Structural view of hexagonal non-perovskite AMnO$_3$

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We refined the crystal structure of AMnO$_3$, with A = Y, Er, Yb and Lu by single crystal x-ray diffraction. Our results show some distinct differences with previous reports on LuMnO$_3$ and YbMnO$_3$. We show that the ferroelectric behaviour is originated in the dipole moment at the A-site, and not, as is the common opinion, at the Mn site.

I. INTRODUCTION

In the search for new composition-properties relations ABO$_3$ compounds have attracted a lot of attention because this structure forms the basis for interesting physical properties such as high $T_c$ superconductivity \cite{2} and colossal magnetoresistance \cite{3}. Non-perovskite AMnO$_3$, with A = Y, Ho,...,Lu, attracted interest, due to their ferroelectric properties \cite{4}. These hexagonal AMnO$_3$ have a basically different structure than most ABO$_3$ compounds, that are distorted perovskites. These properties arise due to the strong correlation of the 3$d$ electrons with the O 2$p$ orbitals. We will show in this paper that the ferroelectricity is mostly due to the anomalous oxygen surrounding of the lanthanide position. Note that some perovskite ABO$_3$ compounds, like Sr-doped LaMnO$_3$ and LaCoO$_3$, can have a rhombohedral-hexagonal structure. However, the hexagonal ABO$_3$ we report here, have a profoundly different structure than the perovskite based ABO$_3$ compounds.

This structure, including atomic positions, reported in literature before. Yakel \cite{5} initiated research. Isobe et al. reported the str YbMnO$_3$ \cite{6}. Muñoz et al. used neutron powder to study YMnO$_3$ and ScMnO$_3$ \cite{7}. Lukaszewicz reported the high temperature P63/mmc \cite{8}. Remarkably the structural transition is some 300 K higher than the ferroelectric order temperature. Note that we use O$_{X,\text{ap}}$ and O$_{X,\text{eq}}$ to denote apical and equatorial positions, respectively, with X = A or Mn. We observe crystal structure at ambient temperature different aspects from the previous reports, where electric dipole moments were ascribed to the Mn environment. We show that it is caused by the coordination of the Y ion.

II. CRYSTAL STRUCTURE

To give an introduction to the hexagonal structure, we first take a look at the centrosymmetric structure. The Mn ions are surrounded by a trigonal bipyramid of oxygen ions. The bipyramids are linked by corner sharing the equatorial oxygens. Between these slabs of bipyramids...
III. ELECTRONIC STRUCTURE

We have calculated the crystal field splitting of a trigonal bipyramidal field. The Mn $3d$ levels are split according to their magnetic quantum number. This yields the $xz, yz$ doublet with the lowest energy, followed by the $xy, x^2-y^2$ doublet. The $z^2$ orbital has the highest energy. For YMnO$_3$, with Mn$^{3+}$ $3d^4$, the $z^2$ orbital is unoccupied. In Fig. 3, the $z^2$ orbitals are shown for two layers.

IV. HT VS. LT

All hexagonal AMnO$_3$ are reported to be ferroelectric with transition temperatures between 800 and 1000 K. For YMnO$_3$, the temperature dependence of the structure is studied by observing the temperature dependence of the integrated intensity of some reflections. The study showed that above the transition temperature a structural transition to higher symmetry is observed. The increase in symmetry yields a smaller unit cell volume, from $Z=6$ to $Z=2$. The main difference in atomic positions between the high and low temperature structure is that in the HT phase all atoms are constrained to planes, parallel with the $ab$ plane. Below the transition temperature the structure loses the mirror planes parallel to the $ab$ plane and all inequivalent atoms get a refinable $z$ position. The deviations from these planes are sketched in Fig. 4.

The deviations yield different bond lengths for A-O$_{A, ap}$. One bond adopts a regular value $\sim 2.4 \text{ Å}$ while the other becomes about 1 Å larger. The asymmetric $A$ environment is the main reason for the ferroelectric behaviour. As we have two inequivalent lanthanide positions in $P6_3cm$, we have two inequivalent, although similar, dipole moments as a result of the movement of the O$_{A, ap}$ ions. This movement can also be expressed as a tilting of the MnO$_5$ bipyramids. Two out of three O$_{Mn, eq}$ positions in the triangular base of the bipyramid are constraint by symmetry, note O$_{A, ap}=O_{Mn, eq}$. The two equivalent O ions move down, the other moves up. This yields, for the two layers in the unit cell, four upwards pointing local dipole moments, whereas the other two point downwards.
V. DATA

Single crystals of AMnO$_3$, A=Y, Yb, Er and Lu, were obtained using a flux method by weighing appropriate amounts of A$_2$O$_3$ and MnO$_2$ with Bi$_2$O$_3$ in a 1:12 ratio. The powders were thoroughly mixed and heated for 48 h at 1523 K in a Pt crucible. The separation of the crystals from the flux has been done by increasing the temperature to 1723 K and evaporating the Bi$_2$O$_3$ flux.

We have studied the crystal structure by single crystal x-ray diffraction. Details of the measurement and the refinement are published elsewhere, cf. YMnO$_3$ [10], ErMnO$_3$ [11], YbMnO$_3$ and YMnO$_3$ [12]. The general atomic coordinates are given in table I. The exact data in table II. In table III the lattice parameters of the studied compounds are shown.

**TABLE I.** General atomic positions of the ambient temperature phase of hexagonal AMnO$_3$. $\delta$ indicates a shift of the order of 0.02 lattice parameter.

| atom | x | y | z |
|------|---|---|---|
| A(1) | 0 | 0 | $\frac{1}{3}$ $\delta$ |
| A(2) | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{1}{3}$ $\delta$ |
| Mn   | $\sim$ $\frac{1}{3}$ | 0 | $\sim$ 0 |
| O1   | $\frac{1}{3}$ $\delta$ | 0 | $\sim$ $\frac{1}{3}$ |
| O2   | $\frac{1}{3}$ $\delta$ | 0 | $\sim$ $\frac{1}{3}$ |
| O3   | 0 | 0 | $-\delta$ |
| O4   | $\frac{1}{3}$ $\delta$ |

**TABLE II.** Values for the refinable position in AMnO$_3$. The z-coordinate of Mn is fixed at zero.

| atom | Y | Er | Yb | Lu |
|------|---|----|----|----|
| A(1)-z | 0.2743 | 0.2746 | 0.2753 | 0.2746 |
| A(2)-z | 0.2335 | 0.2320 | 0.2326 | 0.2311 |
| Mn-x   | 0.3352 | 0.3396 | 0.3333 | 0.3355 |
| O1-x   | 0.3083 | 0.3113 | 0.3030 | 0.3070 |
| O1-z   | 0.1627 | 0.1645 | 0.1636 | 0.1650 |
| O2-x   | 0.3587 | 0.3593 | 0.3610 | 0.3614 |
| O2-z   | -0.1628 | -0.1620 | -0.1639 | -0.1630 |
| O3-x   | -0.0218 | -0.0225 | -0.0249 | -0.0277 |
| O4-z   | 0.0186 | 0.0186 | 0.0211 | 0.0198 |

**TABLE III.** Lattice parameters and unit cell volume for AMnO$_3$.

|       | Y   | Er   | Yb   | Lu   |
|-------|-----|------|------|------|
| a (Å) | 6.1387 | 6.1121 | 6.0584 | 6.0380 |
| c (Å) | 11.4071 | 11.4200 | 11.3561 | 11.3610 |
| $V_{mol}$ (Å$^3$) | 372.27 | 369.47 | 360.97 | 358.70 |

VI. DETAILED STRUCTURE ANALYSIS

In section [I] we regarded the structure as layers of corner linked MnO$_5$ trigonal bipyramids, with the A ions between the layers. In section [IV] the ferroelectric properties were explained using AO$_7$ polyhedra. In this section, the link between the two approaches will be made. The two polyhedra are shown in Fig. [I].

![Fig. 5. Sketch view of the local environment, showing AO$_7$, left side, and MnO$_5$, right side. The arrow indicates the distance between two oxygen planes. The dashed line indicates the Mn-O$_{Mn,ap}$ distance. Atoms marked with "*" and with "@" are identical, the double line indicates the shared edge.](image)

The high temperature phase of the hexagonal AMnO$_3$ consists of 8-fold coordinated A ions in bicapped antiprisms. The stacking of the AO$_6$ antiprism is identical to that of three cubic close packed [111] layers, ABC. The 'bicapping' O$_{A,ap}$ are again located on a B layer, both above C and below A. In Fig. [2] the ABC stacking can be seen by going from the O$_{Mn,ap}$ of the bottom layer, via the A ion, to the O$_{Mn,ap}$ of the top layer. Note that the in-plane bond lengths between the O ions and between the A ions is too large to speak of a true close packed system. In this notation one A ion environment makes up a BABCB stack, or in chemical elements: OOAO. The top O$_{A,ap}$ and the bottom O$_{A,ap}$ of the next layer are one and the same. Therefore, each B is also the end-member of the next stack, but with the opposite order i.e. BCBA, in elements: OOCBBA. This yields BCBCABBCBABCBA, in elements:OOAOOOAOOOAOOOAOOO. Conventionally, the holes between two close packed layers are tetrahedral sites, cf. the spinel structure. In our loosely packed layers, two tetrahedra from adjacent layers join to form a trigonal bipyramidal site. In AMnO$_3$ this occurs in the "OOO" stack. Half of the bipyramidal holes are occupied by Mn. In Fig. [5] two neighbouring polyhedra are sketched, where the shared edge is shown. The O$_{Mn,ap}$ ions are identical with the oxygens that
make up the antiprisms. The Mn-O$_{\text{Mn,ap}}$ distance is thus equal to the distance between the antiprism oxygen layer and the O$_{A,ap}$ layer. The Mn-O$_{\text{Mn,ap}}$ distance is minimal. Therefore, the steric hindrance of the Mn restricts this layer separation and increases the A-O$_{ap}$ bond length. Thus, the eightfold co-ordination is not uniform. The two A-O$_{A,ap}$ have slightly larger bond lengths, i.e. $\sim 2.7\text{Å}$.

We conclude that hexagonal AMnO$_3$ consists of MnO$_5$ trigonal bipyramids, stacked in layers, alternated with layers of A ions. This yields a capped trigonal antiprism as coordination polyhedra for the A ion. In the ferroelectric phase, the capping is effectively single. This asymmetric coordination of the A ion yields the ferroelectric properties.

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