Structurally Based Predictions of Ferroelectricity in Seven Inorganic Materials with Space Group *Pba2* and Two Experimental Confirmations

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Abstract

Application of structural criteria presented previously, to all entries in the Inorganic Crystal Structure Database for materials crystallizing in space group *Pba2*, has led to the prediction of seven new ferro-electrics. These materials, with estimates of their respective predicted transition temperatures (T_c) to an assumed paraelectric phase, are: $Na_{13}Nb_{35}O_{94}$ (340 K), $K_3Fe_5F_{15}$ (535 K), $Mo_{17}O_{47}$ (1750 K), $Bi_3Nb_{17}O_{47}$ (500 K), $Ba_{15}Pr_{38}Ti_{72}O_{216}$ (650 K), $K_3Sb_5O_{14}$ (340 K) and $Ca_2Ge_7O_{16}$ (close to room temperature if the structure determination is correct). Experimental confirmation has now been made for two of these predictions, with a T_c of 320 (10) K found in Na_{13}-$Nb_{35}O_{94}$ and 490 (10) K found in $K_3Fe_5F_{15}$. Five of the newly predicted ferroelectrics are related to the tetragonal-bronze structure.

Introduction

Structural criteria have been presented by Abrahams (1988) for the prediction of ferroelectricity in inorganic crystals. Preparatory to undertaking a systematic investigation of the atomic coordinates of all inorganic crystals in each of the polar point groups for which the structure has been reported in the Inorganic Crystal Structure Data (ICSD) numerical database (see *Crystallographic Databases*, 1987), an analysis was made in 1987 of all such data for materials listed therein as crystallizing in space group *Pba2*. This test space group was selected since two well-known ferro-electric crystals form in it.

The latest release of ICSD, both in 1987 and at the original time of writing this paper, contains 20 entries in space group *Pba2*.† Three entries are without atomic coordinates, four refer to the two familiar ferroelectrics $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$ and one identifies the known antiferroelectric $PbZrO_3$. Three of the remaining entries are to separate refinements reported for Mo_{17}-O_{47}, leaving ten different structures to be examined for

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† An additional entry, concerning $In_2Ga_2Fe_2O_9$, is contained in the current release of ICSD with nominal date July 1988, see below.

possible evidence of ferroelectricity in terms of the criteria presented previously.

The validity of the prediction that seven new ferroelectric crystals may be found in space group *Pba2*, as set forth below, depends closely on the quality of the structural determinations. A brief account of each is hence included in lieu of a shorter, but as adequate a quality, descriptor. It may, however, be noted that experimental confirmation has now been presented for the first two materials of which single crystals were grown, and that the measured and predicted phase-transition temperatures agree within 20 K for each of these two.

Ferroelectrics predicted in space group *Pba2*

$Na_{13}Nb_{35}O_{94}$

The atomic coordinates of the tungsten-bronze-type structure $Na_{13}Nb_{35}O_{94}$ have been reported by Craig & Stephenson (1971). Earlier authors had variously described this material as $NaNb_3O_8$, $Na_2Nb_8O_{21}$ and $Na_{12}Nb_{34}O_{90}$. The unit-cell dimensions at room temperature are $a = 12\cdot364$ (1), $b = 36\cdot992$ (4) and $c = 3\cdot955$ (1) Å. Refinement by Craig & Stephenson of a model with anisotropic thermal parameters for all atoms, using 1651 symmetry-independent reflections in which $I_o > 3\sigma(I_o)$ and with correction only for the real component of the Cu $K\alpha$ anomalous scattering, resulted in $R = 0\cdot045$. Examination of their atomic coordinates shows that all are close to the paraelectric set xyz', with $z' = 0$ or $\frac{1}{2}$, corresponding to the structure in space group *Pbam*. The atomic displacements along the polar axis, between the room-temperature set and the predicted set in the paraelectric phase, may be taken here and elsewhere in this paper as $\Delta z = z - z'$. The temperature T_c, at which all Δz displacements that contribute to the spontaneous polarization become zero, denotes the phase-transition temperature.

All cations in $Na_{13}Nb_{35}O_{94}$ are displaced either in the same sense along the polar c axis or have $\Delta z = 0$ within 2σ, except for Nb(9) which is the only Nb atom to occupy a pentagonal bipyramid; all others occupy octahedra of O atoms. Similarly, the O atoms are all displaced in the opposite sense, or have $\Delta z = 0$ within 2σ, except for O(1). Furthermore, all Δz displacements

are less than 0·3 Å. The average magnitude of the six largest Nb-atom displacements from the nearest average plane of octahedrally bonded O atoms, excluding Nb(9), is 0·13 (3) Å. It is noted that Craig & Stephenson (1971) report in their text that the displacement for this atom is 0·15 Å, in the opposite sense, from the basal plane of its polyhedron.

The average Δz displacement leads to $T_c = 340$ K, based on the Abrahams, Kurtz & Jamieson (1968) relationship $T_c = (\mathcal{K}/2k)(\Delta z)^2$ K, where $\mathcal{K}$ is a force constant and k is Boltzman's constant with $\mathcal{K}/2k \simeq 2\cdot0 \times 10^4$ K Å^{-2}. This ratio remains rather constant in structures built up from O- and/or halogen-atom octahedra; it is, however, not a universal constant and may vary appreciably in ferroelectrics of widely differing structural type. A forthcoming paper will consider such variations and the structural limits of applicability of the underlying relationship.

Experimental confirmation of ferroelectric-like properties in $Na_{13}Nb_{35}O_{94}$ has now been reported by Abrahams, Brandle, Berkstresser, O'Bryan, Bair, Gallagher & Drotning (1989), see below, who also present all Δz values for this structure.

$K_3Fe_5F_{15}$

The xyz atomic coordinates of the tungsten-bronze-type structure $K_3Fe_5F_{15}$, as reported by Hardy, Hardy & Ferey (1973), are included in Table 1. All atomic positions determined are within 0·25 Å of the corresponding positions in ferroelectric tetragonal tungsten-bronze-type $Ba_3TiNb_4O_{15}$ (Jamieson & Abrahams, 1968). The unit-cell dimensions of the material with the formula given by Hardy et al. as $K_{0.6}FeF_3$ are $a = 12\cdot750$ (2), $b = 12\cdot637$ (2) and $c = 3\cdot986$ (2) Å. Their refinement of a model with isotropic thermal parameters was based on 297 independent visually estimated intensities, and led to a final $R = 0\cdot107$. A related set of $x'y'z'$ coordinates is also presented in Table 1, in which the sense of the polar direction is reversed, as discussed below. The difference between corresponding sets of coordinates gives the displacements $2\Delta x = x - x'$, $2\Delta y = y - y'$ and $2\Delta z = z - z'$. It is noted that the factor of two in Δz between $z - z'$ here and for $Na_{13}Nb_{35}O_{94}$ is due to z' representing a reversed polar displacement sense in $K_3Fe_5F_{15}$ and zero polar displacement in $Na_{13}Nb_{35}O_{94}$. The largest magnitude of $2\Delta x$ or $2\Delta y$ is 0·011 Å, for F(7) and F(8). The magnitudes of $2\Delta z$ are given in Table 1.

The equivalence among the positions xyz; $\bar{x}\bar{y}z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, z; and $\frac{1}{2}+x$, $\frac{1}{2}-y$, z in space group $Pba2$ is used in deriving the $x'y'z'$ coordinates of Table 1 together with an exchange of identity between atoms Fe(2) and Fe(3), F(3) and F(4), F(5) and F(6), and also F(7) and F(8). In addition, the sign of the y coordinate is reversed in deriving x'. The resulting two sets of coordinates are

Table 1. Atomic coordinates (x and y, x' and $y' \times 10^4$; z and $z' \times 10^3$) of $K_3Fe_5F_{15}$ in two spontaneous polarization and strain states at room temperature, with corresponding atomic polar displacements

	x	y	z	x'	y'	z'	$2\Delta z$ (Å)
K(1)	0	0	0	0	0	0	0
K(2)	1729 (9)	6729 (9)	8 (11)	1729	6729*	−8	0·064
Fe(1)	0	$\frac{1}{2}$	501 (9)	0	$\frac{1}{2}$*	499	0·008
Fe(2)	763 (4)	2135 (4)	541 (7)	763	2136†	459	0·327
Fe(3)	7864 (4)	763 (4)	541 (7)	7865	763†	459	0·327
F(1)	0	$\frac{1}{2}$	30 (61)	0	$\frac{1}{2}$	−30	0·239
F(2)	2785 (14)	7783 (14)	549 (19)	2783	7785*	451	0·391
F(3)	734 (18)	2067 (18)	41 (23)	734	2065‡	−43	0·335
F(4)	7935 (17)	734 (18)	43 (22)	7933	734‡	−41	0·335
F(5)	3502 (14)	65 (13)	580 (12)	3497	66‡	420	0·638
F(6)	9934 (13)	3497 (14)	580 (12)	9935	3502‡	420	0·638
F(7)	1372 (15)	728 (14)	527 (18)	1374	719‡	471	0·223
F(8)	9281 (14)	1374 (15)	529 (18)	9272	1372‡	473	0·223

* $x' = \frac{1}{2} - y$ and $y' = \frac{1}{2} + x$ in $Pba2$, with the sign of y in the former equality reversed, see text.

† Fe(2) and Fe(3) exchange identity, see text.

‡ F(3) and F(4), F(5) and F(6), and F(7) and F(8) exchange identity, see text.

related by $xyz = \bar{y}x\bar{z} + \Delta$, where the vectorial displacement $\Delta = 2\Delta x + 2\Delta y + 2\Delta z$ with $2\Delta x = x - x'$, $2\Delta y = y - y'$ and $2\Delta z = z - z'$. This coordinate relationship may also be expressed in terms of the unit-cell transformation $abc = \bar{b}a\bar{c} + \Delta$, i.e. the original a axis is replaced in the transformation by the transposed b axis with a change in sense, the original b axis is replaced by the transposed a axis without a change in sense, and the polar c axis is reversed in sense.

The transformation is physically interpretable either as allowing a ferroelastic interchange of the a and b axes under an applied stress as the polar axis consequently reverses direction ferroelectrically, or as a reorientation of spontaneous strain following a reversal of the spontaneous-polarization sense in an external electric field, since the maximum value of $\Delta z = 0\cdot32$ Å [for F(5) and F(6)] lies well within the required structural range for ferroelectric crystals. Taking the largest value of Δz for Fe, regarded here as the critical atom that forms the shortest and least ionic bonds in the structure, then T_c is predicted to be 535 K from the Abrahams et al. (1968) relationship.

Confirmation of the coupled ferroelectric and ferroelastic properties of $K_3Fe_5F_{15}$ has now been made and the transition temperature to a paraelectric paraelastic phase has been measured as 490 (10) K by Ravez, Abrahams & de Pape (1989), see below. The observation of optical isotropy along [001] in the phase above T_c and a consideration of the resulting atomic arrangement leads to the choice of $P4/mbm$ as the most likely space group for this phase.

$Mo_{17}O_{47}$

Three reports have appeared on the structure of $Mo_{17}O_{47}$, by Kihlborg (1960), Kihlborg (1963) and Yamazoe, Ekström & Kihlborg (1975). The two earlier

studies, on the pure material, are based on visually estimated photographically recorded intensities; the later investigation is on a composition in which 7% of the Mo is substituted by V, and is based on diffractometer data. The unit-cell dimensions of $Mo_{17}O_{47}$ at room temperature are $a = 21 \cdot 615$ (5), $b = 19 \cdot 632$ (5) and $c = 3 \cdot 9515$ (5) Å (Kihlborg, 1960). The final structural model included isotropic thermal parameters for each atom and refinement made use of 773 independent reflections, giving $R = 0 \cdot 057$. The atomic coordinates considered here are those of Kihlborg (1963), but with his origin along the polar axis translated by 0·002, *e.g.* $z[Mo(1)] = 0 \cdot 5770$, to set the largest and smallest Δz atomic displacements for Mo equal. The corresponding z' coordinate of each atom in the hypothetical paraelectric phase, for which *Pbam* is the most likely choice of space group, is either 0 or $\frac{1}{2}$. With no Δz displacements greater than $\pm 0 \cdot 33$ Å, the structure of $Mo_{17}O_{47}$ readily satisfies the structural criteria for ferroelectric behavior. The range in Δz for the nine independent Mo atoms, eight of which occupy distorted MoO_6 octahedra but with Mo(9) in a distorted pentagonal bipyramid, is large. Substitution of V causes changes in Δz of as much as 0·1 Å (Yamazoe *et al.*, 1975). The uncertainty in Δz suggests the use of $\langle |\Delta z| \rangle = 0 \cdot 297$ Å in predicting the temperature at which $Mo_{17}O_{47}$ becomes ferroelectric, rather than Δz_{max}, hence T_c is estimated to be about 1750 K with an uncertainty of about 800 K caused by the O atom e.s.d.'s.

$Bi_3Nb_{17}O_{47}$

The structure of this tungsten-bronze-type crystal has been determined by Keve & Skapski (1971). The unit-cell dimensions at room temperature are $a = 12 \cdot 516$ (5), $b = 37 \cdot 14$ (2) and $c = 3 \cdot 922$ (2) Å and generally resemble those of $Na_{13}Nb_{35}O_{94}$ above. Their 1971 refinement was based on visually estimated intensities; 1278 independent reflections were used, with a model that included anisotropic thermal parameters and variable site-occupancy factors for the Bi sites, to give a final $R = 0 \cdot 097$. None of the six Bi sites is fully occupied, but instead each is reported to contain from 0·5 to 0·1 Bi atom per site, leading to the given overall formula. The resulting atomic coordinates, but with atom Nb(1) defining the origin set at $z = \frac{1}{2}$ rather than the previous $z = 0 \cdot 553$, are close to those in the hypothetical high-temperature phase with space group *Pbam* for which all z' coordinates are 0 or $\frac{1}{2}$. These coordinates show that all Bi atoms are within 0·11 Å of the paraelectric phase z' coordinates and all other atoms are within 0·5 Å. The crystal hence satisfies the necessary structural criteria for ferroelectricity. The largest Δz displacement for Nb is 0·157 Å, corresponding to $T_c \simeq 500$ K if the O-atom displacements from their paraelectric positions are neglected in view of their

large e.s.d.'s. Keve & Skapski (1971) recognized that $Bi_3Nb_{17}O_{47}$ might be ferroelectric and calculated the spontaneous polarization from the atomic displacements as about 8(2) μC cm⁻².

$Ba_{15}Pr_{38}Ti_{72}O_{216}$

The atomic coordinates of this tungsten-bronze-type structure (the given formula represents the contents of one unit cell) were reported by Matveeva, Varfolomeev & Il'yushchenko (1984). The unit-cell dimensions at room temperature are $a = 22 \cdot 360$ (7), $b = 12 \cdot 181$ (4) and $c = 3 \cdot 832$ (4) Å. Refinement of a model with variable occupancy factors for the Ba and Pr atom sites, based upon 1990 reflections measured with a diffractometer, resulted in $R = 0 \cdot 090$. Weak reflections corresponding to a superstructure with doubled c axis were observed but not included in the model. The present structure is hence to be regarded as an average of the supercell atomic arrangement. An examination of these 1984 coordinates, in which all atoms are translated along the polar axis to place the origin at $z[Pr, Ba(1)] = \frac{1}{2}$ rather than the previous 0·530, shows that all z coordinates are close to the predicted paraelectric phase z' coordinates in space group *Pbam*, *i.e.* 0 or $\frac{1}{2}$. The largest value of Δz is less than 0·32 Å; hence this complex titanate satisfies the structural criteria for ferroelectricity. The maximum atomic displacement for Ti is 0·180 Å, neglecting the contribution by the O atoms, which hence leads to a predicted T_c of about 650 K.

In addition to the Pr compound, an isostructural series has been reported by Gens, Varfolomeev, Kostomarov & Korovin (1981) in which Pr is successively replaced by each rare-earth element from La to Gd.

$K_3Sb_5O_{14}$ *and family*

The atomic coordinates of $K_3Sb_5O_{14}$ at room temperature, as reported by Aurivillius (1966), are presented in Table 2. The unit-cell dimensions are $a = 24 \cdot 211$ (5), $b = 7 \cdot 153$ (2) and $c = 7 \cdot 322$ (2) Å. Structure refinement of a model with isotropic thermal parameters for each atom was based on 1768 visually estimated and photographically recorded reflections. The final value of R was 0·130 in space group *Pba*2 and 0·131 in space group *Pbam*. The polar space group was chosen in view of coordinate deviations from centrosymmetry, following refinement, that were deemed to be significant. Physical measurements to support the polar choice were not reported; assuming the choice is correct, Table 2 also gives the z' coordinate for each atom in a structure with reversed sense for the spontaneous polarization. Atoms Sb(4) and Sb(5); O(8) and O(9); O(10) and O(11); O(12) and O(13); and also O(14) and O(15) exchange identity in this reversal of the polar-axis sense. Table 2 also

Table 2. *Atomic coordinates* (K, Sb $\times 10^4$; O $\times 10^3$) *of* $K_3Sb_5O_{14}$ *in two spontaneous polarization states at room temperature, with corresponding atomic polar displacements*

	x	y	z	z'	$2\Delta z$(Å)
K(1)	144 (5)	2189 (21)	302 (30)	−302	0·442
K(2)	3837 (5)	1001 (20)	9868 (29)	132	−0·193
K(3)	2940 (6)	1091 (23)	5064 (60)	4936	0·094
Sb(1)	9381 (1)	961 (4)	5000	5000	0
Sb(2)	5571 (1)	837 (3)	5085 (9)	4915	0·124
Sb(3)	2562 (1)	3246 (3)	121 (110)	−121	0·177
Sb(4)	1456 (1)	1101 (4)	2458 (5)	2274*	0·135
Sb(5)	1450 (1)	1073 (5)	7726 (5)	7542*	0·135
O(1)	0	$\frac{1}{4}$	346 (8)	295	0·37
O(2)	0	$\frac{1}{2}$	705 (6)	654	0·37
O(3)	122 (1)	175 (5)	6 (13)	−6	0·09
O(4)	143 (1)	35 (4)	515 (12)	485	0·22
O(5)	17 (1)	163 (3)	523 (7)	477	0·34
O(6)	91 (1)	662 (5)	534 (7)	466	0·50
O(7)	218 (1)	566 (3)	10 (11)	−10	0·15
O(8)	99 (2)	322 (7)	312 (7)	300*	0·09
O(9)	107 (1)	345 (5)	700 (5)	688*	0·09
O(10)	75 (1)	954 (5)	248 (6)	240*	0·06
O(11)	73 (1)	946 (5)	760 (6)	752*	0·06
O(12)	211 (2)	268 (6)	246 (7)	209*	0·27
O(13)	211 (1)	256 (5)	791 (6)	754*	0·27
O(14)	314 (1)	376 (6)	202 (6)	168*	0·25
O(15)	315 (1)	385 (5)	832 (6)	798*	0·25

* An exchange of atomic identity is made, see text.

Table 3. *Atomic coordinates* ($\times 10^4$) *of* $Ca_2Ge_7O_{16}$ *at room temperature in two spontaneous polarization and strain states, with atomic polar displacements*

	x	y	z	x'	y'	z'	$2\Delta z$(Å)
Ge(1)	0	0	0	0	0	0	0
Ge(2)	1335 (1)	1336 (1)	4996 (3)	1336	1335	5004	−0·002
Ge(3)	666 (1)	3122 (1)	−107 (1)	667	3123	−95*	−0·006
Ge(4)	3123 (1)	667 (1)	95 (3)	3122	666	107*	−0·006
Ca	3350 (1)	3348 (1)	4970 (6)	3348	3350	5030	−0·028
O(1)	12	1167 (5)	7467 (13)	6	1171	7579*	−0·052
O(2)	1171 (5)	6 (5)	2421 (12)	1167	12	2533*	−0·052
O(3)	288 (5)	2197 (5)	2695 (13)	282	2198	2820*	−0·058
O(4)	2198 (5)	282 (5)	7180 (13)	2197	288	7305*	−0·058
O(5)	1686 (5)	2658 (5)	7246 (13)	1697	2657	7355*	−0·051
O(6)	2657 (5)	1697 (5)	2645 (13)	2658	1686	2754*	−0·051
O(7)	1398 (5)	4316 (5)	1548 (13)	1403	4327	1694*	−0·068
O(8)	4327 (5)	1403 (5)	8306 (14)	4316	1398	8452*	−0·068

* An exchange of atomic identity is made, see text.

$z' = \bar{z}$, with atoms Ge(3) and Ge(4); O(1) and O(2); O(3) and O(4); O(5) and O(6); and also O(7) and O(8) exchanging identity. The original atomic numbering has been modified in Table 3. If the experimental structural solution is indeed correct, then $Ca_2Ge_7O_{16}$ is ferroelectric and ferroelastic, with two states for the unit cell as expressed by the cell transformation $\mathbf{abc} = \mathbf{ba\bar{c}} + \mathbf{\Delta}$. However, the given RMS amplitude of thermal displacement for each atom is comparable to the displacement required that transforms each value of xyz into $x'y'z'$; such an atomic arrangement may well be unstable and the crystal symmetry may hence differ from that assumed at room temperature.

It is apparent that the magnitudes of the atomic displacements in Table 3 are also inconsistent with the development of ferroelectricity at room temperature, since the minimum polar displacement of a Ge atom is expected to be about 0·12 Å from consideration of the Abrahams *et al.* (1968) relationship. Corrections by this magnitude or more, to at least some of the present z coordinates, are necessary to bring the Δz displacements into conformity with ferroelectric behavior. Alternatively, if the crystal is not ferroelectric, then all Δz displacements as given in Table 3 should be zero and the possibility of tetragonal symmetry should be reinvestigated for an improved structure solution (with xyz and $yx\bar{z}$ thereupon becoming equivalent positions). Further measurements on $Ca_2Ge_7O_{16}$ are in order.

includes the doubled value of atomic displacement for each atom along the polar axis that is necessary for the structure to form the paraelectric phase, with likely space group *Pbam*, at room temperature.

Table 2 contains no Δz magnitude greater than 0·25 Å; hence, if the crystal is indeed polar, it satisfies the criteria for structural ferroelectricity. The largest Sb atomic displacement of 0·089 Å [for Sb(3)] is, however, too small to represent a phase transition above room temperature; nevertheless, allowing for the additional 0·04 Å displacement necessary to place Sb(3) in the center of its octahedron leads to $T_c \simeq 340$ K. Further experimental investigation of $K_3Sb_5O_{14}$ is clearly appropriate.

$Rb_3Sb_5O_{14}$ is also reported by Aurivillius (1966) to be isomorphous with $K_3Sb_5O_{14}$.

$Ca_2Ge_7O_{16}$

The atomic coordinates of $Ca_2Ge_7O_{16}$ at room temperature, as reported by Nevskii, Il'yukhin, Ivanova & Belov (1979), are contained in Table 3. With unit-cell dimensions $a = b = 11·340$ (2) and $c = 4·640$ (1) Å, the crystal symmetry was initially thought to be tetragonal, but the structure was finally solved in space group *Pba2*. Refinement based on 866 independent non-zero reflections and isotropic thermal parameters gave $R = 0·024$. Examination of Table 3 shows that for each atom at xyz, there is an equivalent atom at $x'y'z'$, with all values of $2\Delta x = x - x'$, $2\Delta y = y - y'$ and $2\Delta z = z - z'$ less than 0·07 Å.

These equivalent atomic coordinates are related to those of Nevskii *et al.* (1979) by $x' = y$, $y' = x$ and

Confirmation of ferroelectric phase transition in $Na_{13}Nb_{35}O_{94}$ and in $K_3Fe_5F_{15}$

$Na_{13}Nb_{35}O_{94}$

Single crystals of $Na_{13}Nb_{35}O_{94}$ have been grown with maximum dimensions of 2 cm diameter and 5 cm length (Abrahams *et al.*, 1989). A reversible phase transition, with very small entropy change, is detected calorimetrically at 308 K. Dilatometry reveals a phase transition at a temperature of about 318 K. Thermal cycling results in T_c varying between 315 and 335 K. A

broad but minor anomaly is also found in the dielectric permittivity at about 340 K over a range of frequencies. The transition, which appears to be second or higher order and rather gradual, is comparable to those often found in glasses.

$K_3Fe_5F_{15}$

The dielectric permittivity in $K_3Fe_5F_{15}$ passes through a sharp anomaly at 495 (10) K as the dielectric loss undergoes a change in slope (Ravez *et al.*, 1989). The heat capacity exhibits a λ-type anomaly at 490 (10) K, with an entropy change of 5·5 (2) J mol^{-1} K^{-1}; the value calculated from the predicted change in structure is 5·42 J mol^{-1} K^{-1}. The ferroelastic domains disappear abruptly on heating above 490 (10) K and reappear on cooling below 480 (10) K.

Nonferroelectric structures determined in *Pba*2

The atomic coordinates of $Au_2(SeO_3)_2O$, $K[Al_2F(H_2O)_4(PO_4)_2]$ and $Mn(NH_2NHCOO)_2(H_2O)_2$ are listed by ICSD in space group *Pba*2, in addition to those mentioned in the *Introduction* and those predicted above to be ferroelectric. These final three structures do not satisfy the criteria for ferroelectricity.

Additional entry in ICSD release of 1988

The structure of $In_2Ga_2Fe_2O_9$, reported by Nodari, Malaman & Evrard (1985), forms the 21st entry in space group *Pba*2 of ICSD. With unit-cell dimensions, at room temperature, of $a = 19·253$ (3), $b = 7·2176$ (2) and $c = 3·2581$ (1) Å, 420 independent reflections with $I > 3\sigma(I)$ were measured by means of Ag $K\alpha$ radiation; absorption corrections were neglected as were anomalous-dispersion corrections. Refinement of a model with isotropic thermal parameters for all atoms gave $R = 0·037$. An origin translation along the c axis

by 0·323 reveals that no atom is displaced from a mirror plane at $z = 0$ or $\frac{1}{2}$ by more than 2·8 e.s.d. It may hence be concluded that the given structure does not differ significantly from the alternative arrangement in space group *Pbam* in which atoms In(1), Fe(3), Ga(3), O(1) and O(5) have $z = 0$ and the remaining atoms have $z = \frac{1}{2}$. The structure, with maximum atomic displacement by a metal atom of 0·033 Å from a mirror plane, is hence not predicted to be ferroelectric; further structural investigation is appropriate.

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Electron Density Distribution in Cs3CoCl5

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Abstract

An X-ray diffraction data set was collected at 115 K from a crystal of Cs_3CoCl_5, which contains the $CoCl_4^{2-}$ anion. A 63-parameter multipole analysis based upon 1713 unique reflections of wavevector $< 1·08$ Å^{-1} yielded $wR(I) = 0·026$ with $\chi^2 = 0·731$; $R(F) = 0·013$ for 1384 data with $I > 3\sigma(I)$. The multipole parameters are consistent with the cobalt $3d$ orbital expanded radially by 7 (1)% and populated $e^{4·3 (2)} t_2^{3·2 (2)}$. The

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