

Hexagonal YMnO<sub>3</sub>

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The crystal structure of hexagonal yttrium trioxomanganate has been determined at room temperature and at 180 K. It is isomorphous with LuMnO<sub>3</sub>. The Mn displacement vector has a frustrated component in the *ab* plane and a ferroelectric part along the *c* axis. The net ferroelectricity is zero due to inversion twinning, with 1:1 twin fractions.

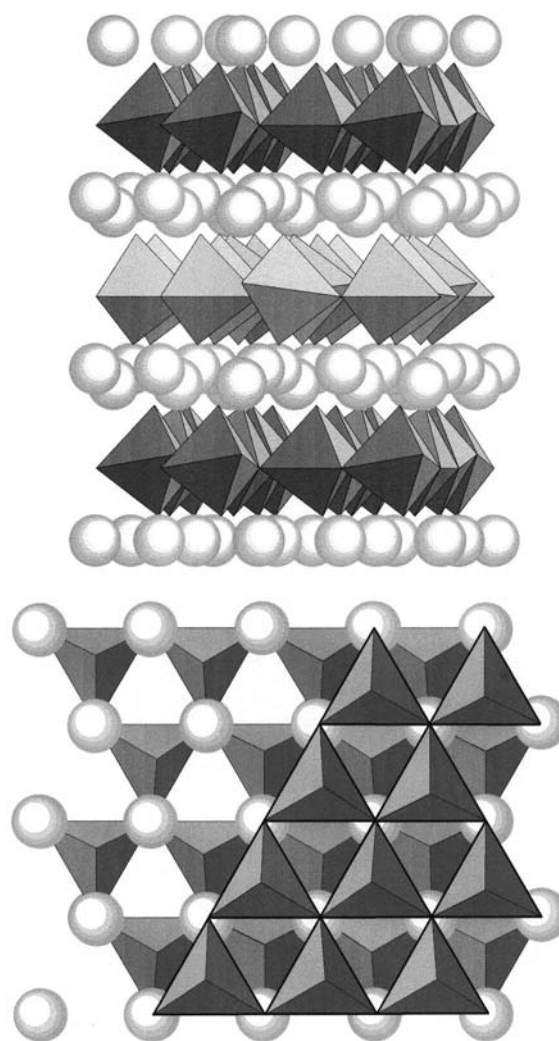
## Comment

The compounds LnMnO<sub>3</sub>, where Ln is a lanthanide, have attracted much interest in two different fields of materials science. The large ionic radius lanthanides, La and Ce–Dy, crystallize in a distorted orthorhombic perovskite structure (Yakel, 1955). These compounds have recently received enormous interest because of the colossal magnetoresistance effect, *i.e.* a metal–insulator transition that changes the conductivity by many orders of magnitude at the Curie temperature (Ramirez, 1997). The Mn atom is octahedrally coordinated by O atoms. The octahedra form a corner-shared three-dimensional network. The small ionic radius lanthanides, Ho–Lu, crystallize in a hexagonal structure (Yakel *et al.*, 1963). Here, the Mn ions are coordinated by a trigonal bipyramid of O atoms, forming a pseudo-layered structure by corner sharing of the trigonal basal plane O atoms. These compounds are of interest because of the combination of ferroelectric and magnetic ordering (Smolenskii & Bokov, 1964). The intermediate ionic radius of Y allows both crystal structures; under ambient conditions, the hexagonal structure is obtained. However, the orthorhombic structure can be stabilized by either low-temperature (Brinks *et al.*, 1997) or high-pressure synthesis (Waintal & Chevanas, 1967), or epitaxial thin film growth (Salvador *et al.*, 1998).

The magnetic properties of hexagonal YMnO<sub>3</sub> were reported by Bertaut & Mercier (1963) from powder neutron diffraction experiments. They found a frustrated triangular basal plane spin structure at 4.2 K. The measurements allowed two stacking sequences for the basal planes spin structure, only one of which allows a ferromagnetic canting. Because ceramic samples showed a ferromagnetic component in the magnetization below 45 K, this stacking sequence was

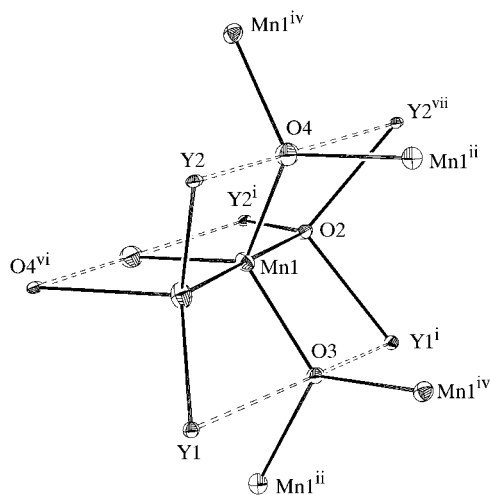
favoured. However, this conclusion was withdrawn when it was realized that the ferromagnetic component originates from small amounts of the impurity phase Mn<sub>3</sub>O<sub>4</sub> (Bertaut *et al.*, 1965). Despite various reports on single-crystal growth of YMnO<sub>3</sub> (Yakel *et al.*, 1963; Bertaut *et al.*, 1963), we could find in the open literature neither the crystallographic structure determination nor the temperature-dependent magnetization of phase-pure samples. We report here the details of the refinement of the crystal structure of YMnO<sub>3</sub>. We will show the magnetic behaviour in a separate publication; these single crystals exhibit an antiferromagnetic anomaly at  $T_N = 75$  K, and a large magnetic anisotropy as expected for this crystal structure (van Aken *et al.*, 2001).

In Table 1, the metal–oxygen bond lengths are given. Both yttrium positions and the manganese position have unusual oxygen environments. In the centrosymmetric high-tempera-

**Figure 1**

A schematic view of the crystallographic structure of YMnO<sub>3</sub>. The top panel shows a view along the basal plane. Y atoms are represented by shaded spheres and the MnO<sub>5</sub> clusters are represented by trigonal bipyramids. This panel highlights the two-dimensional nature of the structure. The lower panel depicts a view along the *c* axis of two layers to show the stacking of the bipyramids.

ture phase,  $T_s = 1283$  K (Łukaszewicz & Karut-Kalicinska, 1974), the single Y atom has an eightfold coordination in the form of a bicapped trigonal antiprism. In the non-centrosymmetric structure, the capping O atoms are displaced with respect to the yttrium in such a way that the Y—O bond length changes from two equivalent values of 2.7 Å to 2.4 and 3.3 Å. The Mn atom is surrounded by five O atoms in a trigonal bipyramidal environment. The difference in bond length between in-plane and out-of-plane bonds is striking,  $\approx 2.05$  and  $\approx 1.86$  Å, respectively. The origin of this difference is the orbital occupation given by the crystal-field splitting of  $\text{Mn}^{3+}$ . The three-dimensional states split in a trigonal bipyramidal field according to the magnetic quantum number (van Aken *et al.*, 2001). This yields an empty  $z^2$  orbital, which is in agreement with the shorter Mn—O distances along the  $c$  axis than in the  $ab$  plane. It can easily be shown that the  $3d^4$  ground state is non-degenerate and thus not Jahn–Teller active.



**Figure 2**  
An ORTEP (Johnson, 1976) view of the unit cell.

The non-equivalent Mn—O atomic distances, both within the basal plane and to the apices, have smaller differences than in isomorphous  $\text{LuMnO}_3$ . Nevertheless, the Mn ion is not located in the centre of the trigonal bipyramid. It is both displaced in the  $ab$  basal plane, and along the  $c$  axis. The three Mn displacement vectors within the basal plane cancel each other in a triangular fashion. The displacement along the  $c$  axis is the same for all Mn ions in the unit cell. Furthermore, the Y ions are also non-symmetrically surrounded by the O atoms. This means that  $\text{YMnO}_3$  is ferroelectric and an ordering temperature of  $\approx 920$  K has been reported (Smolenskii & Chupis, 1982). The macroscopic electric polarization is cancelled by an inversion twin. The origin of the ferroelectricity is not known at the moment. One possibility could be the fact that this hexagonal  $\text{YMnO}_3$  is less dense than the perovskite  $\text{YMnO}_3$ . This could mean that there is some excess volume in the centrosymmetric high-temperature phase. The excess volume can be reduced by rotating or deforming the oxygen polyhedra around the metal ions. This could lead to the disappearance of the inversion centre.

We conclude that  $\text{YMnO}_3$  is ferroelectric with a frustrated displacement pattern. Both the Y and Mn ions are shifted along the  $c$  axis. The electric polarization is cancelled by inversion twinning. Both methods of synthesis result in single crystals of the same quality.

## Experimental

Single crystals of  $\text{YMnO}_3$  were obtained using a flux method by weighing appropriate amounts of  $\text{Y}_2\text{O}_3$  and  $\text{MnO}_2$  with  $\text{Bi}_2\text{O}_3$  in a 1:12 ratio (Yakel *et al.*, 1963). The powders were mixed thoroughly and heated for 48 h at 1523 K in a Pt crucible. The separation of the crystals from the flux was performed by two methods (Bertaut *et al.*, 1963): (i) by increasing the temperature to 1723 K and evaporating the  $\text{Bi}_2\text{O}_3$  flux and (ii) by slowly cooling ( $50 \text{ K h}^{-1}$ ) through the solidification of the flux. The single crystals then segregated on top of the flux. Both methods were used and the results are equal within the error of the structure determination. We report here only on crystals prepared by slow cooling.

## Compound $\text{YMnO}_3$ at 290 K

### Crystal data

$\text{YMnO}_3$   
 $M_r = 191.85$   
Hexagonal,  $P6_3cm$   
 $a = 6.1387(3) \text{ \AA}$   
 $V = 372.27(4) \text{ \AA}^3$   
 $Z = 6$   
 $D_x = 5.135 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation

Cell parameters from 22 reflections  
 $\theta = 29.82\text{--}39.73^\circ$   
 $\mu = 28.07 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
Platelet, black  
 $0.150 \times 0.150 \times 0.024 \text{ mm}$

### Data collection

Enraf–Nonius CAD-4F diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: analytical (Meulenaer & Tompa, 1965)  
 $T_{\min} = 0.053$ ,  $T_{\max} = 0.511$   
3385 measured reflections  
865 independent reflections  
658 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$   
 $\theta_{\max} = 39.95^\circ$   
 $h = 0 \rightarrow 11$   
 $k = -11 \rightarrow 0$   
 $l = -20 \rightarrow 20$   
3 standard reflections  
frequency: 180 min  
intensity variation: 0.5%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.037$   
 $wR(F^2) = 0.107$   
 $S = 1.117$   
865 reflections  
32 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 3.11 \text{ e \AA}^{-3}$  (0.12 Å from Y2)  
 $\Delta\rho_{\min} = -1.17 \text{ e \AA}^{-3}$  (1.62 Å from O2)  
Extinction correction: *SHELXL97* (Sheldrick, 1997)  
Extinction coefficient: 0.025 (3)

**Table 1**

Selected bond lengths (Å) for  $\text{YMnO}_3$  at 290 K.

Y1—O1	2.281 (7)	Y2—Y2 <sup>iii</sup>	3.5442 (3)
Y1—O2 <sup>i</sup>	2.316 (6)	Mn1—O1	1.863 (8)
Y1—O3 <sup>i</sup>	2.326 (14)	Mn1—O2	1.862 (7)
Y2—O1	2.275 (6)	Mn1—O3	2.073 (3)
Y2—O2	2.300 (4)	Mn1—O4	2.052 (3)
Y2—O4 <sup>ii</sup>	2.451 (13)		

Symmetry codes: (i)  $x - y, x, \frac{1}{2} + z$ ; (ii)  $1 + x - y, 1 + x, \frac{1}{2} + z$ ; (iii)  $y - 1, x, z$ .

## Compound YMnO<sub>3</sub> at 180 K

### Crystal data

YMnO <sub>3</sub>	Cell parameters from 22 reflections
$M_r = 191.85$	$\theta = 29.83\text{--}39.81^\circ$
Hexagonal, $P6_3cm$	$\mu = 28.16\text{ mm}^{-1}$
$a = 6.1277(5)\text{ \AA}$	$T = 180\text{ K}$
$V = 371.06(5)\text{ \AA}^3$	Platelet, black
$Z = 6$	$0.150 \times 0.024 \times 0.015\text{ mm}$
$D_x = 5.151\text{ Mg m}^{-3}$	
Mo $K\alpha$ radiation	

### Data collection

Enraf–Nonius CAD-4F diffractometer	$R_{\text{int}} = 0.040$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 39.93^\circ$
Absorption correction: analytical (Meulenaer & Tompa, 1965)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.065$ , $T_{\text{max}} = 0.510$	$k = -11 \rightarrow 0$
3336 measured reflections	$l = -18 \rightarrow 20$
853 independent reflections	3 standard reflections
658 reflections with $I > 2\sigma(I)$	frequency: 180 min
	intensity variation: 0.5%

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R(F) = 0.037$	$\Delta\rho_{\text{max}} = 2.31\text{ e \AA}^{-3}$ (0.64 \AA from Y1)
$wR(F^2) = 0.109$	$\Delta\rho_{\text{min}} = -1.36\text{ e \AA}^{-3}$
$S = 1.094$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
853 reflections	Extinction coefficient: 0.018 (2)
32 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

The space group was determined to be  $P6_3cm$ , taking into consideration the unit-cell parameters, statistical analyses of intensity distributions and, where appropriate, systematic extinctions ( $h\bar{h}l$ :  $l \neq 2n$ ;  $00l$ :  $l \neq 2n$ ). Other space groups that satisfy the same extinction conditions were discarded during the refinement. Attempts to fit the data on a crystal structure with space group  $P63/mcm$  were unsuccessful. Anisotropic displacement parameters indicated that the atoms at the mirror plane ought to be split over two positions on each side of the mirror plane.

The structure was solved by Patterson methods with *SHELXS97* (Sheldrick, 1997) and subsequent difference Fourier maps. The initial coordinates were comparable with the isomorphous structure of LuMnO<sub>3</sub>. The positional and anisotropic displacement parameters were refined. All the occupied sites were checked for partial occupancy and the Y and Mn sites were checked for mixed occupancy with Bi; partial occupancy or mixed population did not improve the refinement.

The Flack parameter (Flack, 1983) of an initial refinement indicated that the crystal was twinned. Therefore, an inversion twin was added to the structure model. An initial attempt gave a twin fraction of 47 (3)%. We expect a 50/50 distribution because this yields no net electrical polarization (Rao & Gopalakrishnan, 1997). We fixed the twin fraction at 50(–)%, which had no significant influence on any other parameter.

For both compounds, data collection: *CAD-4-UNIX Software* (Enraf–Nonius, 1994); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1994); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1421). Services for accessing these data are described at the back of the journal.

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