>4.286</td>
<td>7.897</td>
</tr>
<tr>
<td>Mn-R1</td>
<td>3.265(17)</td>
<td>3.293(14)</td>
<td>3.174(8)</td>
<td>3.264(3)</td>
</tr>
<tr>
<td>Mn-R2 x 4</td>
<td>3.398(12)</td>
<td>3.622(14)</td>
<td>3.377(11)</td>
<td>3.475(11)</td>
</tr>
<tr>
<td>Mn-R2 x 2</td>
<td>3.407(2)</td>
<td>3.420(14)</td>
<td>3.350(11)</td>
<td>3.509(7)</td>
</tr>
<tr>
<td>Mn-R2 x 2</td>
<td>3.418(17)</td>
<td>3.345(10)</td>
<td>3.232(6)</td>
<td>3.305(4)</td>
</tr>
<tr>
<td>Mn-R1</td>
<td>3.701(18)</td>
<td>3.647(15)</td>
<td>3.627(8)</td>
<td>3.721(3)</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>3.401</td>
<td>3.555</td>
<td>3.368</td>
<td>3.486</td>
</tr>
<tr>
<td>$\varepsilon$$_{Mn-Mn}^{\text{max}}$</td>
<td>0.424</td>
<td>9.522</td>
<td>1.273</td>
<td>1.603</td>
</tr>
<tr>
<td>R1-O1 x 3</td>
<td>2.254(26)</td>
<td>2.264(13)</td>
<td>2.126(6)</td>
<td>2.234(11)</td>
</tr>
<tr>
<td>R1-O2 x 3</td>
<td>2.261(13)</td>
<td>2.353(9)</td>
<td>2.232(3)</td>
<td>2.294(14)</td>
</tr>
<tr>
<td>R1-O3</td>
<td>2.52(10)</td>
<td>2.344(25)</td>
<td>2.157(12)</td>
<td>2.244(14)</td>
</tr>
<tr>
<td>R1-O2</td>
<td>2.295</td>
<td>2.314</td>
<td>2.172</td>
<td>2.261</td>
</tr>
<tr>
<td>$\varepsilon$$_{R-O}^{\text{max}}$</td>
<td>9.191</td>
<td>4.303</td>
<td>4.532</td>
<td>2.864</td>
</tr>
<tr>
<td>R2-O1 x 3</td>
<td>2.192(20)</td>
<td>2.260(7)</td>
<td>2.160(3)</td>
<td>2.227(12)</td>
</tr>
<tr>
<td>R2-O2 x 3</td>
<td>2.153(19)</td>
<td>2.323(11)</td>
<td>2.182(5)</td>
<td>2.277(11)</td>
</tr>
<tr>
<td>R2-O4</td>
<td>2.512(69)</td>
<td>2.459(13)</td>
<td>2.312(10)</td>
<td>2.401(10)</td>
</tr>
<tr>
<td>(R-O)</td>
<td>2.220</td>
<td>2.315</td>
<td>2.191</td>
<td>2.273</td>
</tr>
<tr>
<td>$\varepsilon$$_{R-O}^{\text{max}}$</td>
<td>12.065</td>
<td>6.547</td>
<td>5.038</td>
<td>5.705</td>
</tr>
</tbody>
</table>

\textsuperscript{5} Hexagonal YMnO$_3$ and ScMnO$_3$ generated from the data in Ref. 22 (a) and LuMnO$_3$ data obtained from Ref. 22 (b). The distortion parameters $\varepsilon$$_{Mn-O}$, $\varepsilon$$_{Mn-Mn}$ and $\varepsilon$$_{R-O}$ are defined as $\varepsilon$ = [(1/N)$\Sigma$(R - $\bar{R}$)$^2$]$^{1/2}$.

TABLE I. Structural parameters from single crystal refinement.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>In1</td>
<td>0</td>
<td>0</td>
<td>0.2623(4)</td>
</tr>
<tr>
<td>In2</td>
<td>1/3</td>
<td>2/3</td>
<td>0.2328</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3339(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>0.3206(12)</td>
<td>0</td>
<td>0.1545(41)</td>
</tr>
<tr>
<td>O2</td>
<td>0.6355(19)</td>
<td>0</td>
<td>0.3244(33)</td>
</tr>
<tr>
<td>O3</td>
<td>0</td>
<td>0</td>
<td>0.0182(87)</td>
</tr>
<tr>
<td>O4</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0135(62)</td>
</tr>
</tbody>
</table>

Uij (In1) 0.0180(16) 0.0180(16) 0.0096(28) 0.0000 0.0090(8) Uij (In2) 0.0165(11) 0.0165(11) 0.0140(22) 0.0000 0.0082(5) Uij(Mn) 0.0183(13) 0.0156(15) 0.0049(13) 0.0001(5) 0.0078(7) Uiso(O1) 0.0206(51) Uiso(O2) 0.030(5) 0.041(8) 0.000(5) 0.000(2) 0.021(4) Uiso(O3) 0.013(13) Uiso(O4) 0.013(11) 0.013(11) 0.024(25) 0.0000 0.006(5)

Space group: P6$_3$cm

\textsuperscript{4} Atomic displacement parameters Uij are in the order: U$_{11}$, U$_{22}$, U$_{33}$, U$_{13}$, U$_{12}$, (U$_{33}$ = 0 for all atoms by symmetry). For O1 and O3, only U$_{iso}$ values obtained.

![FIG. 3. Remanent P-E hysteresis loops of an InMnO$_3$ single crystal measured at 1 kHz at room temperature.](https://example.com/fig3)
polarization at room temperature. The smaller value is possibly due to defect/voids formed during the quenching procedure. Alternative methods could be developed to prepare defect-free crystals or films for applications. We note that defects result in a range of values of the remanent polarization in YMnO$_3$ single crystals $\sim 4.5$ to $5.5$ $\mu$C/cm$^2$.

Finally, for comparison with other systems in terms of electronic, magnetic, and atomic properties of as prepared samples, the heat capacity of InMnO$_3$ single crystals is shown in Fig. 4(a) with the Néel temperature near 118 K identical with the result of Belik et al.$^{11}$ on powder samples. We have also found a peak near 42 K consistent with the spin rotation on Mn seen in HoMnO$_3$ (see Ref. 26). However, we did not find a magnetic transition near 41 K. However, we did not find evidence for this in synchrotron base powder diffraction measurements on the samples. No un-indexed peaks were observed. A magnetic transition near 40 K in InMnO$_3$ was observed by Greedan et al.$^{76}$

Low temperature fitting of heat capacity gave $\gamma = 2.87 \pm 0.09$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 0.06 \pm 0.01$ mJ mol$^{-1}$ K$^{-2}$, and $\beta_T = 0.0014 \pm 0.0002$ mJ mol$^{-1}$ K$^{-6}$ with fit by $C_p/T = \gamma + \beta T^2 + \beta_T T^4$ in Fig. 4(b). The terms correspond to electronic phonon, and magnetic/anharmonic contributions to the heat capacity, respectively.$^{29}$ We note that neglecting the third term produced only small changes in the Sommerfeld coefficient $\gamma$ given by $\pi^2 k_B^2 N(E_F)/3$, where $N(E_F)$ is the density of states at the Fermi level.$^{28}$ Values of $\gamma = 1.6$ or $3.6$ mJ mol$^{-1}$ K$^{-2}$ (two samples) for YMnO$_3$ single crystals$^{29}$ and $\gamma = 1.0$ mJ mol$^{-1}$ K$^{-2}$ for LuMnO$_3$ single crystals$^{5}$ have been reported. The similar value of $\gamma$ (associated with the number free carriers) for InMnO$_3$ to the other well studied systems, suggests that the main determinant in the polarization is the R-O distribution.

Single crystal synthesis, heat capacity, structure, and electric polarization measurements of hexagonal InMnO$_3$ reveal that this small R ion material has space group $P6_3cm$ and is ferroelectric. Point-charge estimates of electric polarization based on the single crystal derived structure predict an electrical polarization of $7.8 \mu$C/cm$^2$, 26% larger than the standard RMnO$_3$ systems. This system with enhanced room temperature polarization values may serve as possible replacement for YMnO$_3$ in device applications and, due to its interesting magnetic ordering, it may serve as a test-bed for theoretical studies of magnetic ordering.

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18Space groups were tested by PLATON, a set of tools developed by the National Single Crystal Service Facility in the Netherlands.