Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Hexagonal $ErMnO_3$

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Received 3 May 2001
Accepted 14 May 2001
Online 22 May 2001

The crystal structure of hexagonal $ErMnO_3$, erbium manganese trioxide, has been determined at room temperature. It is isomorphous with $YMnO_3$. Although we observed inversion twinning, similar to $YMnO_3$, the twin fractions do not have a 1:1 ratio, and the crystals are expected to show net ferroelectricity.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.005 Å
R factor = 0.034
wR factor = 0.079
Data-to-parameter ratio = 23.0

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

Comment

The compounds $LnMnO_3$, 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 gained enormous interest, because of a colossal magneto-resistance effect, *i.e.* a metal–insulator transition that changes the conductivity by many orders of magnitude at the Curie temperature (Ramirez, 1997). The Mn is octahedrally coordinated by O. 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, forming a pseudo-layered structure by corner sharing of the trigonal basal plane O ions. These compounds are of interest because of the combination of ferroelectric and magnetic ordering (Smolenskii & Bokov, 1964).

Despite various reports on single-crystal growth of $ErMnO_3$ (Yakel *et al.*, 1963; Bertaut *et al.*, 1963), we could not find in the literature the crystallographic structure determination. We report here the details of the refinement of the crystal structure (Fig. 1).

The metal–oxygen bond lengths are given in Table 1. Both erbium positions and the manganese position have unusual oxygen environments. Manganese is surrounded by five O ions in a trigonal bipyramid. There is a striking difference in bond length between in-plane and out-of-plane bonds, respectively $\simeq 2.05$ and $\simeq 1.87$ Å. The origin of this difference is the orbital occupation given by the crystal-field splitting of Mn^{3+}. The $3d$ states split in a trigonal bipyramidal field according to the magnetic quantum number (Van Aken, Bos *et al.*, 2001), with the z^2 orbital highest in energy and two doublets. Thus the $3d^4$ ground state is non-degenerate and therefore not Jahn–Teller active. The empty z^2 orbital is in agreement with the shorter Mn–O distances along the c axis than in the ab plane. The non-equivalent Mn–O atomic distances, both within the basal plane and to the apices, have smaller differences than in isomorphous $YbMnO_3$ (Isobe *et al.*, 1991).

The erbium has a distorted eightfold co-ordination, in the form of a bicapped trigonal antiprism. Due to this distortion

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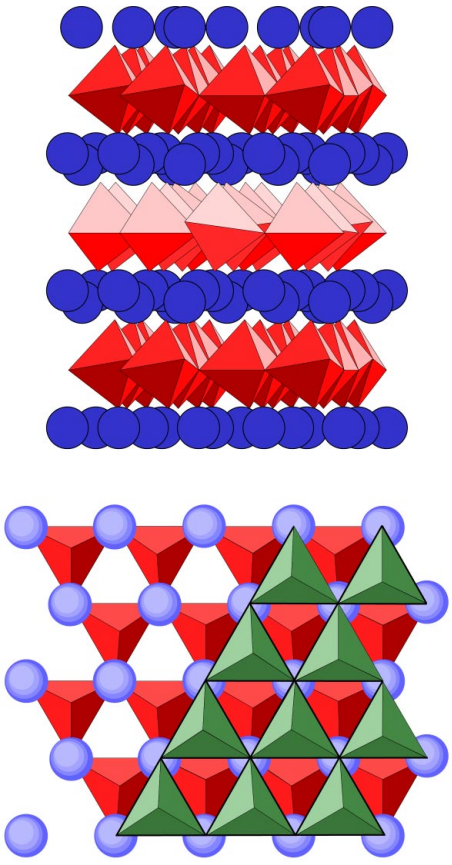

Figure 1
Schematic view of the crystallographic structure of $ErMnO_3$. The upper view is along the basal plane. Er is represented by blue spheres, and the MnO_5 clusters are represented by red trigonal bipyramids. This panel highlights the two-dimensional nature of the structure. The lower view depicts a view along the *c* axis of two layers to show the stacking of the bipyramids. The bipyramids below the Er layer are shown in red, the ones above in green.

the capping O ions are displaced with respect to the erbium in such a way that the Er–O bond length changes from twice 2.9 Å to 2.4 Å and 3.3 Å. As a result the erbium ions are non-centrosymmetrically surrounded by the O ions. Both erbium positions have a similar distorted environment, which are 180° rotated with respect to each other. The combined environment yields a ferrielectric configuration with four Er2 parallel dipole moments antiparallel to the two Er1 dipole moments. Consequently, $ErMnO_3$ is ferroelectric and an ordering temperature of ≃833 K has been reported (Smolenskii & Chupis, 1982). The macroscopic electric polarization is cancelled by an inversion twin, as found in $YMnO_3$ (Van Aken, Meetsma & Palstra, 2001). The origin of the ferroelectricity is not known at present, although the hexagonal manganites are less densely packed than the perovskite manganites.

We conclude that $ErMnO_3$ is ferrielectric. Both erbium positions have a dipole moment parallel to the *c* axis and antiparallel to each other. The electric polarization is cancelled by inversion twinning.

Experimental

Single crystals of $ErMnO_3$ were obtained using a flux method by weighing appropriate amounts of Er_2O_3 and MnO_2 with Bi_2O_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 carried out by increasing the temperature to 1723 K and evaporating the Bi_2O_3 flux (Bertaut *et al.*, 1963).

Crystal data

$ErMnO_3$
M_r = 270.20
Hexagonal, $P6_3cm$
a = 6.1121 (5) Å
c = 11.4200 (14) Å
V = 369.47 (6) Å^3
Z = 6
D_x = 7.286 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3929 reflections
θ = 3.5–38.4°
μ = 38.68 mm^{-1}
T = 293 K
Triangular platelet, black
0.11 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEX diffractometer
Area-detector scans
Absorption correction: Gaussian (*XPREP*, Bruker, 2000)
T_{min} = 0.018, T_{max} = 0.083
7178 measured reflections
759 independent reflections
569 reflections with $F > 4\sigma(F)$
R_{int} = 0.068
θ_{max} = 38.5°
$h = -6 \rightarrow 10$
$k = -10 \rightarrow 8$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.079
S = 1.03
759 reflections
33 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 3.8 (9) e Å^{-3}
$\Delta\rho_{min}$ = −6.4 (9) e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0223 (11)

Table 1
Selected geometric parameters (Å, °).

Er2—O4	2.437 (15)	Er1—O2^{iii}	2.281 (8)
Er2—O2	2.244 (7)	Er1—O3^{iii}	3.39 (3)
Er2—O1^{i}	2.306 (5)	Mn1—O3	2.092 (4)
Er2—O4^{ii}	3.273 (15)	Mn1—O4	2.030 (2)
Er1—O3	2.32 (3)	Mn1—O1	1.854 (8)
Er1—O1	2.312 (6)	Mn1—O2	1.886 (8)
O3—Mn1—O4	119.49 (7)	O1—Mn1—O2	178.5 (3)
O4—Mn1—O4^{iv}	120.76 (13)	Mn1—O3—Mn1^{v}	118.5 (4)

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

The space group is determined to be $P6_3cm$, taking into consideration the unit-cell parameters, statistical analyses of intensity distributions and, 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 with a crystal structure in space group $P6_3/mcm$ were unsuccessful with wR = 0.479 and R = 0.195. Furthermore, the principal mean-square atomic displacements of Er1 have a ratio of 14:1 for the perpendicular and parallel directions in this 'wrong' space group. *SHELXL*97 suggests a splitting of this atom in a position above and

below the mirror plane. The structure was solved by using initial coordinates, which are taken from a previous reported hexagonal manganite, $YMnO_3$ (Van Aken, Meetsma & Palstra, 2001). The positional and anisotropic displacement parameters were refined. The principal mean-square atomic displacements for the cations in the right space group do not show any significant anisotropy. The final difference Fourier map showed a peak of 3.9 (9) e $Å^{-3}$ near the Er1 position and a hole of 6.4 (9) e $Å^{-3}$ also near the Er1 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. The model without a twin yielded a Flack parameter $x = 0.3484$ and $x = 0.6147$ for the inverse structure. The R values are $wR = 0.0811$ and $R = 0.0355$, $wR = 0.0857$ and $R = 0.0363$, respectively. Therefore, an inversion twin was added to the structure model, similar to the one reported for $YMnO_3$ (Van Aken, Meetsma & Palstra, 2001). The final refinement gave a twin fraction of 36 (5)%. We expect a 50–50% distribution because this yields no net electrical polarization (Rao & Gopalakrishnan, 1997). The deviation from the 50–50% can be caused during the cutting process of the crystals.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *XPREP* (Bruker, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Farrugia, 2000); software used to prepare material for publication: *PLATON* (Spek, 2001).

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