

Systematic prediction of new inorganic ferroelectrics in point group 4

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Abstract

The latest release of the Inorganic Crystal Structure Database contains a total of 87 entries corresponding to 70 different materials in point group 4. The structures reported for 11 materials in space group $P4$ satisfy the criteria for ferroelectricity, as do four in $P4_1$, one each in $P4_2$ and $P4_3$, 12 in $I4$, including seven that form three families, and another three in $I4_1$. Three previously known ferroelectrics were also listed in $I4$ and one in $I4_1$. In addition, the listing for point group 4 contains 22 entries for nonferroelectric materials and three with misassigned space groups. Among the newly predicted ferroelectrics in point group 4, assuming the validity of the underlying structural reports, are $Ce_5B_2C_6$, modulated $NbTe_4$, $Na_3Nb_{12}O_{31}F$, Ca_2FeO_3Cl , $K_4CuV_5O_{15}Cl$, $TiBO_2$, $CrOF_3$, $PbTeO_3$, $VO(HPO_3)(H_2O).3H_2O$, $MgB_2O(OH)_6$, β -tetragonal boron, $CuBi_2O_4$, $WOBr_4$, Na_8PtO_6 , SbF_2Cl_3 , $Ba_{1.2}Ti_8O_{16}$, $Ni[SC(NH_2)_2]_4Cl_2$, $Ca_2SiO_3Cl_2$, the mineral caratiite, $NbAs$, β - NbO_2 and Ag_3BiO_3 .

1. Introduction

Criteria developed for predicting ferroelectricity in polar crystals on the basis of crystal structure include (a) that no i th atom forming the shortest and least ionic bonds in the unit cell of such a crystal shall have a displacement $\Delta z \gtrsim 1 \text{ \AA}$, where $\Delta z = (z_i - z_{P_i=0})_c$, along the polar direction between the location reported at xyz and that at which the resulting spontaneous polarization $P_s = 0$, and (b) that the largest $\Delta z \gtrsim 0.1 \text{ \AA}$ or its r.m.s. thermal or static displacement u (Abrahams, 1988). The upper limit in criterion (a), based on the atomic displacements characteristic of known ferroelectrics, is associated with the height of the largest potential barrier that may be crossed by application of an external electric field; that in criterion (b) is associated with barrier heights comparable to the thermal energy kT . The corresponding Curie temperature T_c is related to Δz_i by (1), as given by Abrahams *et al.* (1968), hereafter AJK

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

where κ is a force constant, k is Boltzmann's constant, Δz_i is the largest displacement by the i th atom along the

polar c axis, as defined in criterion (a), and $\kappa/2k = 2.00(9) \times 10^4 \text{ K \AA}^{-2}$ for structures in which the i th atom occupies an octahedron of O or F atoms. These criteria have been applied to all entries in the Inorganic Crystal Structure Database (ICSD), see Bergerhoff & Brown (1987), listed under space group $Pba2$ (Abrahams, 1989) and also to all entries under point group $6mm$ (Abrahams, 1988), point group 6 (Abrahams, 1990) and point group $4mm$ (Abrahams, 1996). In consequence, seven new ferroelectrics have been predicted in space group $Pba2$, ~ 40 in point group $6mm$, ~ 50 in point group 6 and ~ 40 in point group $4mm$. The uncertainty in the number of reliable predictions is due to the possibility that some structure determinations may be erroneous, see for example Abrahams *et al.* (1998). Further uncertainty is caused by the undetermined number of isostructural members in many predicted families.

The value of a predicted new ferroelectric is greatly enhanced if the ferroelectric property can be confirmed experimentally. Confirmation, which requires sample preparation followed by measurement of the appropriate dielectric and related properties, has been presented for $Na_{13}Nb_{35}O_{94}$ (Abrahams *et al.*, 1989) and $K_3Fe_5F_{15}$ (Ravez *et al.*, 1989) in space group $Pba2$. The property of ferroelasticity, in addition to ferroelectricity, was also predicted in $K_3Fe_5F_{15}$; both properties were confirmed by Ravez *et al.* (1989), as was the direct coupling between them. Among recent systematic predictions of new ferroelectrics are those of the semiconductor Sr_2SbMnO_6 (Foster, Brown *et al.*, 1997), the tungsten-bronzes $Ba_6CoNb_9O_{30}$ and $Ba_6FeNb_9O_{30}$ (Foster, Nielson *et al.*, 1997), the mineral fresnoite $Ba_2TiOSi_2O_7$ (Foster *et al.*, 1999a) and $K_2(NbO)_2Si_4O_{12}$ (Foster *et al.*, 1999b) in point group $4mm$; other newly predicted ferroelectrics have been prepared and their ferroic properties confirmed in a series of ongoing investigations in the undergraduate laboratories at Southern Oregon University.

The present total number of unique known ferroelectrics, *i.e.* excluding solid solutions between two or more known end members, may be extrapolated to ~ 240 from the estimate made by Nakamura (1989) of ~ 200 pure ferroelectrics. The strong demand for an increased selection of ferroelectric materials exhibiting more advantageous nonlinear optic and electronic properties than currently available may be better met by the

Table 1. Wyckoff positions, occupancy factors and atomic coordinates for $Ce_5B_2C_6$ at room temperature with hypothetical z' coordinates and polar displacements (\AA)

$a = 8.418$ (3), $c = 12.077$ (4) \AA . $z^* = \text{authors' } z + 0.0040$; $\Delta z = (z' - z^*)c$.

Atom	Wyckoff position $P4, P4/m$	Occupancy	x	y	z^*	z'	Δz
Ce1	4(<i>d</i>), 4(<i>j</i>)	1	0.4029 (2)	0.2072 (2)	-0.0264 (2)	0	-0.319
Ce2	4(<i>d</i>), 4(<i>k</i>)	1	0.2053 (2)	0.4036 (3)	0.4671 (2)	$\frac{1}{2}$	0.397
Ce3	4(<i>d</i>)	1	0.2941 (2)	0.0976 (3)	0.2534 (2)	0.2467	0.081
	8(<i>l</i>)						
Ce4	4(<i>d</i>)	1	0.0971 (3)	0.2960 (3)	0.7601 (2)	0.7533	0.081
Ce5	1(<i>b</i>)	1	$\frac{1}{2}$	$\frac{1}{2}$	0.2340 (6)	0.2455	-0.139
	2(<i>h</i>)						
Ce6	1(<i>b</i>)	1	$\frac{1}{2}$	$\frac{1}{2}$	0.7430 (5)	0.7545	-0.139
Ce7	1(<i>a</i>), 1(<i>b</i>)	1	0	0	0.4953 (5)	$\frac{1}{2}$	0.057
Ce8	1(<i>a</i>), 1(<i>b</i>)	1	0	0	0.0040	0	-0.048
C1	4(<i>d</i>), 4(<i>j</i>)	1	0.090 (6)	0.291 (6)	-0.020(4)	0	0.242
C2	4(<i>d</i>), 4(<i>k</i>)	1	0.288 (5)	0.103 (5)	0.449 (4)	$\frac{1}{2}$	0.616
C3	4(<i>d</i>)	1	0.191 (6)	0.386 (6)	0.228 (4)	0.267	-0.477
	8(<i>l</i>)						
C4	4(<i>d</i>)	1	0.379 (5)	0.187 (5)	0.693 (4)	0.733	-0.477
C5	4(<i>d</i>)	$\frac{1}{4}$	$\frac{1}{2} + \delta$	$\frac{1}{2} + \delta'$	0.433†	0.446	-0.145
	8(<i>l</i>)						
C6	4(<i>d</i>)	$\frac{1}{4}$	$\frac{1}{2} + \delta$	$\frac{1}{2} + \delta'$	0.542	0.554	-0.145
C7	4(<i>d</i>)	$\frac{1}{4}$	0.538	0.519	-0.060	-0.045	-0.175
	8(<i>l</i>)						
C8	4(<i>d</i>)	$\frac{1}{4}$	0.538	0.519	0.029	0.045	-0.175
C9	4(<i>d</i>)	$\frac{1}{4}$	0.019	0.038	0.203	0.200	0.036
	8(<i>l</i>)						
C12	4(<i>d</i>)	$\frac{1}{4}$	$0 + \delta$	$0 + \delta'$	0.803	0.800	0.036
C10	4(<i>d</i>)	$\frac{1}{4}$	0.019	0.038	0.293	0.299	-0.072
	8(<i>l</i>)						
C11	4(<i>d</i>)	$\frac{1}{4}$	$0 + \delta$	$0 + \delta'$	0.695	0.701	-0.072
B1	4(<i>d</i>), 4(<i>j</i>)	1	0.153 (6)	0.341 (6)	0.110 (5)	0	-1.328
B2	4(<i>d</i>), 4(<i>k</i>)	1	0.310 (6)	0.140 (6)	0.567 (5)	$\frac{1}{2}$	-0.809

† Authors did not vary coordinates without e.s.d.'s in refinement; δ, δ' is small, see text.

present approach, in which ~ 140 new candidate materials have already been predicted, than by traditional methods. The results of analysing all 87 entries in point group 4 are given below.

2. New inorganic ferroelectrics predicted in space group $P4$

A total of 21 entries for 16 different materials are listed under $P4$ in the current (1998/1) release of ICSD. Nine materials are potentially new ferroelectrics, six are probably nonpolar and the structure determination of one material is incomplete. The order in which the analyses in this and later sections are presented follows that of the ICSD and is without further significance. Comments on the entries that remain, after the predictions in §§2.1–2.7, are given in §2.8 and also follow ICSD order.

2.1. $Ce_5B_2C_6$ family

Two isostructural materials, $Ce_5B_2C_6$ and $La_5B_2C_6$, have been reported in space group $P4$ with an atomic arrangement derived from that of CaC_2 (Bauer & Bars,

1982, 1983). Each was measured diffractometrically and structure refinement gave $R(F) = 0.052$, $wR(F) = 0.074$ for $Ce_5B_2C_6$, with $R(F) = 0.079$, $wR(F) = 0.117$ for $La_5B_2C_6$. The Ce atoms form corner-sharing chains of octahedra along the polar direction; the dimensions of the octahedra are reported by Bauer & Bars (1982) as alternating in length along the chains. Table 1 provides, in addition to the atomic coordinates, the corresponding Wyckoff positions and occupancy factors of all atoms; all C atoms are treated as located in 4(*d*) positions. It may be noted that Ce5 and Ce6 are in Wyckoff positions 1(*b*), Ce7 and Ce8 in 1(*a*); C11 and C12 have $\delta, \delta' = 0$ in $Ce_5B_2C_6$; both δ and δ' are small but $\neq 0$ in $La_5B_2C_6$.

Table 1 shows the z coordinate of every atom, except B1, to be less than $\sim 0.8 \text{ \AA}$ from a hypothetical location z' in space group $P4/m$ with corresponding $P_s = 0$; B1 is $\sim 1.3 \text{ \AA}$ from the expected location at $z' = 0$. This distance exceeds the upper limit of structural criterion (*a*) for ferroelectricity, but, in view of the expected uncertainties in the location of this lighter atom, $Ce_5B_2C_6$ is likely to fulfil these criteria. In that case $Ce_5B_2C_6$ and $La_5B_2C_6$ are predicted to be new ferroelectrics, provided both determinations are free from major error. Since $Gd_5B_2C_6$, $Y_5B_2C_6$ and $Dy_5B_2C_6$ are

reported by Bauer & Bars (1982) to be isostructural with $Ce_5B_2C_6$, these materials may also be ferroelectric. The unusual structure of the $Ce_5B_2C_6$ family is associated with an unknown force constant, preventing a reliable estimate of Curie temperature T_c by (1).

2.2. Ba_3SbReO_9

The structure of Ba_3SbReO_9 was determined by Kemmler-Sack & Treiber (1982) from powder data and refined in space group $P4$ by the use of a single isotropic value of $B = 2 \text{ \AA}^2$ for all atoms to give $R2 = 0.161$. The resulting atomic coordinates in Table 1S,† except for the magnitude of $z(\text{Ba}1)$, may be seen as fully consistent with the symmetry of space group $P4/m$, in which Wyckoff position 1(c) becomes occupied by O4, 1(d) by Ba4; 2(f) by O3; 2(g) by Ba2, Ba3; 2(h) by Re1, Sb1; also Re2, Sb2; and O5, O6; and 4(i) by O1, O2. If the stated value of $z(\text{Ba}1) = 0.025$, corresponding to $\Delta z(\text{Ba}1) = 0.366 \text{ \AA}$, indeed departs significantly from Wyckoff position 1(a) in space group $P4/m$, then the phase is ferroelectric; however, no estimate of standard uncertainty was presented in the paper. The structure should be redetermined with higher reliability or investigated dielectrically.

2.3. Modulated $NbTe_4$

The tetragonal structure of $NbTe_4$ has been reported by Böhm & von Schnering (1985) as modulated with a periodicity of 16/5, a result of the introduction of Nb_2 pairs into chains of Nb_3 groups; it has three entries in the ICSD. The final coordinates obtained from refinement, assuming a modulation periodicity of 3, are reproduced in Table 2S and correspond to a value of $R = 0.034$. The largest value of $|\Delta z|$, for Nb2 and Nb11, is 0.137 \AA ; the complementary average r.m.s. amplitude $u(\text{Nb}2, \text{Nb}11)$ is given as 0.112 \AA . The next largest $|\Delta z|$ in Table 2S is 0.115 \AA for Nb5 and Nb8, all others being less than 0.072 \AA . If the largest displacements in fact exceed their r.m.s. u amplitudes, then modulated $NbTe_4$ is ferroelectric. Further investigation of the assumed polar space group by structural or dielectric measurement is advisable in order to clarify the material properties.

An intermediate incommensurate $NbTe_4$ phase is reported to develop below room temperature, with no substantial changes to below 100 K, in space group $P4$ (a phase transition at $\sim 50 \text{ K}$ is also found; Kusz & Böhm, 1994). Atomic coordinate positions refined at 100 K are closely related to those in the room-temperature structure, see Table 3S, with most atoms located in pairs near Wyckoff positions 8(l), 4(k), 4(j), 4(i), 2(g) and 2(h) in space group $P4/m$, but with eight of the Te atoms

forming four pairs with coordinates near the nonspace-group-related positions xyz and $\bar{x}, y, \frac{1}{2} - z$. The polarization of these atomic pairs cancels as effectively as pairs in Wyckoff position 8(l) and are expected to correspond equally to a minimum in the thermodynamic potential; the displacements in Table 3S are hence indicative of ferroelectricity.

2.4. $Na_3Nb_{12}O_{31}F$

The structure of this tetragonal tungsten-bronze, with three entries in the ICSD, was determined by Li (1988) from 2132 diffractometer-measured reflections and refined in space group $P4$ to give a final $R = 0.140$. Most of the atomic coordinates reported, see Table 4S, are consistent with locations in space group $P4/m$; the exceptions are Nb4, O1, O4, O5, O7, O8 and O10, each of which have Δz displacements ranging from 4 to 7 estimated s.u.'s. The apparent polar displacement $|\Delta z|(\text{Nb}4)$, however, is less than its r.m.s. u amplitude; the O atoms have values of u ranging from 0.01 to 0.27 \AA , the latter being comparable to the largest $\Delta z(\text{O})$. The x and y coordinates obtained from high-resolution electron microscopy (Li & Hovmöller, 1988) were in good agreement with the X-ray results, but the study provided no information concerning the z coordinates. Independent evidence in favor of the polar space group has not been presented. Some 22 diffraction and physical tests, by use of which possible ambiguities between noncentrosymmetric and corresponding centrosymmetric space groups may be resolved, have been given by Abrahams *et al.* (1998).

If the application of such tests show $Na_3Nb_{12}O_{31}F$ to be without inversion centers at room temperature, then the criteria for ferroelectricity would be satisfied. The largest $\Delta z(\text{Nb})$ is 0.189 \AA for Nb6, corresponding to $T_c = 714 (130) \text{ K}$ from the AKJ relation in (1). A more reliable structural redetermination would improve the estimation of T_c . Alternatively, dielectric investigation of $Na_3Nb_{12}O_{31}F$ would show directly if it is ferroelectric, although the recently reported (Ravez, 1999) absence of calorimetric anomaly between 77 and 850 K does not lend support to the possibility.

2.5. Ca_2FeO_3Cl

The structure of this calcium iron oxychloride, determined diffractometrically by Ackerman (1991) as one of a series of alkaline earth iron oxyhalides, resulted in $R = 0.0537$ for the refined coordinates in Table 5S. The origin in this table has been shifted 0.0407 (*i.e.* 0.556 \AA) along the polar axis, an average of the distances that members of the atomic pairs Fe1, Fe2; Ca1, Ca3; Ca2, Ca4; and Cl1, Cl2 are displaced from the planes at $z = 0$ or $\frac{1}{2}$. An array with all atoms at $0, 0, z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$ or $0, \frac{1}{2}, z; 0, \frac{1}{2}, \frac{1}{2} - z$, thereby giving equal but opposite displacements from one that is symmetric, would result in polarizations that cancel antiferroelectrically

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR0086). Services for accessing these data are described at the back of the journal. From hereon tables labeled S refer to the supplementary material.

and hence correspond to a thermodynamic potential minimum. It may be noted that both Fe1 and Fe2, the atoms with the shortest and least ionic bonds in this structure and therefore most likely to determine T_c , see §1, also Abrahams (1990), occupy distorted octahedra consisting of five O and one Cl atoms.

Bond lengths are Fe1—O1 1.960 ($\times 4$), Fe1—Cl1 3.054 and Fe1—O3 1.692 Å, with Fe1 displaced 0.374 Å from the equatorial plane toward O3; Fe2 is displaced 0.299 Å from its equatorial plane toward O4, with Fe2—O2 1.947 ($\times 4$), Fe2—Cl2 2.907 and Fe2—O4 1.900 Å. These distances differ in part from those reported. Assuming the atomic coordinates are not misreported and correcting for the difference in radii of O^{2-} and Cl^- as 0.41 Å (Shannon, 1976), Fe1 is displaced $\Delta z = 0.408$ Å, while Fe2 is similarly displaced 0.299 Å from their respective mean octahedral z coordinates. If these displacements become zero at the phase transition from ferroelectric to antiferroelectric, then $\Delta z(\text{Fe1})$ gives $T_c = 3330$ (300) K from the AJK relation. $\text{Ca}_2\text{FeO}_3\text{Cl}$ is prepared at 1125 K and may not remain stable at temperatures approaching the predicted T_c . It is however possible that dielectric hysteresis is observable at lower temperatures, provided the resistivity and breakdown strength allow the application of fields that are adequate to reverse the polarity.

2.6. $\text{Ba}_{0.65}\text{Ru}_{2.7}\text{Cr}_{1.3}\text{O}_8$

The atomic coordinates of the experimental composition in the title material, close to ideal $\text{BaRu}_4\text{Cr}_2\text{O}_{12}$, were determined from powder X-ray and electron diffraction photographs by Cadée & Prodan (1979) on the basis of an assumed simple hollandite structure with tripled short axis, as given in Table 6S. It may be noted that $z = n/6$ for all atoms, where n is an integer; the preferred orientation prevented structural refinement, but the structure is claimed as the only one found that gave a good intensity fit. It may be noted that the polarization contribution by the Ba, Ru and Cr atoms becomes zero for an origin shift of $c/12$, assuming identically charged Ru and Cr ions. However, P_s cannot be zero unless an even number of O atoms is present (11 O atoms only were determined) or all locations are not fully occupied. If fully occupied, then the composition would correspond to $\text{Ba}_{0.73}\text{Ru}_{2.91}\text{Cr}_{1.45}\text{O}_8$ rather than that given by the title (a single formula unit corresponds to $A_xB_{4-2x}C_{2x}O_8$); if O12 were also present, then the structural formula would become $\text{Ba}_{0.71}\text{Ru}_{2.84}\text{Cr}_{1.42}\text{O}_8$. The authors note that models with mirror planes normal to the c axis may be constructed if random cation distributions are assumed. Polarizations associated with the structure in Table 6S are not expected to change strongly as a function of temperature; confirmation of the space group together with modifications to the model such as noted above may, however, be consistent

with ferroelectricity. Further structural and/or physical study is necessary for property characterization.

2.7. $\text{K}_4\text{CuV}_5\text{O}_{15}\text{Cl}$ family

A total of 682 independent $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$ from a $\text{K}_4\text{CuV}_5\text{O}_{15}\text{Cl}$ crystal were measured diffractometrically and refined to $R1 = 0.034$ by Martin & Müller-Buschbaum (1994), with atomic coordinates as given in Table 7S. It may be seen that an origin shift of 0.1360 places all atoms except O5 within 0.91 Å of a special position in space group $P4/m$; although this shift locates O5 a distance of 1.19 Å from the corresponding $1(d)$ Wyckoff position at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; its r.m.s. displacement amplitude $u = 0.56$ Å is the largest reported and the stated uncertainty in $z(\text{O5})$ may be substantially underestimated. V1 forms V_2O_7 double tetrahedra with common O4 atoms, V2 occupies VO_5 square pyramids and Cu forms CuO_4Cl_2 octahedra. If Δz displacements as large as those in Table 7S are possible, then the structure is ferroelectric; they are, however, at the upper limit of structural criterion (a). The unknown force constant corresponding to the unusual V_2O_7 geometry prevents an estimate of T_c from (1). Dielectric or further structural investigation is necessary to resolve the matter.

The material is isostructural with $\text{K}_4\text{CdV}_5\text{O}_{15}\text{Cl}$ (ZNBSE 51 493),[†] $\text{Tl}_4\text{CdV}_5\text{O}_{15}\text{Cl}$ (ZNBSE 52 453) and $\text{Rb}_4\text{CdV}_5\text{O}_{15}\text{Cl}$ (ZNBSE 52 453) and is also closely related to $\text{K}_2\text{V}_3\text{O}_8$; the latter was predicted previously to be ferroelectric (Abrahams, 1996). The mineral fersnoite, $\text{Ba}_2\text{TiSi}_2\text{O}_8$, is isostructural with $\text{K}_2\text{V}_3\text{O}_8$ and has very recently been shown to exhibit ferroelectricity (Foster *et al.*, 1999a).

2.8. Nonpolar and incomplete structure determinations reported in $P4$

The atomic arrangements reported in $\gamma\text{-PdH}_{1.33}$ (KRISA 25 1162), a disordered structure determined by electron diffraction, $\text{Ba}_{5.5}\text{Ta}_{21.8}\text{O}_{60}$ (BUFCA 90 172), $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$ (JCSOA 1932 2527) and PdO (GCITA 56 388) are nonpolar since all atoms are reportedly located on actual or pseudosymmetry mirror planes. The positions of two atoms only were reported in TISCN (CGITA 64 400); many of the above determinations were made early and should probably be repeated with improved techniques.

Refinement of the $\text{Bi}_3\text{PbWO}_8\text{Cl}$ structure by Ackerman (1986), based on single-crystal diffraction, led to the indicators $R1 = 0.053$, $wR2 = 0.064$. The atomic coordinates, presented in Table 8S, place all

[†] Coden-type references are given throughout this paper for most structure determinations mentioned, but for which atomic coordinates are not reproduced, see Notes for Authors (1996). The ICSD omits the final check letter of the journal abbreviation, providing only five letters in each coden. The year of publication is given implicitly in the coden by the volume number following the journal's modified acronym.

Table 2. Atomic coordinates for $TlBO_2$ at room temperature with hypothetical z' coordinates and polar displacements in \AA

$$a = 7.380 (6), c = 9.350 (8) \text{ \AA}. z^* = z + 0.0463; \Delta z = (z' - z^*)c.$$

	Wyckoff positions $P4_1, P4/m$	x	y	z^*	z'	Δz
Tl1	4(a), 4(j)	0.2618 (3)	0.2634 (3)	0.0463	0	0.43
Tl2	4(a), 4(k)	0.2611 (3)	0.0225 (3)	0.4537 (4)	$\frac{1}{2}$	-0.43
O1	4(a)	0.213 (5)	0.501 (6)	0.338 (4)	0.383	-0.42
	8(l)					
O3	4(a)	0.257 (5)	0.426 (7)	0.572 (5)	0.617	-0.42
O2	4(a), 4(k)	0.515 (6)	0.460 (5)	0.423 (4)	$\frac{1}{2}$	-0.72
O4	4(a), 4(k)	0.042 (5)	0.454 (6)	0.487 (4)	$\frac{1}{2}$	-0.12
B1	4(a), 4(k)	0.135 (7)	0.455 (6)	0.471 (6)	$\frac{1}{2}$	-0.15
B2	4(a), 4(k)	0.461 (6)	0.402 (6)	0.560 (6)	$\frac{1}{2}$	0.56

Table 3. Atomic coordinates for $CrOF_3$ at room temperature with hypothetical z' coordinates and polar displacements in \AA

$$a = 5.174 (2), c = 8.921 (6) \text{ \AA}. z^* = z + 0.018, \text{ to give equal but opposite displacements for F1 and F2; } \Delta z = (z' - z^*)c.$$

	Wyckoff positions $P4_1, P4/m$	x	y	z^*	z'	Δz
Cr	4(a), 4(j)	-0.1096 (1)	-0.4171 (1)	0.018	0	0.161
F1	4(a)†	0.1563 (7)	-0.4272 (7)	0.1381 (4)	0.1238	0.128
F2	4(a)†	0.0617 (7)	-0.1960 (6)	-0.1094 (4)	-0.1238	0.128
F3	4(a), 4(j)	-0.4333 (7)	-0.3136 (6)	-0.0754 (4)	0	-0.672
O	4(a), 4(j)	-0.0745 (9)	-0.6686 (9)	-0.0725 (5)	0	-0.647

† F1 and F2 are related very nearly as x,y,z is to $\frac{1}{2} + y, \bar{x}, \bar{z}$ rather than through Wyckoff position 8(l) relationships; the former is, however, not a space group $P4/m$ relation.

atoms in Wyckoff positions 1(a), 1(b) or 2(c). The corresponding z coordinates in space group $P4/m$ differ from the experimental $z' = z + 0.0012$ values by no more than $\sim 0.07 \text{ \AA}$ for Cl with an r.m.s. amplitude $u \simeq 0.19 \text{ \AA}$, or by $0.33 (13) \text{ \AA}$ for O3 with $u \simeq 0.23 \text{ \AA}$. With W at the origin, all xyz' coordinates hence correspond to one or other of Wyckoff positions 1(a), 1(d), 2(e), 2(g) or 2(h) in space group $P4/m$. It may be concluded that Bi_3PbWO_8Cl forms in the latter space group, hence is nonpolar.

3. New inorganic ferroelectrics predicted in space group $P4_1$

A total of 26 entries for 21 different materials are listed under $P4_1$ in the current release of the ICSD. Four materials, $TlBO_2$, $CrOF_3$, $PbTeO_3$ and $VO(HPO_3)(H_2O)_2 \cdot 3H_2O$ are potentially new ferroelectrics, 16 are polar but cannot be ferroelectric and one structure determination is not complete enough to allow conclusions to be drawn.

3.1. $TlBO_2$

The atomic coordinates of $TlBO_2$, thallium catenaborate, as refined by Touboul & Amoussou (1978) with $638 F_o > 4\sigma(F_o)$ to give $R = 0.090$ and $wR = 0.102$, are presented in Table 2. An origin shift along the polar axis of 0.0463 produces equal but opposite displacements by

Tl1 and Tl2 from planes with $z = 0$ and $\frac{1}{2}$, respectively. This shift leads to an atomic array in which all displacements are less than $\sim 0.7 \text{ \AA}$ from the structure as transformed to space group $P4/m$ with $P_s = 0$, satisfying criterion (a) for ferroelectricity; with $0.17 \geq u \geq 0.09 \text{ \AA}$, criterion (b) is also satisfied. The structure at room temperature consists of $B_2O_2^{2-}$ ions formed by planar $B1O_3$ and tetrahedral $B2O_4$ ions sharing O1 and O2 atoms. The Δz magnitudes are expected to correspond to a rather high Curie temperature; since the AKJ relationship in (1) applies only to Δz displacements within O or F octahedra, it is inapplicable to the present geometry.

3.2. $CrOF_3$

The structure of bright-purple $CrOF_3$ was refined by McHughes *et al.* (1986) using 644 unique $F_o > 2\sigma(F_o)$ to give $R1 = 0.053$, $wR2 = 0.056$ for the atomic coordinates listed in Table 3. The polar-coordinate origin has been displaced by 0.018 from that reported to give equal but opposite displacements by F1 and F2. The Cr atom coordination is square pyramidal, with F1, F2 and F3 ($\times 2$) in a basal position and the O atom in apical positions; an F2 atom in another molecule at a distance of 2.185 \AA completes a highly distorted octahedron about the Cr. It may be noted that, although F1 and F2 are not related by a symmetry operation of space group $P4/m$, $z'(\text{F1}) = -z'(\text{F2})$; the thermodynamic potential

minimum that develops at $P_s = 0$ is expected to stabilize the structure corresponding to the xyz' coordinates. Table 3 shows that no atom is more than ~ 0.67 Å from the nonpolar arrangement, fulfilling structural criterion (a) for ferroelectricity. The nominal threefold axis of the octahedron is approximately parallel to the polar axis, with the Cr atom displaced 0.131 Å from its mean z coordinate; application of the AKJ relation in (1) gives $T_c = 345$ (25) K. Investigation of the dielectric properties of CrOF_3 is hence indicated.

3.3. PbTeO_3

A total of 1181 reflections with $F_o^2 > 3\sigma(F_o^2)$ were measured and refined by Sciau *et al.* (1986) to give a final $R1 = 0.048$, $wR1 = 0.035$ for the atomic coordinates in Table 9S; the origin in the table has been displaced 0.37 Å along the polar axis to set the average z coordinate for the TeO_3^{2-} anion at $\frac{1}{2}$. The tellurite anion forms a slightly distorted trigonal pyramid, with an average Te—O distance of 1.86 Å; the O atoms are shared by Pb to form three shorter (average 2.40 Å) and three longer (average 2.66 Å) Pb—O bonds. It may be seen in Table 9S that the largest atomic displacement from an arrangement with $P_s = 0$ is $\Delta z(\text{O}2) = 0.93$ Å. With the largest r.m.s. displacement $u \simeq 0.14$ Å, the structure satisfies both criteria for ferroelectricity; PbTeO_3 is also reported to generate second harmonics. It is, however, unlikely that the transition to paraelectric will occur below an irreversible phase transition at 758 K, see Sciau *et al.* (1986), in view of the large magnitudes of $\Delta z(\text{Pb}, \text{Te}) = 0.372$ and 0.501 Å, respectively, in addition to that of $\Delta z(\text{O}2)$. Investigation of such dielectric properties as hysteresis at room temperature may reveal the predicted ferroelectricity.

3.4. $\text{VO}(\text{HPO}_3)(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$

Refinement of the $\text{VO}(\text{HPO}_3)(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ structure,† based on the measurement of 1261 independent reflections, was reported by Zakharova *et al.* (1994) to give the atomic coordinates in Table 10S, with final $R1 = 0.044$, $wR2 = 0.092$. The V atom occupies an octahedron of six O atoms, two of which are water O atoms; the P atom occupies a tetrahedron of three O and one H atoms corresponding to HPO_3 . Octahedra and tetrahedra share three O atoms to form chains. All non-H atoms may be seen in Table 10S as displaced from the plane at $z = 0$ by no more than 0.55 Å, except for O2 and O3 which are displaced 1.22 and 1.23 Å, respectively; these two atoms, however, are in locations related as x, y, z is to x, y, \bar{z} with resulting displacements only 0.006 Å from zero polarization. The largest H atom displacement from the plane at $z = 0$ is 0.89 Å, with each H having an r.m.s. displacement $u \simeq 0.25$ Å. The structural criteria for ferroelectricity are hence satisfied. The average z

coordinate displacement in the VO_6 octahedron and in the PO_3H tetrahedron from a mirror plane at $z = 0$ is 0.015 Å or less. Each of the remaining three water O atoms, however, is displaced more than 0.5 Å from this plane, with r.m.s. amplitudes $u \simeq 0.21$ Å. If the given locations are correct, T_c is likely to be high; in that case, the waters of hydration may be lost at $T \ll T_c$. Dielectric investigation will reveal if ferroelectricity is exhibited at room temperature.

3.5. Nonferroelectric materials in space group $P4_1$

The atomic arrangements reported in PbTi_3Cl_5 (ZAACA 432 141), isostructural $\beta\text{-Sr}_2\text{V}_2\text{O}_7$ (JSSCB 4 87), low- $\text{Pr}_2\text{Si}_2\text{O}_7$ (ZEKGA 133 364; NATWA 57 669; STBGA 13 150), $\text{Sm}_2\text{Si}_2\text{O}_7$ (KRISA 15 256) and $\text{La}_2\text{Si}_2\text{O}_7$ (DANKA 252 1117), in the duplicate entry for ISbCl_8 (ACCRA 12 859) and in Cs_3P_7 (ZAACA 552 69), $\text{Cs}_4(\text{P}_4\text{O}_{12})(\text{H}_2\text{O})_4$ (ACSCE 42 131), $\text{Na}_2\text{K}_2\text{P}_4\text{O}_{12}(\text{H}_2\text{O})_2$ (JSSCB 58 119), LaRhC_2 (KRISA 33 345), CeRhC_2 (CMATE 1 581), $\text{Rb}_4\text{Li}[\text{H}_3(\text{SO}_4)_4]$ (ACSCE 46 1199), $\text{Sr}_{1.58}\text{Ca}_{0.42}\text{V}_2\text{O}_7$ (ZNOKA 38 428), $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (ACCRA 21 942), $\text{Co}[\text{F}_2(\text{NH}_3)_4]\text{ClO}_4$ (BCSJA 64 1743) and Tl_3PbBr_5 (JCOMA 78 281) are unable to become nonpolar under displacements less than ~ 1 Å. Each of these materials hence correspond to polar but non-ferroelectric structures.

3.6. Nonpolar and incomplete structure determinations reported in $P4_1$

The atomic arrangement reported in $\text{Cs}_2\text{O}(\text{B}_2\text{O}_3)_9$ (ARKEA 12 247 and 14 451) is incomplete, allowing no property inferences to be drawn.

4. New inorganic ferroelectrics predicted in space group $P4_2$

A total of eight entries for four different materials (two of which are H_2S and D_2S) are listed under $P4_2$ in the current release of the ICSD. The mineral $\text{MgB}_2\text{O}(\text{OH})_6$ is either misassigned to a polar space group or is potentially ferroelectric. The structure of H_2S and D_2S , as determined, is nonpolar, that of NH_4NO_3 at 125 K is not complete enough to allow the inference of property attributes.

4.1. $\text{MgB}_2\text{O}(\text{OH})_6$

The structure of the mineral pinnoite, $\text{MgB}_2\text{O}(\text{OH})_6$, was refined by Genkina & Malinovskii (1983) in space group $P4_2$ to give $R = 0.033$, based on an earlier determination in space group $P4_2/n$. Inspection of Table 11S shows that, apart from the atoms Mg, O5 and O6 which are nearly at $x, y, 0$ or $x, y, \frac{1}{2}$ and O7 and O8 which are nearly at $0, 0, z, \frac{1}{2}, \frac{1}{2}, \bar{z}$, all other atoms form pairs very close to x, y, z and $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$. Such relationships are characteristic of space group $P4/n$, as indicated by the z'

† Formula given as $[\text{VO}(\text{HPO}_3)(\text{H}_2\text{O})_2]_n \cdot 3n\text{H}_2\text{O}$.

magnitudes in Table 11S derived on the basis of a 0.228 origin shift along the polar axis that places Mg at $xy0$. The largest differences along the polar direction between the refined z magnitudes and their values if the space group were $P4/n$ are given under Δz in Table 11S. It is notable that, while all atomic displacements are less than 0.07 Å, the r.m.s. u amplitudes lie between 0.09 and 0.12 Å for all atoms except H, for which $0.05 < u < 0.22$ Å. The assumption by Genkina & Malinovskii (1983) that the point group of pinnoite is polar may be subject to problems similar to those discussed recently in a study of $\text{Sr}_5\text{Nb}_5\text{O}_{17}$ by Abrahams *et al.* (1998); pinnoite is hence a candidate for possible space-group reassignment rather than ferroelectric behavior. The structure should be reinvestigated using as many as possible of the 14 diffraction and eight physical tests discussed in the latter work.

4.2. H_2S/D_2S

Three of the four entries for H_2S or D_2S in the ICSD give only the coordinates of the independent S atom in two of the three phases identified at low temperatures. The coordinates of the two independent D atoms in the $P4_2$ structure at 102 K have been refined from neutron powder patterns in the most recent entry (NATUA 224 905), with $R(F^2) = 0.056$. Placing $z(\text{S}) = 0$, $z(\text{D1})$ was found equal to $-z(\text{D2})$; the structure as given is hence nonpolar. If redetermination at higher accuracy reveals $z(\text{D1}) \neq -z(\text{D2})$, then the structure may be ferroelectric.

4.3. Nonferroelectric structure in space group $P4_2$

The remaining entry under space group $P4_2$ is for the structure of NH_4NO_3 at 125 K (ZEKGA 117 92), many z coordinates of which were determined by trial and error. The investigation revealed evidence of considerable disorder, leading to partial centrosymmetry. In the absence of disorder, the magnitude of the rotations required for polarity reversal by all independent ions at low temperatures appears unlikely. Further investigation is needed to clarify the structural details reported.

5. New inorganic ferroelectrics predicted in space group $P4_3$

Two entries, each for a different material, are listed under $P4_3$ in the current release of the ICSD. One of these, β -tetragonal boron, is possibly ferroelectric, whereas the other, $[\text{Hg}_7(\text{HgBr})_2\text{As}_4](\text{Bi}_2\text{Br}_{10})$, cannot be ferroelectric.

5.1. β -tetragonal boron ($B_{21} \cdot 2B_{12} \cdot B_{2.5}$)

The structure of β -tetragonal boron, related to α - AlB_{12} , was reported by Vlasse *et al.* (1979) on the basis of 1250 independent reflections measured diffractome-

trically and refined to a final $R = 0.096$. The order of presentation in Table 12S follows that of Vlasse *et al.* (1979), except for the final seven atoms. The atoms from B1 to B44 are given in pairs, with the coordinates for each pair related as xyz is to $\sim(y - \frac{1}{2}, x + \frac{1}{2}, 1 - z)$; B45–B47 have $z \simeq \frac{1}{2}$, B48 has $z \simeq 3/4$ and B49 has $z \simeq 0$. The polarization due to B48 on undergoing displacement to $z = 3/4$ is cancelled by the equivalent atom at $z = 1/4$ generated by the screw axis. Five atoms only in the table are displaced more than 0.09 Å from positions that satisfy the relationships above exactly, which would result in an antiferroelectric array. These displacements are 0.20 Å for the B19, B20 pair, 0.52 Å for B47, 0.30 Å for B48 and 0.45 Å for B49 in a unit cell that contains eight B_{12} icosahedra, four B_{21} -twinned icosahedra sharing a face and ten single B atoms, of which B47, B48 and B49 are reported to be $\sim 50\%$ occupied. If the occupancy of each related pair of atoms is identical, and if all Δz displacements in Table 12S significantly exceed zero, then β -tetragonal boron would satisfy the structural criteria for ferroelectricity. The magnitudes of many of the r.m.s. u amplitudes, particularly the seven largest which range from 1.42 (B15) to 2.41 Å (B48), may need structural reevaluation. A dielectric study will show if tetragonal boron exhibits ferroelectricity.

5.2. Nonferroelectric structure in space group $P4_3$

The only other entry under space group $P4_3$ is to the structure of $[\text{Hg}_7(\text{HgBr})_2\text{As}_4](\text{Bi}_2\text{Br}_{10})$ (ZAACA 518 120), for which the atomic displacements necessary to achieve nonpolarity significantly exceed the structural criteria.

6. New inorganic ferroelectrics predicted in space group $I4$

A total of 23 entries for 20 different materials is listed under $I4$ in the 1998 release of ICSD. Two are to the known ferroelectric BaFeF_5 and SrAlF_5 (Abrahams *et al.*, 1981), and a third to $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$ (Abrahams *et al.*, 1987); three new families (including three isomorphous members of the WOB_4 family, two each in the SbCl_3F_2 family and two in the hollandite mineral families) and three other materials are predicted to be ferroelectric. Two further materials are possibly ferroelectric, another is nonpolar and the space group of four more may have been misassigned.

6.1. CuBi_2O_4

The atomic coordinates of CuBi_2O_4 , determined by Arpe & Müller-Buschbaum (1976) and refined to $R = 0.094$ on the basis of 674 independent reflections, are presented in Table 13S. The origin has been shifted 0.0868 along the polar axis to give displacements that are approximately equal but of opposite sense for the two independent Cu atoms with respect to that of the unique

Bi atoms. In consequence, no atom is displaced more than 0.52 Å from an equivalent location in space group $I4/m$. The structure of CuBi_2O_4 , with $0.03 \leq u \leq 0.09$ Å, hence satisfies the criteria for ferroelectricity. The Cu atoms occupy square coplanar CuO_4^{6-} ions, forming multiple links to the distorted trigonal prism of O atoms coordinated to each Bi, with $2.19 < d(\text{Bi}-\text{O}) < 2.70$ Å. Since $z(\text{Bi})$ is displaced by only ~ 0.05 Å along the polar axis from the mean $z(\text{O})$ coordinate of the prism, the entire BiO_6^{9-} ion must be displaced by ~ 0.5 Å before the paraelectric state can be achieved. The corresponding T_c is hence expected to be high, but the unknown force constant associated with the structural geometry prevents estimation by use of the AJK relation in (1).

6.2. WOBr_4 family

Hess & Hartung (1966) first reported the structure of WOBr_4 in addition to that of isomorphous WOCl_4 and WOCl_3Br . The former two were also reported by Boorman *et al.* (1968). A total of 269 independent absorption-corrected WOBr_4 reflections were subsequently measured and refined by Müller (1984) to give $R = 0.0495$ with atomic coordinates as in Table 14S; the origin in this table is shifted by 0.0356 to equalize the distribution of differences between the experimental z coordinates and those predicted in a paraelectric phase. The W atom in this structure occupies a distorted octahedron of four Br and two O atoms. On correction for the difference in radii of 0.61 Å between O^{2-} and Br^- (Shannon, 1976), a displacement of the octahedral center along the polar axis relative to W by 0.201 Å would result in zero polarization for WOBr_4 . The resulting value of T_c from the AKJ relation in (1) is 805 (350) K. The displacements for WOCl_3Br and WOCl_4 are comparable but less well defined. Decomposition temperatures are unknown but, possibly, not greater than T_c . Investigation of the dielectric properties will show if the expected ferroelectric property is present.

6.3. Na_8PtO_6

The atomic coordinates of the unique Pt and both independent O atoms in a model reported by Hauck (1976) on the basis of a trial-and-error fit to the powder pattern are fully consistent with space group $I4/m$, as shown in Table 15S. Assuming 50% occupancy of the Pt and O2 sites, the 26 reflections used led to $R = 0.12$. The z coordinate of the unique Na atom, however, may be seen in the table as displaced from the mirror-plane location at $z = 0$ by 0.32 Å. If this Δz displacement can be confirmed, then the structure fulfils the criteria for ferroelectricity with a value of T_c that is expected to be rather high; no estimate of the r.m.s. amplitude u was given. It is noted that the Pt atom has zero polar displacement from the center of its slightly distorted octahedron of O atoms. Reinvestigation of the reported

structure, or dielectric measurement, will determine whether Na_8PtO_6 exhibits ferroelectricity or whether the structural model reported requires modification.

6.4. $\text{SbF}_{1.6}\text{Cl}_{3.4}$ and SbCl_3F_2

The structure of $\text{SbF}_{1.6}\text{Cl}_{3.4}$ was determined by Müller (1979) and refined to $R = 0.036$ with 637 independent reflections to give the atomic coordinates presented in Table 16S. The coordinates of atoms Cl1 and $\text{Cl1}'$, each in Wyckoff position 8(c) of space group $I4$, were reported with values corresponding to a 16(i) position in space group $I4/m$, but in which $\text{Cl1}'$ is only 40% occupied; the symmetry of the 16(i) position requires equally occupied x,y,z and x,y,\bar{z} sites. The nearby F2 site (located ~ 0.13 Å distant from $\text{Cl1}'$) is reported as being 60% occupied, thereby corresponding to the chemical formula found analytically. All atoms are located within 0.175 Å of sites that would result in zero polarization if occupied. The $\text{Cl1}'$, F2 sites are taken as randomly occupied by the two types of atom. Under these conditions, $\text{SbF}_{1.6}\text{Cl}_{3.4}$ satisfies the structural criteria for ferroelectricity. The structure of SbCl_3F_2 [JCDTB 1977 1472] is closely isomorphous with $\text{SbF}_{1.6}\text{Cl}_{3.4}$ and, if confirmed, is similarly expected to be ferroelectric. The Sb atom in both materials occupies a distorted octahedron of approximately three F and three Cl atoms, depending on the composition. The net displacement for Sb in the $\text{SbF}_{1.6}\text{Cl}_{3.4}$ octahedron may be estimated as $\Delta z \simeq 0.16$ Å, corresponding to $T_c \simeq 500$ (300) K on the basis of the AJK relationship in (1). Dielectric measurements will either confirm this result or indicate the advisability of further structural study.

6.5. Hollandite family

Both the 'average' and the modulated structures of $\text{Ba}_{1.2}\text{Ti}_8\text{O}_{16}$, a new mineral member of the hollandite family in which the Ba site contains $\sim 4\%$ K and the Ti site $\sim 17\%$ V, $\sim 4\%$ Cr and smaller proportions of Fe, Mn and Al have been refined by Bolotina *et al.* (1992) using 660 independent $F_o > 0$, the former to $R = 0.0415$ and the latter to $R = 0.0428$. The Ba and Ti sites are considered hereafter as occupied only by Ba and Ti atoms, respectively, for simplicity. The 'average' structure was refined by use of 244 reflections from a subcell in which $c = c'/5$, leading to the atomic coordinates in Table 17S, as modified by an origin shift of 0.063 along the polar axis to midway between the two independent Ba atoms. The commensurate modulated structure is assumed to be a result of variations both in the occupancy and z coordinates of the Ba atoms. Using a four-dimensional primitive space group based on $I4$, the Ba atoms are described as occupying nine distinct positions along the polar axis, the Ti and O atoms each occupying another five distinct sets of positions. The polar axis is approximately normal to one of the linear O—Ti—O axes of the TiO_6 octahedron, for which $1.920 <$

Table 4. Atomic coordinates for $Ni[SC(NH_2)_2]_4Cl_2$ at room temperature with hypothetical z' coordinates and polar displacements in Å

$a = 9.606$ (2), $c = 9.083$ (2) Å. $\Delta z = (z - z')$.

	Wyckoff positions $I4, I4/m$	x	y	z^*	z'	Δz
Ni	2(a), 2(a)	0	0	0	0	0
Cl1	2(a)	0	0	-0.2646 (1)	-0.2709	0.057
	4(e)					
Cl2	2(a)	0	0	0.2771 (1)	0.2709	0.057
S	8(c), 8(h)	0.0303 (1)	0.2535 (1)	0.0318 (1)	0	0.289
C	8(c), 8(h)	0.1541 (1)	0.3271 (1)	-0.0794 (2)	0	-0.721
N1	8(c), 8(h)	0.1983 (2)	0.4543 (2)	-0.0492 (3)	0	-0.447
N2	8(c), 8(f)	0.2071 (2)	0.2614 (2)	-0.1934 (2)	0	0.514
H1	8(c), 8(h)	0.1620 (26)	0.4932 (25)	0.0258 (25)	0	0.234
H2	8(c), 8(h)	0.2644 (35)	0.4712 (38)	-0.0777 (38)	0	-0.706
H3	8(c), 8(f)	0.2684 (31)	0.2963 (27)	-0.2512 (29)	0	-0.011
H4	8(c), 8(f)	0.1786 (35)	0.1774 (36)	-0.2250 (37)	0	0.227

$d(Ti-O) < 2.025$ Å in the subcell structure, and bisects the angle between the two other linear O—Ti—O axes. The Ti atom in the subcell structure is displaced ~ 0.04 Å from the octahedral center in the same sense as its displacement of ~ 0.21 Å from the origin, hence T_c may be estimated as 880 (100) K from (1) by means of the AJK relationship. The modulated structure gives a similar result.

A new lead aluminosilicate hollandite $Pb_{0.8}Al_{1.6}Si_{2.4}O_8$ synthesized at 16.5 GPa and 1725 K is reported by Downs *et al.* (1995) to have atomic coordinates closely comparable to the mineral $Ba_{1.2}Ti_8O_{16}$, as shown in Table 18S, based on a refinement of 433 $F(hkl) > 4\sigma[F(hkl)]$ that gave $wR = 0.045$. The resulting Si, Al atomic displacement from a nonpolar array may be seen in Table 18S as identical to that of O1 and O2 at 0.162 Å, with T_c estimated from the AJK relationship as 525 (40) K.

6.6. $Ni[SC(NH_2)_2]_4Cl_2$

A charge density study of dichlorotetrakis(thiourea) nickel(II) at 140 K by Figgis & Reynolds (1986) led to $R = 0.021$ for 1512, that at 295 K to $R = 0.022$ for 2492, independent absorption-corrected observed reflections. The atomic coordinates determined at 295 K are listed in Table 4, those at 140 K are very similar. The two independent Cl atoms in general positions are seen to be only 0.057 Å from the corresponding 4(e) location in space group $I4/m$, the Ni atom remaining in position 2(a), while the z coordinates of all other atoms are less than 0.73 Å from either an 8(h) or an 8(f) position in $I4/m$. The structure of $Ni[SC(NH_2)_2]_4Cl_2$ thus satisfies criterion (a) for ferroelectricity; the quoted $0.105 < u < 0.217$ Å amplitudes at 140 K,† however, are unusually large. The center of the octahedron formed by the two

Cl and four S atoms about Ni is located at $z = 0.0233$, corresponding to $\Delta z(Ni) = 0.211$ Å. If $Ni[SC(NH_2)_2]_4Cl_2$ is ferroelectric, then the resulting $T_c = 890$ (20) K from (1), by the AKJ relation. This temperature is likely to exceed that at which $Ni[SC(NH_2)_2]_4Cl_2$ decomposes, hence the possibility of ferroelectricity may best be investigated by determination of the dielectric hysteresis, if measurable, at room temperature. Magnitudes of Δx and Δy displacements comparable to Δz show that $Ni[SC(NH_2)_2]_4Cl_2$ is most likely a three-dimensional ferroelectric, in the event the above measurements give positive results.

6.7. $Ca_2SiO_3Cl_2$

The structure of $Ca_2SiO_3Cl_2$ reported by Golovastikov & Kazak (1977) was refined in space group $I4$ by the use of 1037 reflections to give $R = 0.0768$ for the atomic coordinates listed in Table 19S; isotropic u parameters were also varied. The origin has been shifted by 0.0046 to give Ca1 and Ca2 equal displacements of $\Delta z = 0.007$ Å. Table 19S shows that all atoms are within 0.036 Å of the corresponding locations in space group $I4/m$, except Cl2 which is 0.218 Å from its 4(d) Wyckoff position. If Cl2 is indeed at the location reported, then $Ca_2SiO_3Cl_2$ is expected to be ferroelectric; it may be noted, however, that the r.m.s. amplitudes for all Cl atoms are large, with $u(Cl2) = 0.12$ Å. Golovastikov & Kazak (1977) investigated the alternative space group $I4/m$, but since it led to $R = 0.1064$ on refinement with $u(Cl2)$ increasing to 0.15 Å, it was rejected. It is, however, possible that the better fit may be an artefact; more extensive methods for distinguishing between nonpolar and ferroelectric crystals have been presented elsewhere (Abrahams *et al.*, 1998). The AKJ force constant in (1) for structures with distorted SiO_4 tetrahedra is presently unknown, hence an estimate of T_c is unavailable. Ferroelectric behavior should be readily detectable by dielectric investigation.

† The authors' \bar{u} magnitudes, e.g. 470 pm² for N, are assumed to be identical with the mean amplitudes of thermal or static displacement u .

Table 5. Atomic coordinates for $K_4Cu_4O_2(SO_4)_4Cu_{0.5}Cl$ at room temperature with hypothetical z' coordinates and polar displacements in Å

$a = 13.60$ (2), $c = 4.98$ (2) Å. $\Delta z = (z - z')c$.

	Wyckoff positions in $I4$, $I4/m$	x	y	z^*	z'	Δz
K	8(c), 8(h)	0.1905 (1)	0.1279 (1)	-0.0379 (6)	0	-0.189
Cu1	8(c), 8(h)	0.05627 (6)	0.40789 (6)	0	0	0
O1	4(b), 4(d)	0	$\frac{1}{2}$	0.7572 (23)	$\frac{3}{4}$	0.036
S	8(c), 8(h)	0.4426 (1)	0.2347 (1)	-0.0179 (6)	0	-0.089
O2	8(c)	0.4230	0.2103 (5)	0.2705 (15)	0.2295	0.204
	16(i)					
O3	8(c)	0.3807 (5)	0.1706 (5)	-0.1884 (18)	-0.2295	0.204
O4	8(c), 8(h)	0.5456 (4)	0.2157 (4)	-0.0778 (17)	0	-0.387
O5	8(c), 8(h)	0.4158 (5)	0.3369 (4)	0.0531 (20)	0	0.264
Cu2, Na	2(a), 2(b)†	0	0	0.4482 (12)	$\frac{1}{2}$	-0.258
Cl	2(a), 2(a)	0	0	-0.0513 (18)	0	-0.255

† Site may contain one-half Cu or one Na atom.

6.8. $K_4Cu_4O_2(SO_4)_4Cu_{0.5}Cl$

The structure of the mineral caratiite was determined by Effenberger & Zemann (1984) on the basis of 654 absorption-corrected $F_o > 6\sigma(F_o)$ to give $R = 0.035$ and the atomic coordinates in Table 5. The z coordinates of all atoms are within 0.40 Å of their corresponding Wyckoff positions in space group $I4/m$, the independent x, y coordinates of O2 and O3 in position 8(c) of space group $I4m$ being even closer to those in Wyckoff position 16(i); with $0.12 \leq u \leq 0.20$ Å, the structural criteria for ferroelectricity are hence satisfied. Cu1 occupies a distorted tetragonal pyramid within which it is slightly displaced towards the interior from the noncoplanar basal four O atoms, with $d(\text{Cu}-\text{O}) < 2.069$ Å; the apical fifth atom O4 has $d(\text{Cu}-\text{O}) = 2.292$ Å. The force constant in (1) for this atomic arrangement is unknown. The nominal Cu2 site lies within a rather regular octahedron, with four nearest O atoms at 2.496 Å and two Cl at 2.49 Å. The metal atom, which the authors suggest may consist of an Na instead of half a Cu atom, is displaced only 0.003 Å from the octahedral center along the polar axis, hence is unlikely to determine T_c if a phase transition exists. Dielectric measurement is necessary to confirm the possibility of ferroelectricity in caratiite.

6.9. Nonferroelectric and incorrectly assigned structures in $I4$

$\text{AgBi}(\text{Cr}_2\text{O}_7)_2$, with two entries for the same reference [ACBCA 36 1327], does not satisfy the criteria for and hence is not expected to exhibit ferroelectricity. The atomic coordinates of the single independent atom in elementary Pa [ACCRA 5 19], given as 0,0,0, satisfy space group $I4m$, as do the special coordinates of ThH_2 and ZrH_2 [ACCRA 5 22]. Their authors state only that these materials are body-centered tetragonal; the space group should probably not be assigned to $I4$. No atom in $(\text{PbCl}_4)_2(\text{PbCl}_6)\text{Br}$ is further than 0.1 Å [JCDTB 1995

2719] from the corresponding location in space group $I4/m$, hence it is likely the space group has been misassigned in the course of the determination.

7. New inorganic ferroelectrics predicted in space group $I4_1$

A total of seven entries, for as many materials, is listed under space group $I4_1$ in the 1998/1 release of the ICSD. One entry is for the known ferroelectric $\text{Sr}_3(\text{FeF}_6)_2$, see Abrahams *et al.* (1984); three others are predicted to be possible new ferroelectrics and the remaining three materials to be polar, but not ferroelectric.

7.1. NbAs

The structure of this simple material was reported by Furuseh & Kjekshus (1964) with Nb at the origin and As at 0,0,0.416 (1) in a unit cell with $a = 3.4517$ and $c = 11.680$ Å (uncertainties not given). If the origin is displaced 0.042 Å (*i.e.* placing Nb at 0,0,0.042 and As at 0,0,0.458), then a displacement of each atom by 0.49 Å in opposite directions from Wyckoff position 4(a) in space group $I4_1$ to 0,0,0 and $0,0,\frac{1}{2}$ would result in a phase transition to space group $I4_1/a$ with its zero spontaneous polarization, the atoms occupying positions 4(a) and 4(b), respectively. Boller & Parthé (1963) previously reported NbAs as forming in space group $I4_1md$ with $z(\text{As}) = 5/12$, which would leave the result above unchanged. NbAs hence satisfies structural criterion (a) for ferroelectricity, with Δz magnitudes suggestive of high T_c , although values of u are unreported. The resistivity is presently unknown, but is anticipated to be low, with a potential for causing difficulties with dielectric measurements; detection of a band-gap anomaly might provide an alternative approach, as used successfully in the case of $\text{Sr}_2\text{SbMnO}_6$ (Foster, Nielson *et al.*, 1997).

Table 6. Atomic coordinates for $\beta\text{-NbO}_2$ at room temperature with hypothetical z' coordinates and polar displacements in Å

$a = 9.693$ (3), $c = 5.985$ (1) Å. $z^* = z - 0.0052$; $\Delta z = (z^* - z')c$.

	Wyckoff positions in $I4_1, I4/m$	x	y	z^*	z'	Δz
Nb1	8(<i>b</i>), 8(<i>h</i>)	0.2621 (2)	0.5076 (3)	0.0247 (4)	0	0.148
Nb2	8(<i>b</i>), 8(<i>h</i>)	0.2455 (2)	0.4909 (2)	0.4752 (4)	$\frac{1}{2}$	-0.148
O1	8(<i>b</i>), 8(<i>h</i>)	0.397 (1)	0.150 (1)	0.003 (3)	0	0.018
O2	8(<i>b</i>), 8(<i>h</i>)	0.110 (3)	0.364 (3)	-0.014 (6)	0	-0.084
O3	8(<i>b</i>), 8(<i>h</i>)	0.609 (1)	0.361 (1)	0.501 (3)	$\frac{1}{2}$	0.006
O4	8(<i>b</i>), 8(<i>h</i>)	-0.104 (3)	0.150 (3)	0.493 (7)	$\frac{1}{2}$	-0.042

O4 transformed to equivalent location at $\bar{y}\frac{1}{2} + x\frac{1}{4} + z$.

7.2. $\beta\text{-NbO}_2$

Schweizer & Gruehn (1982) reported that $\beta\text{-NbO}_2$ has a deformed rutile structure-type and refined the structure with 849 independent reflections to $R = 0.103$. The atomic coordinates are given in Table 6 with the origin shifted 0.0052 along the c axis to equalize the Nb atomic Δz displacements. Although $\Delta z(\text{O}) < u(\text{O})$ for each O atom on the basis of x, y, z' coordinates corresponding to space group $I4/m$, both $\Delta z(\text{Nb1})$ and $\Delta z(\text{Nb2}) \gg u(\text{Nb})$. The reported structure of $\beta\text{-NbO}_2$ hence fully satisfies the structural criteria for ferroelectricity. The observation that $u(\text{O4})$ is anomalously high at ~ 0.6 Å may be an indicator that further structural investigation is advisable. Assuming the present results, the value of T_c may be estimated from (1) by the AJK relation as 690 (350) K, using the larger of the two effective $\Delta z(\text{Nb})$ displacements with respect to their octahedra, *i.e.* $\Delta z(\text{Nb1}) \simeq 0.190$ Å. Dielectric and calorimetric measurements are necessary for confirmation of the predicted ferroelectricity.

7.3. Ag_3BiO_3

The atomic coordinates reported by Bortz & Jansen (1993) for the structure of Ag_3BiO_3 , prepared under 0.1 GPa oxygen pressure at ~ 1060 K, were refined to $R = 0.060$ based on 1729 independent absorption-corrected $F_o \geq 2\sigma(F_o)$, as given in Table 20S. The origin has been shifted along the polar axis to midway between the two independent Bi atoms and the order of some atoms has been rearranged in the table. The maximum atomic displacement is $\Delta z(\text{Ag4}) = 0.79$ Å, with all other $\Delta z \lesssim 0.23$ Å from the nonpolar antiferroelectric array represented by the x, y, z' locations; $0.08 < u_{33} < 0.13$ Å for all atoms except Ag6, for which $u_{33} = 0.21$ Å. If the x, y, z' array is stable at and above T_c , as expected from the resulting thermodynamic potential minimum associated with $P_s = 0$, then the criteria for ferroelectricity below T_c are satisfied. Both independent Bi atoms exhibit square pyramidal coordination by five O atoms, with one O shared between like Bi atoms and two O shared between independent Bi atoms to form a three-dimensional network. Lack of an applicable force

constant in (1) to this structural geometry prevents the estimation of T_c . Dielectric investigation is necessary to show if this material is ferroelectric.

7.4. Nonferroelectric materials in space group $I4_1$

$\text{Na}_2\text{ZrW}_3\text{O}_{12}$ (ZSTKA 22 6) and isomorphous $\text{Ag}(\text{In}_{3/4}\text{Ag}_{1/4})_2(\text{MoO}_4)_3$ (KRISA 29 701) are clearly polar, but the displacement magnitudes required for ferroelectricity exceed criterion (a) sufficiently so that neither is likely to be ferroelectric. $\text{Cs}_5\text{NaW}_4\text{N}_{10}$ (ZAACA 622 881) also fails to satisfy the structural criteria for ferroelectricity with three N atomic displacements from nonpolarity that exceed 1 Å.

8. Phase transitions and ferroelectricity

More than one-third of the entries under point group 4 in the current release of the ICSD, corresponding to about half the number of different materials listed, satisfy the structural criteria for ferroelectricity as presented above. About one-quarter of all entries in both point groups 4*mm* and 6 were shown to satisfy the structural criteria (Abrahams, 1990, 1996), as did about one-third of all entries in point group 6*mm* (Abrahams, 1988). The ICSD currently contains 5182 entries to materials in point groups that include a polar axis. The total number that might eventually be found to satisfy the structural criteria and subsequently confirmed as new ferroelectrics could hence approach an order of magnitude more than the number of ferroelectrics now known, see §1. Associated with each predicted ferroelectric is the probability that it will undergo a phase transition at T_c as $P_s \rightarrow 0$; for some materials, T_c may be higher than the m.p. or the decomposition temperature. Two major types of ferroelectric phase transition may be distinguished, from ferroelectric to paraelectric and from ferroelectric to antiferroelectric.

The transition from a ferroelectric to a paraelectric phase generally results in the addition of one or more symmetry elements, with the space group of the paraelectric structure becoming a supergroup of the ferroelectric space group. $\text{Ce}_5\text{B}_2\text{C}_6$ in space group $P4$ is

typical, see §2.1, with Δz displacements consistent with a transition from space group $P4$ to space group $P4/m$, the former being a subgroup of the latter. $\text{Ni}[\text{SC}(\text{NH}_2)_2]_4\text{Cl}_2$ is predicted to be another typical ferroelectric that undergoes a subgroup–supergroup transition to the paraelectric phase at T_c , see §6.6, with Δz displacements for all atoms consistent with a transition from space group $I4$ at room temperature to space group $I4/m$ at higher temperatures.

Transitions from a ferroelectric to a paraelectric phase, however, need not be subject to a subgroup–supergroup relationship as, for example, in the case of TlBO_2 (§3.1) from $P4_1$ to $P4/m$ and $\beta\text{-NbO}_2$ (§7.2) from $I4_1$ to $I4/m$. A similar nonsubgroup–supergroup relation was found earlier in the case of $\text{Sr}_3(\text{FeF}_6)_2$; with space group $I4_1$ at 295 K it was predicted to have $T_c = 1160$ (290) K at a phase transition to space group $I4/m$. Experimentally, $T_c = 922$ (1) K in $\text{Sr}_3(\text{FeF}_6)_2$, see Abrahams *et al.* (1984). All nonsubgroup–supergroup ferroelectric to paraelectric phase transitions are likely to be of first order.

The ferroelectric to paraelectric phase transition predicted in CrOF_3 (§3.2) is without symmetry change, but is otherwise typical of materials characterized by asymmetric potential minima, *cf.* Abrahams (1990). The calorimetric investigation of many previously unknown phase transitions at T_c , as the physical properties of new ferroelectrics systematically predicted on the basis of structural criteria are determined concomitantly, is expected to enrich the study of both phase transitions and ferroelectricity.

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