

Ferroelectricity and structure in the YMnO_3 family

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The 1963 discovery of ferroelectricity in YMnO_3 was accompanied by an experimental Curie temperature (T_c) reported as 913 K; this value was revised to 1270 K in the following decade. Subsequently, YInO_3 was shown to be isostructural with YMnO_3 and later demonstrated to satisfy the structural criteria for ferroelectricity; recent unpublished measurements give $T_c(\text{YInO}_3) = 835(15)$ K. The experimental T_c value of 913 K for YMnO_3 is in satisfactory agreement with the calculated 1220 (100) K value as derived from a very recent structural refinement, the experimental T_c of 835 (15) K for YInO_3 with the calculated 760 (120) K. The full YMnO_3 family includes the AMnO_3 subfamily with $A = \text{Y, Ho, Er, Tm, Yb, Lu, Sc, In}$; the AlnO_3 subfamily with $A = \text{Y, Gd, Dy, Ho, Tb}$; and the AGaO_3 subfamily with $A = \text{Y, Ho, Er}$. The T_c values of six family members with known structure, in addition to YMnO_3 and YInO_3 , have been structurally derived as 1310 (110) K for ErMnO_3 , 1290 (165) K for LuMnO_3 , 1270 (110) K for YbMnO_3 , 1220 (105) K for ScMnO_3 , 540 (375) K for InMnO_3 and 1020 (100) K for YGaO_3 . The agreement between predicted and experimental T_c values for ErMnO_3 , LuMnO_3 and YbMnO_3 , in addition to that for YMnO_3 and YInO_3 , leads to the confident prediction that ScMnO_3 , InMnO_3 and YGaO_3 are new ferroelectrics. The remaining six members of the full YMnO_3 family are also expected to be new ferroelectrics.

1. Introduction

The discovery by Bertaut *et al.* (1963) that YMnO_3 and YbMnO_3 are both antiferromagnetic and ferroelectric, following the determination by Yakel (1955) and Bertaut & Forrat (1956) that these manganites have a structure described as that of a distorted perovskite (but see §2), led to substantial interest in their properties. Yakel *et al.* (1963) undertook a single-crystal structure determination of LuMnO_3 and showed, from the powder patterns, that it was isostructural with YMnO_3 and YbMnO_3 . They reported the a axis length in the AMnO_3 family as ranging between 6.136 and 6.042 Å at ~ 300 K for $A = \text{Y, Ho, Er, Tm, Yb}$ and Lu , with a range for the c axis between 11.42 and 11.37 Å.

YGaO_3 was also found to be isostructural with the YMnO_3 family by Geller *et al.* (1975) as well as, probably, HoGaO_3 and ErGaO_3 with similar unit-cell parameters. Soon after, the crystal structure of YInO_3 was reported by Pistorius & Kruger (1976) to be isostructural with YMnO_3 , as were the AlnO_3 subfamily members with $A = \text{Eu, Gd, Tb, Dy}$ and Ho . Additional members of the YMnO_3 family were identified by searching release 2000/2 of the Inorganic Crystal Structure Database (ICSD; Bergerhoff *et al.*, 1983). The atomic coor-

dinates of isostructural YbMnO₃ (Isobe *et al.*, 1991), InMnO₃ and ScMnO₃ (Greedan *et al.*, 1995) were thereby retrieved, together with redeterminations of the ScMnO₃ structure (an X-ray powder diffraction study by Xu *et al.*, 1995, and a neutron powder diffraction study by Bieringer & Greedan, 1999).

The very recent refinements of the YMnO₃ and ErMnO₃ atomic coordinates by van Aken *et al.* (2001*a,b*) were of particular interest in view of the prediction (Abrahams, 1988) that isostructural YInO₃ is ferroelectric with Curie temperature $T_c = 810$ (90) K.

The structurally derived values of T_c in YMnO₃, ErMnO₃, YbMnO₃ and LuMnO₃, a reanalysis of the YInO₃ coordinates leading to a revised value for its T_c , and the structural prediction of ferroelectricity in ScMnO₃, InMnO₃ and YGaO₃ with corresponding values for their calculated T_c , are presented hereafter. Eight additional family members with structures not yet fully refined are also expected to be ferroelectric.

2. Ferroelectric YMnO₃

Prompt confirmation of Bertaut *et al.*'s (1963) discovery was made by Bokov *et al.* (1964) and by Smolenskii & Bokov (1965); they reported an inflection at ~750 K in the inverse magnetic susceptibility thermal dependence, ascribing it to a structural phase transition, but found no ferroelectric transition below 825 K. Ismailzade & Kizhaev (1965) observed a sharp maximum at T_c (YMnO₃) \simeq 935 K in the pyroelectric current thermal dependence with discontinuities at approximately the same temperature in the *a* and *c* axial parameters by powder diffractometer measurement; they also found a small discontinuity in the *c*-axis parameter at ~500 K. Small discontinuities in the thermally dependent dielectric permittivity and loss led Coeuré *et al.* (1966) to report T_c (YMnO₃) = 913 K. Other determinations, however, gave discrepant results for the value of T_c . An Arrhenius plot (Peuzin, 1965) of electric resistance ($\log R$, in Ω , versus $1/T$) for $295 < T \lesssim 930$ K was without significant departures from linearity and hence not indicative of a dielectric change in this thermal range.

Łukaszewicz & Karat-Kalicińska (1974) showed, by single-crystal diffractometry, that YMnO₃ reflections with $h + k \neq 3n$ are weak at room temperature and decrease with increasing temperature to become zero at T_c (YMnO₃) \simeq 1270 K. They note these reflections are observable at 1258 K, but not at 1283 K. The dimensions of the hexagonal unit cell above T_c in phase I correspond to $a_I \simeq 3.61$ Å, $c_I \simeq 11.39$ Å. The polar unit cell in phase II, with space group $P6_3cm$ and dimensions $a_{II} \simeq 6.14$ Å, $c_{II} \simeq 11.41$ Å, undergoes reorientation at $T > T_c$ to a cell with space group $P6_3/mmc$ and $a_I = a_{II}/2\cos 30^\circ$; the resulting volume is one-third that at $T < T_c$, see Fig. S1.¹ Łukaszewicz & Karat-Kalicińska's (1974) data, taken provi-

sionally as more reliable, clearly show a decrease (~ 0.028 Å) in the *c* axis between 300 and 1075 K, with much smaller lattice constant discontinuities in the range 895–955 K, in contrast to Ismailzade & Kizhaev's (1965) results, which indicate a discontinuous increase (~ 0.021 Å) in the *c*-axis dimension between 300 and 935 K. The recommended nomenclature of Tolédano *et al.* (1998) for the prototype and ferroelectric phases of YMnO₃, on the basis on these results, is hence shown below.

I	>1270 K	$P6_3/mmc$ (194)	$Z = 2$	Nonferroic	Reoriented unit cell with volume 1/3 that of ferroelectric phase
II	<1270 K	$P6_3cm$ (185)	$Z = 6$	Ferroelectric	2 variants

The atomic coordinates for phase II < 1270 K of van Aken *et al.* (2001*a*),² or their symmetry equivalents, are given in Table 1 with an origin shift in *z* of 0.2505 to minimize $\sum \Delta z$ [by setting $\Delta z(Y1) + \Delta z(Y2) + \Delta z(Mn) = 0$]; Δz as used in (1) is defined below. A view of the YMnO₃ structure, which differs significantly from that of perovskite, may be found in Fig. S2. It is notable that reorientation of the phase I unit cell, see Fig. S1, is accompanied by a symmetry change at the Y2 site from a rotation triad to an inversion hexad screw axis as the Y1 site symmetry changes from a hexad to an inversion hexad screw axis. The coordinate relationship between a given atom in phase I >1270 K and phase II < 1270 K is $x_I = 2x_{II} - y_{II}$, $y_I = x_{II} + y_{II}$, $z_I = z_{II}$. The coordinates $2/3, 1/3, z$ of atom Y2 at Wyckoff position 4(*b*) in phase II thus transform to $0,0,z; 0,0,\bar{z}; 0,0,\frac{1}{2} + z; 0,0,\frac{1}{2} - z$ in phase I. Since $z(Y2) = \bar{z}(Y2)$ in phase I, both coordinates necessarily become zero as the coordinates of Y2 achieve identity with those of Y1 in the resulting $2(a)$ position of phase I, see Table 1. The two independent Y atoms below T_c hence define the unit-cell origin at $T > T_c$.

The x_I, y_I, z_I coordinates in phase I derived from the symmetry operators of space group $P6_3/mmc$, see Table 1, are identical to those of Łukaszewicz & Karat-Kalicińska (1974), except for $z_I(O1)$ and $z_I(O2)$ which these authors estimated at 0.415 and 0.585, respectively. An inability to refine the structure of YMnO₃ from measurements at 1005 K in space group $P6_3/mmc$ was noted as possibly due to disorder.

Table 1 shows there is no difference between corresponding coordinates in phases I and II greater than 0.28 Å. With all atomic displacements significantly larger than their thermal/static displacements but less than an upper limit of ~ 1 Å, the structural criteria for the prediction of ferroelectricity (Abrahams, 1988) are clearly satisfied. It has been shown that T_c may be estimated from (1) below with acceptable accuracy in the case of well determined structural refinement of oxygen or fluorine octahedral ferroelectrics (Abrahams & Ravez,

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR0107). Services for accessing these data are described at the back of the journal.

² Following initial use of the recommended nomenclature, including all six information fields, Tolédano *et al.* (1998) advise that subsequent use in a paper be reduced to two of the first three fields.

Table 1

Atomic coordinates of YMnO₃ at 290 K (van Aken *et al.*, 2001a), hypothetical $x_{\text{I}}y_{\text{I}}z_{\text{I}}$ coordinates above T_c and atomic (Δx , Δy , Δz) and thermal/static (u_{eq}) displacements in Å.

$a_{\text{II}} = 6.1387$ (3), $c_{\text{II}} = 11.4071$ (9) Å at 290 K; $a_{\text{I}} \simeq 3.61$, $c_{\text{I}} \simeq 11.39$ Å at ~ 1285 K. Wyckoff position 6(c) in $P6_3cm$ is $x,0,z$; $0,x,z$; \bar{x},\bar{x},z ; $\bar{x},0,\frac{1}{2} + z$; $0,\bar{x},\frac{1}{2} + x$; $x,\bar{x},\frac{1}{2} + z$. In position 4(b), it is $1/3,2/3,z$; $2/3,1/3,z$; $1/3,2/3,\frac{1}{2} + z$; $2/3,1/3,\frac{1}{2} + z$ and in position 2(a) it is $0,0,z$ and $0,0,\frac{1}{2} + z$. Atomic coordinates in the unit cell with space group $P6_3/mmc$ are given in italics on the line below, as transformed by the relationship between polar cell II and nonpolar cell I: $x_{\text{I}} = 2x_{\text{II}} - y_{\text{II}}$, $y_{\text{I}} = x_{\text{II}} + y_{\text{II}}$, $z_{\text{I}} = z_{\text{II}}$. $z^* = z_{\text{II}} + 0.25050$; $\Delta z = (z^* - z_{\text{I}})c$, where $x_{\text{I}}y_{\text{I}}z_{\text{I}}$ are hypothetical atomic coordinates in cell I with space group $P6_3/mmc$. In the unit cell at ~ 1285 K with space group $P6_3/mmc$ (Łukaszewicz & Karat-Kalicińska, 1974), see §2, Wyckoff position 4(f) in phase I is $1/3,2/3,z$; $2/3,1/3,\bar{z}$; $2/3,1/3,\frac{1}{2} + z$; $1/3,2/3,\frac{1}{2} - z$. In position 2(c), it is $1/3,2/3,\frac{1}{4}$; $2/3,1/3,\frac{3}{4}$; in 2(b), $0,0,\frac{1}{4},0,0,\frac{3}{4}$, and in 2(a), $0,0,0$ and $0,0,\frac{1}{2}$.

	Wyckoff position in $P6_3cm$	Phase II			Wyckoff position in $P6_3/mmc$	Phase I						
		x_{II}	y_{II}	z^*		x_{I}	y_{I}	z_{I}	Δx	Δy	Δz^*	U_{eq}
Y1	2(a)	0	0	0.52172 (12)	2(a)	0	0	1/2	0	0	0.247	0.062
		<i>0</i>	<i>0</i>	<i>0.52172 (12)</i>								
Y2	4(b)	2/3	1/3	0.98091 (3)	2(a)	0	0	0	0	0	-0.217	0.064
		<i>0</i>	<i>0</i>	<i>0.98091 (3)</i>								
Mn	6(c)	0.3352 (4)	0	0.24738 (12)	2(d)	2/3	1/3	1/4	0.023	0.007	-0.030	0.076
		<i>0.6704</i>	<i>0.3352</i>	<i>0.24738 (12)</i>								
O1	6(c)	0.3083 (12)	0	0.4101 (7)	4(f)	2/3	1/3	0.4127	-0.181	-0.090	-0.030	0.089
		<i>0.6166</i>	<i>0.3083</i>	<i>0.4101 (7)</i>								
O2	6(c)	0.6413 (10)	0	0.5846 (6)	4(f)	1/3	2/3	0.5873	-0.181	-0.092	-0.030	0.070
		<i>0.2826</i>	<i>0.6413</i>	<i>0.5846 (6)</i>								
O3	2(a)	0	0	0.7256 (12)	2(b)	0	0	3/4	0	0	-0.278	0.073
		<i>0</i>	<i>0</i>	<i>0.7256 (12)</i>								
O4	4(b)	2/3	1/3	0.2660 (11)	2(b)	0	0	1/4	0	0	0.182	0.095
		<i>0</i>	<i>0</i>	<i>0.2660 (11)</i>								

1992). In ferroelectric YMnO₃, however, the Y1 and Y2 cations occupy distorted monocapped oxygen octahedra, the Mn distorted oxygen trigonal bipyramids, with two-dimensional arrays of Y separating sheets of MnO₅ groups that share equatorial oxygen corners resulting in a net MnO₃ composition, see Fig. S2. Since ferroelectricity is found in the AMnO₃ subfamily and also in the AGaO₃ and AInO₃ subfamilies, all A atoms may be considered as *i*th atoms in (1) below.

The largest metal atom displacement Δz [where $\Delta z = (z^* - z_{\text{I}})c$, for z^* the atomic z_{II} coordinate in phase II after an origin shift along the polar axis and z_{I} the hypothetical z coordinate in the phase I unit cell] between the two phases is $\Delta z(\text{Y1}) = 0.247$ Å, see Table 1. Using (1) to estimate T_c

$$T_c = (\kappa/2k)(\Delta z_i)^2 \text{ K}, \quad (1)$$

where κ is a force constant, k is Boltzmann's constant, Δz_i is the largest displacement along the polar c axis by the *i*th atom and $\kappa/2k = 2.00$ (9) $\times 10^4$ K Å⁻² (Abrahams *et al.*, 1968), which gives T_c as 1220 (100) K. The uncertainty in T_c includes both that in the atomic position polar coordinate and in the force constant $\kappa = 5.52$ (25) kPa. All values of T_c calculated herein from (1) are rounded to the nearest 5 K.

The theoretical basis for (1) is the double-well potential model (*cf.* Kurtz, 1975) in which each atom occupies a minimum at a distance Δz from the intervening potential barrier, see §6. The barrier height associated with the *i*th atom is proportional to T_c (*cf.* Kurtz *et al.*, 1991). Equation (1) has also been derived from mean field theory (Eisenreigler, 1974) and by the use of pseudospin formalism (Elliot, 1971).

Application of a reliable correction to $\Delta z(\text{Y1})$ for the mean polarization displacement of the monocapped oxygen octahedron is not possible in view of the latter's high asymmetry with respect to the mirror plane at $z = \frac{1}{4}$. It is hence noteworthy

that the use of the metal-atom displacement without such a correction in (1) gives a value of T_c in acceptable agreement with experiment, although the force constant in capped octahedra is not necessarily identical to that in uncapped octahedra.

3. Ferroelectric ErMnO₃

The unit cell and atomic arrangement reported for ErMnO₃ by van Aken *et al.* (2001b), as presented in Table S1, closely resembles that in YMnO₃ and the other members of the YMnO₃ family, see Tables 1 and S1–S7. Unpoled ferroelectric crystals generally have a domain distribution that minimizes the net polarization; a 2:1 ratio of domains with opposite polarity is reported in the ErMnO₃ crystal studied. Examination of the resulting atomic coordinates shows the metal atoms are displaced by $\Delta z(\text{Er1}) = 0.256$ (1), $\Delta z(\text{Er2}) = -0.231$ (1) and $\Delta z(\text{Mn}) = -0.025$ (2) Å, with polar displacements for oxygen that range from -0.29 (3) Å in the case of O3 to 0.010 (8) Å for O1 and O2. The corresponding value of T_c from (1), based on $\Delta z(\text{Er1})$, is 1310 (110) K, see §2 and Table 2.

4. Ferroelectric YInO₃

The prediction that YInO₃ is a new ferroelectric with T_c calculated as 810 (90) K (Abrahams, 1988) was based on an assumed phase transition to a paraelectric phase in space group $P6_3/mcm$ without an integral change in cell volume. This assumption led to its high-temperature preparation and the preliminary measurement of its dielectric properties (Hall *et al.*, 1998). A reproducible calorimetric anomaly was observed at 835 (15) K, followed by melting at 1820 (20) K. Dielectric

Table 2

AMnO₃ and YBO₃ family with maximum cation displacements (Å) and Curie temperatures (*T_c*, K), both from (1) and experimentally.

Neither the structure nor the physical properties of GdInO₃, TbInO₃, DyInO₃, HoInO₃ (Pistorius & Kruger, 1976), HoGaO or ErGaO₃ (Geller *et al.*, 1975) have been reported but, with unit cells of *a*_{II} ≈ 6.0, *c*_{II} ≈ 11.4 Å and space group *P6₃cm* at ~300 K, all six materials are also likely to be ferroelectric, see §6.

Column headed 'Calculated *T_c* from (1)': joint uncertainty in *T_c* as calculated from (1) is based on the uncertainty both in the atomic coordinate and the force constant.

	$ \Delta z(A)_{\max} $	Calculated <i>T_c</i> from (1)	Experimental <i>T_c</i>	Reference
YMnO ₃	0.247 (1)	1220 (100)	1270, 915, 935	(a), (b), (c), (d)
LuMnO ₃	0.254†	1290 (165)	>750	(e), (f)
YbMnO ₃	0.252 (1)	1270 (110)	995	(g), (c)
ScMnO ₃				
SC	0.247 (2)	1220 (105)	–	(h)
XRPD	0.246 (34)	1210 (365)	–	(i)
NPD	0.280 (13)	1570 (235)	–	(j)
InMnO ₃	0.164 (57)	540 (375)	–	(h)
TmMnO ₃	–	–	>750	(f)
ErMnO ₃	0.256 (1)	1310 (110)	835	(k), (c)
HoMnO ₃	–	–	875	(c)
YInO ₃	0.195 (10)	760 (120)	835 (15)	(l), (m)
YGaO ₃	0.226 (6)	1020 (100)	–	(n)

(a) van Aken *et al.* (2001a); (b) Łukaszewicz & Karat-Kalicińska (1974); (c) Coeuré *et al.* (1966); (d) Ismailzade & Kizhaev (1965); (e) Yakel *et al.* (1963); (f) Bertaut *et al.* (1963); (g) Isobe *et al.* (1991); (h) Greedan *et al.* (1995); (i) Xu *et al.* (1995); (j) Bieringer & Greedan (1999); (k) van Aken *et al.* (2001b); (l) Pistorius & Kruger (1976); (m) Hall *et al.* (1998); (n) Geller *et al.* (1975). † Uncertainty in *z*(Lu2) assumed to be 0.012 Å.

permittivity and loss anomalies were observed at ~880 K and frequencies to 100 kHz, with the reproducible demonstration of a.c. dielectric hysteresis at room temperature confirming the prediction; the spontaneous polarization was ~0.5 × 10⁻² C m⁻². Dielectric and associated property measurement methods used to characterize new ferroelectrics may be found in Bauer *et al.* (2001).

Reanalysis of the atomic coordinates reported by Pistorius & Kruger (1976), on the basis that phase II of YInO₃ undergoes a transition to space group *P6₃/mmc* as in the case of YMnO₃, shows that Y1 must undergo a displacement of 0.195 Å, Y2 of -0.187 Å, in the course of the transition, see Table S2. These displacements, and those of the remaining atoms, are close to the original values obtained (Abrahams, 1988) on the assumption that the transition was to the space group *P6₃/mcm*.

The resulting calculated value of *T_c* from (1), based on Δ*z*(Y1) = 0.195 (10) Å, is 760 (120) K in good agreement with experiment.

5. Predicted ferroelectric YMnO₃ family members

The 16 members of the YMnO₃ family presented in Table 2 include seven known ferroelectrics; eight members have structures still to be determined in detail and, if confirmed as isostructural with YMnO₃, each is most likely ferroelectric, see §6. Both ScMnO₃ and InMnO₃ are predicted to be new ferroelectrics, with calculated *T_c* values close to 1220 (105) and 540 (375) K, respectively. With the exception of InMnO₃, the

remaining seven known structures have predicted or experimental values of *T_c* ≥ 800 K. The origin of ferroelectricity in YMnO₃ has long been a subject of speculation, see §6, much of which has centered on the ability of the Mn³⁺ ion to occupy the trigonal bipyramidal site. The role of *dsp*³ hybrid bonding with likely high-spin configuration, for example, was discussed by Yakel *et al.* (1963); this, and related models based on the Mn³⁺ cationic *d*⁴ configuration, are clearly inapplicable to In³⁺ with a filled shell in ferroelectric YInO₃. Hill (2000) has suggested the stability of YMnO₃ is ionic size related. The radii of Y³⁺ (VII) and the rare-earth ions from Tb³⁺ (VII) to Lu³⁺ (VII) listed by Shannon (1976) fall within the range 1.10–1.066 Å; the interpolated radius of Sc³⁺ (VII) is ~0.95 Å, that of In³⁺ (VII) is ~1.00 Å. The magnetic moment of 4.78 μ_B for the Mn³⁺ ion in ScMnO₃ (Xu *et al.*, 1995) corresponds to the high spin state; the interpolated radius of Mn³⁺ (V, HS) is ~0.70 Å with that of In³⁺ (V) at ~0.85 Å and Ga³⁺ (V) at 0.69 Å. The metal ion radius thus has a lower limit at the monocapped oxygen octahedral site of ~0.95 Å and an upper limit at the trigonal bipyramidal site of ~0.85 Å. These restrictions are satisfied by In³⁺ at both sites; however, neither Mn³⁺ nor Ga³⁺ with respective radii of ~0.86 and ~0.82 Å satisfy the lower limit at the seven coordination site, in accord with observation.

The largest Δ*z*(A) displacements are by cations in the 2(*a*) and 4(*b*) sites of phase II. Except for LuMnO₃ and InMnO₃, |Δ*z*(A)| for cations in 2(*a*) sites exceed those in the 4(*b*) sites, see Tables 1 and S1–S7. In all family members |Δ*z*(A)_{max}| ≥ 0.2 Å; the apparent anomaly in the case of InMnO₃ is without significance. Displacements at these two sites are of opposite sense in all members. The reliability of the Δ*z* magnitudes and their derivative *T_c* values in Table 2 is dependent on the reliability of the underlying structural determination. Structures not discussed in §§2–4 are hence briefly considered here.

Yakel *et al.* (1963) measured 1186 independent absorption-corrected LuMnO₃ *F*_{obs}² values to determine and refine the structure to a final *R* = 0.13. Refinement was accompanied by large correlations among the variables, with negative (unrealistic) atomic displacement parameters. Uncertainties in the atomic positions, see Table S3, were unavailable and the resulting reliability is likely to be lower than normal. Remeasurement and new refinement is strongly advisable.

A single crystal of YbMnO₃ ground into a 'rough' sphere gave 742 unique *F*_{obs}² > 1.5σ(*F*_{obs}²); refinement with unit weights led to the atomic coordinates in Table S4, with *R* = 0.036, *wR* = 0.053 (Isobe *et al.*, 1991). Comparison with the following results on ScMnO₃, see Figs. S3 and S4, suggests the value of σ[Δ*z*(Yb)_{max}] in Table 2 may be similarly underestimated.

Three separate studies of ScMnO₃ have been reported. Greedan *et al.* (1995) used a triangular crystal plate in the measurement of 378 averaged absorption-corrected independent reflections; a rejection limit on *F*² was unspecified. Refinement gave the atomic coordinates in Table S5(*a*) with final *R* = 0.0283, *wR*(*F*²) = 0.0731. Independently and simultaneously, Xu *et al.* (1995) subjected the powder diffraction pattern of ScMnO₃ to refinement by the Rietveld method, resulting in the atomic coordinates of Table S5(*b*). Neutron diffraction powder patterns of ScMnO₃ were measured by

Bieringer & Greedan (1999) at room temperature and at 5 K intervals between 130 and 10 K. Rietveld refinement of the crystal structure at 300 K gave the nuclear coordinates in Table S5(c); the magnetic structure was also investigated at low temperatures.

Normal probability analysis (Abrahams & Keve, 1971) of the ranked experimental deviates $|\xi_1 - \xi_2|/[\sigma^2(\xi_1) + \sigma^2(\xi_2)]^{1/2}$, where ξ_1 and ξ_2 are the coordinates of a given atom in Tables S5(a) and (c), allows direct comparison of the refinement results. Fig. S1 reveals a difference of 59.5 joint standard uncertainties between the values of $x(\text{O1})$ reported in the two studies; the value in Table S5(c) is likely in error, with $d(\text{Sc1} - \text{O1}) = 2.662$ and $d(\text{Sc2} - \text{O1}) = 1.944$ Å compared with normal distances of ~ 2.14 Å. Neglecting this deviate, the remaining nine exhibit a slope of 5.79 by linear regression against their normal probabilities. If the joint uncertainties are equally distributed between the two refinements, each given uncertainty is then underestimated in the least-squares fit by a factor of approximately four. The corresponding analysis of the atomic coordinates in Tables S5(a) and (b) reveals a discrepancy in the deviate for $x(\text{Mn})$ with a value of 6.06; the source of its error is unknown but, excluding the deviate, see Fig. S3, the slope of 1.10 indicates the large uncertainties assigned by Xu *et al.* (1995) suffice to produce realistic joint uncertainties in the remaining coordinates.

The crystal structure of InMnO_3 at 295 K was determined by Greedan *et al.* (1995) by the use of neutron powder profile analysis, taking 134 independent points on the profile. The refinement resulted in the nuclear coordinates presented in Table S6, with $R_p = 0.071$ and $R_{\text{WP}} = 0.091$. The stated uncertainties are larger, by factors between two and four, than those in Table S5(c) and are hence less likely, with an average of ~ 0.05 Å, to be underestimated; consequently, they result in a large uncertainty for the predicted T_c value.

Refinement of the YGaO_3 structure determination by Geller *et al.* (1975) suffered from parameter correlations comparable to those reported in LuMnO_3 (Yakel *et al.*, 1963). A total of 266 independent reflections were measured, of which 91 were less than an unspecified threshold value. Failure to achieve convergence if all 29 positional and thermal parameters were simultaneously varied led to the setting of $u^{22}(\text{Ga})$ and the 8 thermal parameters for O1 and O2 at the average of previously obtained values. The assigned uncertainties in the resulting atomic coordinates of Table S7, corresponding to $R = 0.04$, $R_2 = 0.072$, are most likely significantly underestimated.

6. Ferroelectricity in the YMnO_3 family

Spontaneous polarization reversibility in the YMnO_3 family, as demonstrated by dielectric hysteresis loop formation at room temperature, depends, in terms of the double-well potential model outlined in §2, on a separation between minima $\lesssim 0.6$ Å along the polar axis for all atoms in the structure. In each case, the intervening potential barrier can be crossed under the application of electric fields greater than the coercive field.

Values of measured and calculated T_c in Table 2 are in satisfactory agreement for four of the ferroelectrics: YMnO_3 , LuMnO_3 , YbMnO_3 , ErMnO_3 and YInO_3 in which both temperature values are known; the difference in the fifth case, ErMnO_3 , loses its possible significance if the (unstated) experimental uncertainty in $T_c \geq 120$ K. The T_c values for YMnO_3 , ErMnO_3 , HoMnO_3 and YbMnO_3 determined from dielectric permittivity measurements were regarded as approximate by the authors, Coeuré *et al.* (1966), hence redetermination is appropriate. The wide experimental range reported in Table 2 for T_c (YMnO_3) is indicative of difficulties both in preparing single-phase ceramic samples and with the high temperature of the phase transition. In addition to redetermining the experimental values of T_c , as stated for seven family members in Table 2, the undetermined values for ScMnO_3 , InMnO_3 and YGaO_3 should be measured together with T_c for GdInO_3 , TbInO_3 , DyInO_3 , HoInO_3 , HoGaO_3 and ErGaO_3 .

The expectation that each member of the $A\text{InO}_3$ subfamily, with $A = \text{Gd}$, Tb , Dy or Ho , is a new ferroelectric rests entirely upon a shared space group and unit cell similar to that of the known ferroelectric YInO_3 (Hall *et al.*, 1998), see §4. Likewise, both members of the $AGaO_3$ subfamily with $A = \text{Ho}$ or Er are expected to be ferroelectric in view of their comparability with the structurally predicted ferroelectric YGaO_3 , see §5. If preparation and dielectric measurement confirm these six family members to be ferroelectric, then the YMnO_3 family will rank among the largest to exhibit this important property.

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