Hexagonal LuMnO₃ revisited

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The crystal structure of hexagonal LuMnO₃ at room temperature is isomorphous with YMnO₃ and deviates in important details from the early work of Yakel et al. [Acta Cryst. (1963), **16**, 957–962]. Mn is near the centre of its oxygen coordination environment. On the threefold axes, the apical O—Lu bonds have alternating long and short bond lengths, leading to ferroelectric behaviour. The sample studied was composed of almost equal volumes of inversion twins.

Comment

As part of a programme to investigate the origin of the ferroelectric behaviour in the hexagonal LnMnO₃ family, we have determined accurate structural parameters for single crystals of this series (Van Aken et al., 2001a,b,c). Here we report the structure of LuMnO₃. Single-crystal growth of LuMnO₃ has frequently been reported (Yakel et al., 1963; Bertaut et al., 1963) and the structure was reported by Yakel et al. Our refinement shows small but significant differences from the work of Yakel et al. (1963), as discussed below. The hexagonal LnMnO₃ family has been described in great detail previously (Van Aken et al., 2001d).

The M—O bond lengths are given in Table 1. The non-equivalent Mn—O atomic distances, both within the basal plane and to the apices, have smaller differences than in previous reports on LuMnO₃ (Yakel et al., 1963). In-plane differences are 0.023 (7) Å (this work) and 0.09 Å (Yakel et al., 1963), apical 0.031 (7) Å (this work) and 0.08 Å (Yakel et al., 1963). As a result Mn is approximately in the centre of its oxygen environment. Likewise, the equatorial Lu—O1 and Lu—O2 bond lengths show less variation than the result of Yakel et al. (1963). Our data yield equatorial bond lengths of 2.227–2.294 Å, whereas Yakel et al. report 2.18–2.35 Å. The differences in apical bond distances of Lu1 and Lu2 are larger [1.192 (14) and 0.879 (10) Å] respectively, than those reported by Yakel et al. (0.84 and 0.96 Å).

Yakel et al. (1963) only measured reflections of one asymmetric hkl set, i.e. no Bijvoet pairs. Based on the observation of ferroelectricity (Bertaut et al., 1963) and systematic absences, the non-centrosymmetric space group $P6_3cm$ was chosen. Our experiment included over 90% of the Friedel pairs and subsequent analysis confirmed this space group. Yakel et al. also discuss the possibility of the existence of domains with reversed polar direction. Our refinement indicated that our sample contained roughly equal volumes of twin domains.

Experimental

Single crystals of LuMnO₃ were obtained using a flux method by weighing appropriate amounts of Lu₂O₃ and MnO₂ with Bi₂O₃ in a

Figure 2
Perspective *ORTEP*II (Johnson, 1976) drawing of all inequivalent atoms. All atoms are represented by atomic displacement ellipsoids drawn to encompass 50% of the electron density.

Crystal data

$LuMnO_3$	Mo $K\alpha$ radiation
$M_r = 277.90$	Cell parameters from 22
Hexagonal, $P6_3cm$	reflections
$a = 6.038\ (1)$ Å	$\theta = 28.0–28.8°$
$c = 11.361\ (1)$ Å	$\mu = 46.03$ mm^{-1}
$V = 358.70\ (9)$ Å^3	$T = 293$ K
$Z = 6$	Platelet, black
$D_x = 7.719$ Mg m^{-3}	$0.120 \times 0.100 \times 0.004$ mm

Data collection

Enraf–Nonius CAD-4F	$R_{int} = 0.094$
diffractometer	$\theta_{max} = 40.0°$
$\omega/2\theta$ scans	$h = -10 \rightarrow 9$
Absorption correction: analytical	$k = 0 \rightarrow 10$
(de Meulenaer & Tompa, 1965)	$l = -20 \rightarrow 20$
$T_{min} = 0.084$, $T_{max} = 0.759$	3 standard reflections
4711 measured reflections	frequency: 180 min
833 independent reflections	intensity decay: none
610 reflections with $F > 4\sigma(F)$	

Refinement

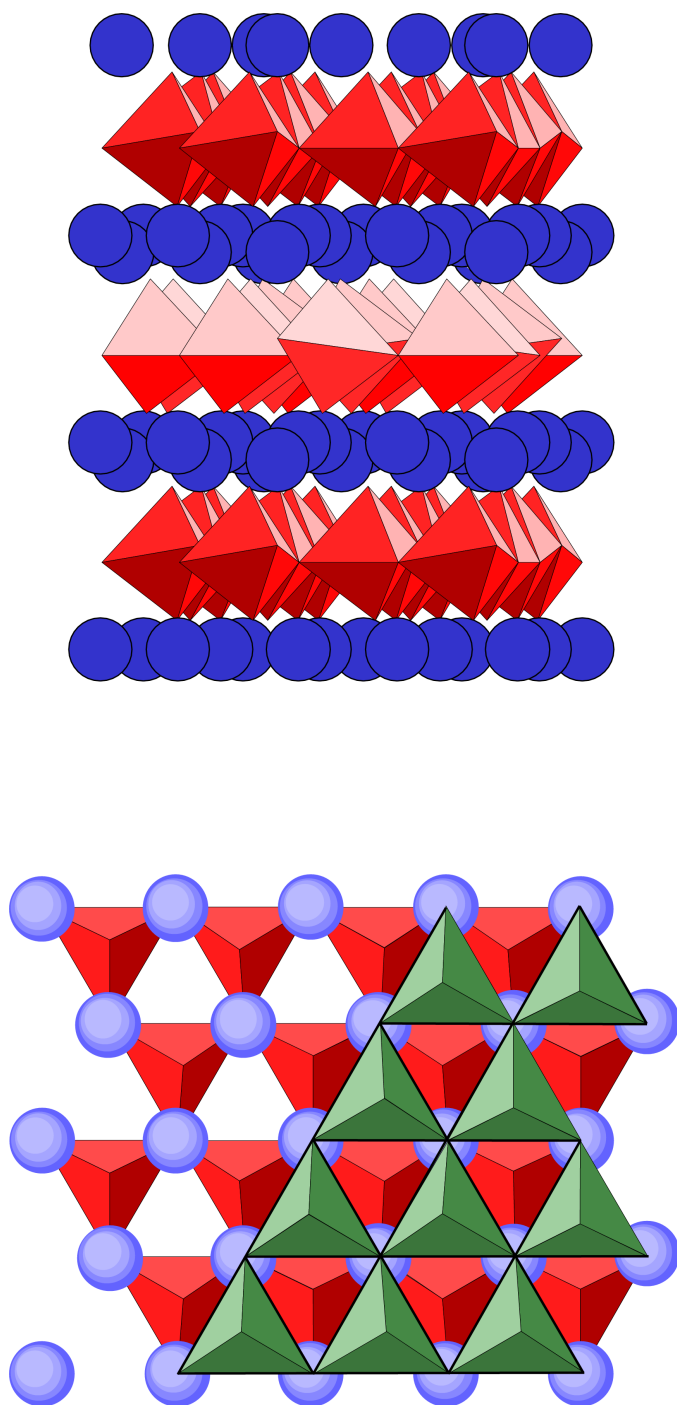|	
Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.027$	$\Delta\rho_{max} = 2.0\ (4)$ e Å^{-3}
$wR(F^2) = 0.065$	$\Delta\rho_{min} = -5.6\ (4)$ e Å^{-3}
$S = 1.05$	Extinction correction: *SHELXL*97
833 reflections	(Sheldrick, 1997)
32 parameters	Extinction coefficient: 0.0024 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Figure 1
Schematic view of the crystallographic structure of LuMnO₃. The top panel shows a view along the basal plane. Lu is represented by shaded spheres, and the MnO₅ 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.

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 Bi₂O₃ flux (Bertaut *et al.*, 1963).
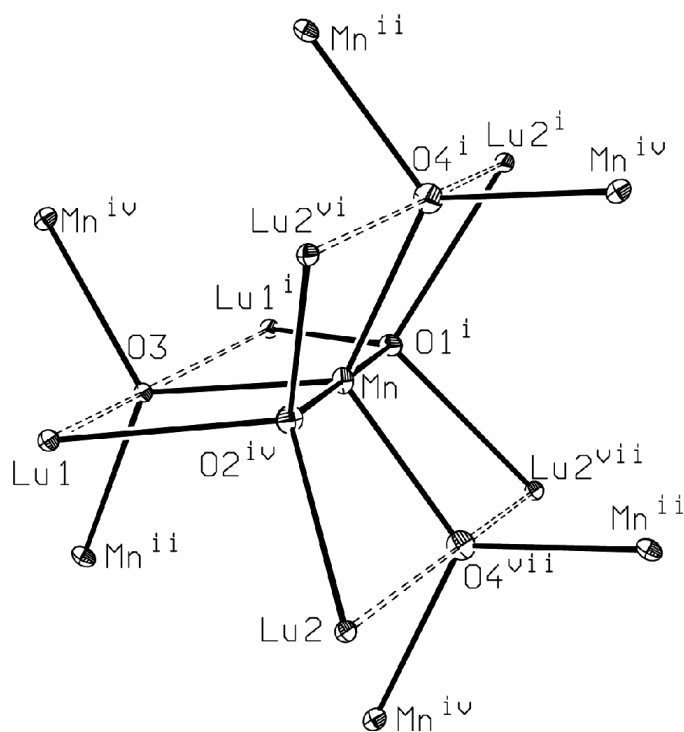
Table 1
Selected geometric parameters (Å, °).

Lu1—O1	2.234 (9)	Lu2—O4[ii]	3.279 (10)
Lu1—O2[i]	2.294 (10)	Lu2—O2[iii]	2.277 (12)
Lu1—O3[i]	2.244 (14)	Mn—O1	1.882 (7)
Lu1—O3	3.436 (14)	Mn—O2	1.859 (7)
Lu2—O1	2.227 (12)	Mn—O3	2.050 (6)
Lu2—O4	2.401 (10)	Mn—O4	2.019 (7)
O1—Mn—O2	179.6 (6)	O4—Mn—O4[iv]	119.4 (3)
O1—Mn—O3	93.6 (5)	Mn—O3—Mn[v]	117.7 (3)
O1—Mn—O4	86.2 (5)	Mn—O4—Mn[vi]	118.8 (3)
O3—Mn—O4	120.2 (3)		

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

The space group is determined to be $P6_3cm$, taking into consideration the unit cell parameters, statistical analyses of intensity distributions and systematic extinctions ($h-hl$: $l \neq 2n$; $00l$: $l \neq 2n$). Attempts to fit the intensities with a crystal structure in space group $P6_3/mcm$ were unsuccessful. Anisotropic displacement parameters and $SHELXL97$ indicated that the Lu ions should be shifted away from the mirror plane perpendicular to the c axis.

The integrated intensities were measured in 'flat mode' as the absorption is very large. In 'flat mode' every reflection is measured in the orientation that minimizes the path length through the crystal and thus the absorption. The minimum transmission factor is therefore larger than expected from the crystal size.

The structure was solved by using initial co-ordinates which were taken from a previous reported hexagonal manganite, YMnO3 (Van Aken *et al.*, 2001a). The positional and anisotropic displacement parameters were refined.

The final difference Fourier map showed a peak of 2.0 (4) e Å^{-3} near the Lu position and a hole of 5.7 (4) e Å^{-3} also near the Lu position. No other significant peaks having chemical meaning above the general background (0.9 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. Therefore an inversion twin was added to the structure model, similar to the one reported for YMnO3 (Van Aken *et al.*, 2001a). An initial attempt gave a twin fraction near 50%. We expect a 50%–50% distribution because this yields no net electrical polarization. We fixed the twin fraction at 50%, which 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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