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Hexagonal $YbMnO_3$ revisited

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The crystal structure of hexagonal ytterbium manganese oxide, $YbMnO_3$, has been refined at room temperature. It is isomorphous with $YMnO_3$. The Mn ions lie near the centre of a trigonal bipyramid. Although the Yb ions lie on threefold axes, the apical oxygen ions are at dissimilar distances, leading to ferroelectric behaviour. The sample studied was composed of almost an equal volume of inversion twins.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.004 Å
R factor = 0.030
wR factor = 0.072
Data-to-parameter ratio = 26.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

As part of a programme to investigate the origin of the ferroelectric behaviour in the hexagonal $LnMnO_3$ family, we have determined accurate structural parameters for several members of this series (Van Aken *et al.*, 2001*a*,*b*,*c*). Here we report the structure of $YbMnO_3$. Single-crystal growth of $YbMnO_3$ has frequently been described (Yakel *et al.*, 1963; Bertaut *et al.*, 1963), but the structure was first reported by Isobe *et al.* (1991). Our refinement shows small but significant differences from the work of Isobe *et al.* (1991), as discussed below.

The hexagonal $LnMnO_3$ family has been described in great detail previously (Van Aken *et al.*, 2001*a*,*b*,*c*). The lattice parameter c of 11.5575 (5) Å reported by Isobe *et al.* (1991) is exceptionally large when compared with other $LnMnO_3$ compounds. However, the value we measured of 11.3561 (7) Å is likely more reliable, as it lies within the range observed for other isostructural compounds, *i.e.* 11.36–11.42 Å (Yakel *et al.*, 1963; Van Aken *et al.*, 2001*a*,*b*,*c*).

The metal–oxygen bond lengths are given in Table 1. In contrast to the report of Isobe *et al.* (1991), the equatorial Mn—O distances are the same within the measured s.u.'s. More importantly, the apical Mn—O distances in our report are also the same within the experimental precision. They differ by only 0.001 (7) Å, whereas Isobe reports a difference of 0.058 (10) Å. As a result, the Mn is approximately in the centre of its oxygen environment. Likewise, the differences between the apical bond distances of Yb1 and Yb2, 1.140 (18) and 0.876 (10) Å, respectively, are significantly larger than those reported by Isobe *et al.* (1991), *viz.* 1.071 and 0.707 Å.

Isobe *et al.* (1991) measured reflections for only one asymmetric *hkl* set and therefore included no Bijvoet pairs, with the result that they could obtain no information about the non-centrosymmetry of their sample. Our experiments included over 90% of the Friedel pairs, allowing us to calculate the Flack (1983) parameter. The refinement indicated that our sample contained roughly equal volumes of inversion twins as was also found for $YMnO_3$ (Van Aken *et al.*, 2001*a*). Our results show the significance of a full data set, for twinned non-centrosymmetric samples.

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Experimental

Single crystals of $YbMnO_3$ were obtained using a flux method by mixing appropriate amounts of Yb_2O_3 and MnO_2 with Bi_2O_3 in a 1:12 ratio (Yakel *et al.*, 1963). The powders were thoroughly mixed and heated for 48 h at 1523 K in a Pt crucible. The crystals were separated from the flux by increasing the temperature to 1723 K and evaporating the Bi_2O_3 flux (Bertaut *et al.*, 1963).

Crystal data

$YbMnO_3$
$M_r = 275.88$
Hexagonal, $P6_3cm$
$a = 6.0584\ (6)$ Å
$c = 11.3561\ (7)$ Å
$V = 360.97\ (6)$ Å^3
$Z = 6$
$D_x = 7.617$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 15.0$–27.9°
$\mu = 43.58$ mm^{-1}
$T = 293$ K
Platelet, black
0.15 × 0.10 × 0.01 mm

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Spek, 1983)
$T_{\min} = 0.059$, $T_{\max} = 0.577$
3264 measured reflections
835 independent reflections
636 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.037$
$\theta_{\max} = 39.9^\circ$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.072$
$S = 1.08$
835 reflections
32 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.5\ (10)$ e Å^{-3}
$\Delta\rho_{\min} = -7.3\ (10)$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0121 (7)

Table 1
Selected geometric parameters (Å, °).

Yb1—O1	2.231 (7)	Yb2—O4$^{\rm ii}$	3.277 (10)
Yb1—O2$^{\rm i}$	2.294 (8)	Yb2—O2$^{\rm iii}$	2.270 (8)
Yb1—O3$^{\rm i}$	2.269 (18)	Mn—O1	1.867 (7)
Yb1—O3	3.409 (18)	Mn—O2	1.868 (7)
Yb2—O1	2.257 (5)	Mn—O3	2.039 (4)
Yb2—O4	2.401 (10)	Mn—O4	2.034 (4)
O1—Mn—O2	179.5 (4)	O4—Mn—O4$^{\rm iv}$	118.62 (19)
O1—Mn—O3	92.3 (6)	Mn—O3—Mn$^{\rm v}$	118.1 (3)
O1—Mn—O4	86.1 (3)	Mn—O4—Mn$^{\rm vi}$	118.6 (2)
O3—Mn—O4	120.54 (8)		

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

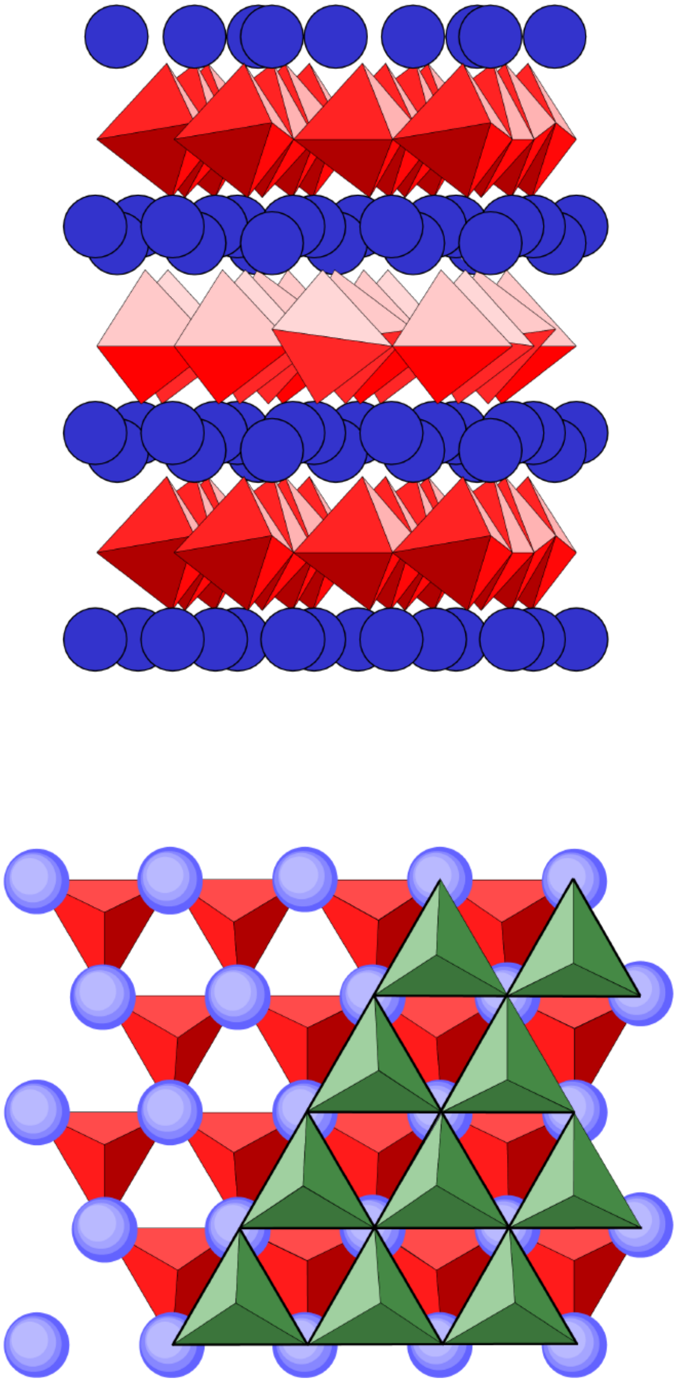

Figure 1
Schematic view of the crystallographic structure of $YbMnO_3$. Top: a view along the basal plane. Yb is represented by blue spheres, and the MnO_5 clusters are represented by red trigonal bipyramids. This panel highlights the two-dimensional nature of the structure. Bottom: a view along the *c* axis of two layers to show the stacking of the bipyramids. The bipyramids below the Yb layer are shown in red, with those above in green.

The space group is determined to be $P6_3cm$, taking into consideration the unit-cell parameters, statistical analyses of intensity distributions and, where appropriate, systematic extinctions (h-hl: $l \neq 2n$; $00l$: $l \neq 2n$). Attempts to fit the data in the space group $P6_3/mcm$ were unsuccessful with $wR^2 = 0.45$ and $R = 0.18$. Anisotropic displacement parameters and *SHELXL97* (Sheldrick, 1997) indicated that the Yb ions should be shifted away from the mirror plane perpendicular to the *c* axis. The structure was solved by using initial coordinates which are taken from a previous reported hexagonal manganite, $YMnO_3$ (Van Aken *et al.*, 2001*a*). The positional and anisotropic displacement parameters were refined. The final difference Fourier map showed a peak of 2.5 (10) e Å^{-3} near the Yb1 position and a hole of 7.3 (10) e Å^{-3} also near the Yb1 position. No other significant peaks having chemical meaning above the general background 1.0 e Å^{-3} were observed in the final difference Fourier map. The Flack parameter (Flack, 1983) of an initial refinement indicated that the crystal was twinned. The model without a twin yielded a Flack parameter of $x = 0.34\,(3)$ and $x = 0.57\,(3)$ for the inverse structure. The R values are $wR^2 = 0.0789$ and $R = 0.0305$, and $wR^2 = 0.086$ and $R = 0.0318$, respectively. Therefore an inversion twin was added to the structure model, similar to the one reported for $YMnO_3$ (Van Aken *et al.*, 2001*a*). The final refinement gave a twin fraction near 50%. We expect a 50/50% distribution because this yields no net electrical polarization (Rao & Gopalakrishnan, 1997). Fixing the twin fraction at 50% had no significant influence on any other parameter.

Data collection: *CAD*-4-*UNIX Software* (Enraf–Nonius, 1994); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 2000); software used to prepare material for publication: *PLATON* (Spek, 2001).

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