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New Ferroelectric Inorganic Materials Predicted in Point Group 4*mm*

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Abstract

The Inorganic Crystal Structure Database contains a total of 209 entries for 128 different materials reported in point group 4*mm*, of which eight are for previously known ferroelectrics. Analysis of the remaining entries, assuming the structure determinations reported are correct, leads to the prediction of an additional 43 new ferroelectric materials. 15 were determined in space group *P*4*mm*, 11 in *P*4*bm*, one in $P4_2nm$, one in *P*4*cc*, two in $P4_2mc$, one in $P4_2bc$, seven in *I*4*mm*, two in *I*4*cm*, one in $I4_1md$ and two in $I4_1cd$. Numerous other structures are shown to have been assigned, most likely, to an incorrect space group. All but one of the materials reported in space group *P*4*bm* are predicted to be ferroelectric. New ferroelectrics predicted in point group 4*mm* include $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$, $Nd_{0.33}TaO_3$, $YBaCuFeO_{5+\delta}$, $Ba_2(TiO)(Si_2O_7)$, $K_2(NbO)_2(SiO_3)_4$, $Ba_6CoNb_9O_{30}$, Sr_2SbMnO_6, $Hg_2AlF_5.(H_2O)_2$, $Rb_5Nb_3OF_{18}$ and $SrNi_2(VO_4)_2$.

1. Introduction

Application of the structural criteria presented by Abrahams (1988) to the atomic coordinates listed in the Inorganic Crystal Structure Database, hereafter ICSD (Bergerhoff & Brown, 1987), led, in the case of the test space group *Pba*2, to the prediction of ferroelectricity in five materials having the orthorhombically distorted tungsten–bronze-type structure and, at a lower confidence level, to the same predicted property in two additional materials (Abrahams, 1989). The first of these tungsten–bronze-type crystals that were grown in order to test the predictions experimentally were $Na_{13}Nb_{35}O_{94}$ and $K_3Fe_5F_{15}$ and both were found to exhibit confirmatory ferroelectric properties. $K_3Fe_5F_{15}$ is of particular interest both as the first known tungsten–bronze-type ferroelectric fluoride (Ravez, Abrahams & de Pape, 1989) and for the electronic order–disorder among the Fe^{2+} and Fe^{3+} ions that accompanies the 490 K ferroelectric–ferroelastic phase transition (Calage, Abrahams, Ravez & de Pape, 1990).

In addition to the prediction of ferroelectricity at room temperature, an estimate of the Curie temperature T_c of the predicted phase transition may be made by means of the Abrahams, Kurtz & Jamieson (1968), hereafter AKJ, relationship given in (1). The applications above assume T_c is a function of the largest Δz displacement from the zero spontaneous polarization structure, along the polar direction, by the metal ion that forms the strongest and least ionic bonds in the ferroelectric structure as given by

$$T_c = (\mathcal{K}/2k)(\Delta z)^2 \text{ K}, \qquad (1)$$

where $\mathcal{K}$ is a characteristic force constant, k is Boltzmann's constant, $\mathcal{K}/k \simeq 2.0 \times 10\,\text{K}^4\,\text{Å}^{-2}$ and c is the polar axis. The estimate holds best for octahedrally coordinated metal ions.

Verification of the two predictions in the test space group *Pba*2 led to the systematic application of the criteria to all entries in the ICSD for point groups 6*mm* and 6. Two new families were found to satisfy the structural criteria for ferroelectricity in space group $P6_3mc$, with eight additional compounds predicted in point group 6*mm* that may also be ferroelectric (Abrahams, 1988). If the space group and structural assignment for each material entered in the 1987 version of the database for this point group were correct, then three further families and four additional materials with this symmetry would be ferroelectric. The systematic examination of all entries in point group 6 led to over 80 additional newly predicted ferroelectrics (Abrahams, 1990), of which *ca* 30 are rare-earth isomorphs. Structural visualization of all atomic coordinate sets in the ICSD is conveniently accomplished by the use of Dowty's (1994) *ATOMS* program.

Ferroelectric crystals grown either from the melt or solution, in the absence of an appropriately applied electric field, are generally polydomain with greatly reduced spontaneous polarization (Abrahams, 1994). Structural refinement based upon X-ray diffraction data measured with a polydomain crystal is subject to increased uncertainty in the relatively small displacements of atoms from their higher-temperature positions (*cf.* the problems associated with $BaTiO_3$ in §2.5). Predictions drawn from the analysis of such refinements are hence subject to a related increase in the uncertainty of T_c.

The results of applying the structural criteria for ferroelectricity to all entries under point group 4*mm* listed in the June 1995 release of the ICSD, many of

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which are based on polydomain measurement, are presented herein. The ICSD was accessed through the Canadian Scientific Numeric Database Service.

2. New inorganic ferroelectrics predicted in space group *P*4*mm*

The 93 entries listed under space group *P*4*mm* in the ICSD constitute by far the largest number for any space group in point group 4*mm*, forming almost half the total. It may be noted, however, that 22 of these entries are to the major ferroelectric $BaTiO_3$, ten are to ferroelectric $PbTiO_3$ and 32 are to other related perovskite-type structures. In addition, 21 entries are to members of the $K_2[Pt(CN)_4]X_{0.3}.3H_2O$ family. The order in which the analyses below, and in the following space groups within point group 4*mm*, are presented largely follows that adopted in the ICSD and is without other significance.

2.1. $K_2[Pt(CN)_4]X_{0.3}.3H_2O$ *family*

The crystal structures of six isomorphous members of this family, with $X = Cl$, Br or the FHF group and in which combinations of Rb or NH_4 may replace K, and D may replace H, have been reported. The combined X-ray and neutron diffraction study of $K_2[Pt(CN)_4X_{0.3}.3H_2O$, with $X = Cl$ or Br, at several temperatures ranging from 31 to ~300 K (Heger, Deiseroth & Schulz, 1978), is taken as representative of all the other studies on the family listed in the ICSD (INOCA 15 782, INOCA 17 834, INOCA 17 839, INOCA 18 1922, ACBCA 34 1965, FEROA 16 135, PRLTA 33 963, PRLTA 33 1079, PRLTA 34 1132, ANYAA 313 516, MRBUA 10 217, MRBUA 10 225 and MRBUA 10 411).* The atomic coordinates in Table 1 were derived from the 417 independent neutron diffraction reflections measured on $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ at room temperature that led to a final refined model with $R = 0.032$. The corresponding model derived by an X-ray diffraction study at room temperature, which in principle gives more accurate coordinates for the Pt and Br atoms than those derived with neutrons, is not considered here since the use of averaged Friedel pairs in polar space groups can introduce systematic bias; indeed, large correlations were reported by Heger *et al.* (1978) between selected *z* coordinates in the X-ray diffraction study. Table 1 also contains the hypothetical paraelectric *z*′ coordinates. The occupancy factors for Br, O2, O3, D2, D3, D4 and D5, given in the neutron study as *ca* 0.6, 0.4, 0.9, 0.1, 0.2, 0.5 and 0.5, respectively, show that Br and O2 share a split 1(*b*) Wyckoff position and that D4 and D5 each occupy only half an 8(*g*) position.

Table 1. *Atomic coordinates for $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ at room temperature, hypothetical z′ coordinates and polar displacements in Å*

$a = 9.897\ (6)$, $c = 5.784(4)$ Å

	Wyckoff position	x	y	z	z'	Δz*
Pt1	1(*a*)	0	0	0	0	0
Pt2	1(*a*)	0	0	0.500 (2)	1/2	0
K	4(*f*)	0.1936 (7)	1/2	0.258 (2)	1/4†	0.046
Br	1(*b*)	1/2	1/2	0.503 (2)	1/2	0.017
C1	4(*e*)	0.2015 (2)	0	0.006 (2)	0	0.035
C2	4(*d*)	0.1428 (2)	0.1428	0.499 (2)	1/2	−0.006
N1	4(*e*)	0.3184 (2)	0	0.009 (2)	0	0.052
N2	4(*d*)	0.2254 (1)	0.2254	0.491 (2)	1/2	−0.052
O1	2(*c*)	1/2	0	0.595 (2)	0.605‡	−0.058
O2	1(*b*)	1/2	1/2	0.385 (6)	0.395	−0.058
O3	4(*d*)	0.3395 (5)	0.3395	−0.064 (2)	0	−0.370
D1	4(*e*)	0.426 (1)	0	0.700 (2)	0.716‡	−0.09
D2	4(*d*)	0.472 (4)	0.472	0.269 (11)	0.284	−0.09
D3	4(*d*)	0.452 (3)	0.452	0.542 (9)	1/2	0.24
D4	8(*g*)	0.402 (1)	0.363 (1)	0.837 (2)	0	0.94
D5	8(*g*)	0.292 (9)	0.286 (9)	0.844 (3)	0	0.90

* $\Delta z = (z - z')c$. † This location corresponds to the centrosymmetric 8(*t*) position in space group *P*4/*mmm* if half occupied by the K atom above the putative transition, see text. ‡ Note the nonpolar *z*, *z*′ relationship with the following atom in table, see text.

Examination of Table 1 also shows, among atoms other than D, that all *z* coordinates are close to 0 or 1/2 with the exception of K and the O1, O2 pair of atoms; in this table, O2 and O3 are interchanged with respect to those given by Heger *et al.* (1978). If the K^+ ions in Wyckoff position 4(*f*) of space group *P*4*mm* become disordered at higher temperatures among positions such as 8(*t*) in space group *P*4/*mmm*, with each location half-occupied, and if the approximately equal but opposite *z* coordinates of D1 and D2 become related as in Table 1, then the resulting assumed higher-temperature phase will be structurally paraelectric. Each of the two independent Pt atoms occupies the center of a slightly nonplanar $Pt(CN)_4$ group. Examination of Table 1 shows that all polar Δz displacements are less than 0.1 Å, except for O3, D3, D4 and D5. It may be noted that O2 is located only 0.68 Å from Br, but with a joint occupancy of unity for the two atoms; movement of O2 toward Br at higher temperatures would decrease Δz(O2). It is concluded that if $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ undergoes a phase transition to a paraelectric state above room temperature, then the change from a ferroelectric state is caused structurally by an order–disorder transformation of the K^+ ions together with a change in hydrogen-bond configuration comparable to that in KH_2PO_4 rather than to atomic displacements within

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* Coden-type references are given thoughout this paper for most structure determinations mentioned, but for which atomic coordinates are not reproduced, see Notes for Authors (1994). The ICSD omits the usual final check letter of the journal abbreviation, providing only five letters in each coden

well defined polyhedra such as those required for the application of (1).

2.2. *$PbTiO_3$*

The ferroelectric properties of $PbTiO_3$ have been known since 1950, with a phase transition to the paraelectric phase occurring at $T_c = 763$ K; the ferroelectric phase stability range is reported by Kobayashi, Uesu & Sakemi (1983) to extend, at lower temperatures, to a new second-order phase transition at 183 K. The corresponding displacement by Ti from the center of its O-atom octahedron at temperatures well below T_c, as given by the AKJ relationship (1), is hence $\Delta z(\mathrm{Ti}) = 0.195$ Å. Four of the ten entries to $PbTiO_3$ in the ICSD are from Glazer & Mabud (1978) and two are from Nelmes & Kuhs (1985). The single-crystal neutron diffraction study by Nelmes & Kuhs (1985) on a single-domain poled crystal gives $\Delta z(\mathrm{Ti}) = 0.323(2)$ Å at 295 K and 0.235 (3) Å at 700 K. A neutron diffraction powder profile refinement by Glazer & Mabud (1978) reports that $\Delta z(\mathrm{Ti}) = 0.32(1)$ Å at 298 K, also that it does not undergo significant change on cooling either to 160 or 90 K. The strong thermal dependence of Δz(Ti) at higher temperatures and the marked anharmonic atomic motion reported in the single-crystal study along the polar axis (highly significant third-order effects were reported) illustrate the need for further high-resolution diffraction studies to clarify the detailed dependence of this structure on temperature.

2.3. *$KNbO_3$*

Ferroelectricity in $KNbO_3$ was first reported in 1949, with $T_c = 691$ K. The space group above T_c is *Pm*3*m*; the structure in the *P*4*mm* tetragonal perovskite phase has been refined by Hewat (1973*a,b*) on the basis of both neutron diffraction single-crystal and powder profile refinement studies. Diffraction by the crystal, which was electric-field poled to be at least 90% single domain, was measured at 543 K. A total of 67 reflections were measured in an octant of reciprocal space, including 18 that were equivalent, to give a final value of $R = 0.019$ on refinement of the 14 parameter model. In the powder diffraction study, also measured at 543 K, the profile was determined at 0.1° steps to 59° 2θ. Refinement of the same 14 parameters led to almost identical values, with $R = 0.043$. High parameter correlations were found in both studies. The average resulting displacement of Nb from the center of its O-atom octahedron at 543 K is 0.167 (9) Å, corresponding to a Curie temperature predicted from (1) of 560 (60) K, in satisfactory agreement with experiment.

2.4. *$Pb_2Cu(OH)_4Cl_2$*

The atomic coordinates of the mineral diaboleite $Pb_2Cu(OH)_4Cl_2$, a distorted perovskite, were determined by Rouse (1971) on the basis of 173 independent reflections obtained by averaging a hemisphere of data including Bijvoet pairs. The starting model used the results of an earlier study [ARKEA 2 397] and led to $R = 0.05$; no improvement was obtained on changing from isotropic to anisotropic atomic displacement parameters. Cu, OH and one Cl atom occupy locations that are within 0.15 Å of the corresponding special positions in space group *P*4/*mmm*, but Pb1 and the other Cl atoms would have to undergo displacements of 1.26 and 0.51 Å, respectively, to transform to the centrosymmetric space group *P*4/*mmm*. An origin change results in other atomic displacements that are comparably long and that exceed those required by the structural criteria for ferroelectricity, hence $Pb_2Cu(OH)_4Cl_2$ is not expected to be ferroelectric, but may possess interesting dielectric properties.

2.5. *$BaTiO_3$*

The structure of $BaTiO_3$ has been intensively studied since this first complex oxide ferroelectric was discovered in 1944, with a total of 22 entries listed in the ICSD. Strong correlations between positional and thermal parameters produced severe problems in the earlier structural determinations (ACCRA 4 377, ACCRA 9 131, ACCRA 14 1019, ACCRA 15 972, MRBUA 16 497 and PHRVA 100 745). The study by Harada, Pedersen & Barnea (1970) is typical in giving good agreement between atomic coordinates determined from the X-ray and neutron diffraction results provided all U_{33} are assumed to be approximately equal; with this assumption, the final $R = 0.024$ for the X-ray and 0.027 for the neutron study. The average displacement of Ti in this study, with respect to the center of its O-atom octahedron, required to achieve a paraelectric state is $\Delta z(\mathrm{Ti}) = 0.128(2)$ Å, corresponding to $T_c = 330(15)$ Å on the basis of (1). With an experimental value of 393–403 K, depending upon crystal purity, the predicted Curie temperature is in acceptable agreement in view of the assumptions made in refinement and not reflected in the stated uncertainty. Two sets of high-precision X-ray diffraction measurements in the most recent study, by Buttner & Maslen (1992), remain characterized by a major correlation between z(Ti) and U_{33}(Ti); this study gives $\Delta z(\mathrm{Ti}) = 0.134(23)$ and 0.112 (77) Å. The Δz(Ti) displacement corresponding to the experimental T_c is 0.142 Å, based on (1), and is within the rather wide limits set by Buttner & Maslen (1992). It is unlikely that the well known correlation between Δz displacements and U_{33} parameters in structural studies of $BaTiO_3$ will be overcome until the study crystal consists of a single domain.

2.6. *PuS_2*

A black powder with the composition PuS_2, prepared by direct reaction of the elements, was reported by

Marcon & Pascard (1966) to be isostructural with Fe_2As. The atomic coordinates determined from the powder pattern are deposited in Table 1S,* but with the authors' z coordinates replaced by $z + 0.018$, thus shifting the origin to give equal but opposite Δz displacements by the two independent Pu atoms. Neither temperature factors, e.s.d.'s nor R factors are given in the paper. With S1 at $0,0,\frac{1}{4} - z$ and S2 at $\frac{1}{2},\frac{1}{2},\frac{1}{4} + z$, two S3 atoms at $\frac{1}{2},0,\frac{3}{4}$, one Pu1 at 000 and one Pu2 at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ in the hypothetical paraelectric structure, the polarization is zero since S1 and S2 are located at an equal but opposite distance on either side of the plane with $z = \frac{1}{4}$. The only nonzero Δz displacements are those of Pu1 and Pu2 at 0.143 Å each, corresponding to $T_c = 410$ K by means of the AKJ relationship (1). These polar displacements are likely to exceed the massive Pu atom r.m.s. amplitudes of thermal or static displacement at room temperature by a significant factor, hence, if the space group is indeed polar, the structure is predicted to be ferroelectric.

2.7. *$CsEuCl_3$ family*

The halide perovskite $CsEuCl_3$ has been reported by Nocera, Morss & Fahey (1980) in space group *P4mm* at room temperature and *Pm3m* at 423 K by Meyer (1978). The atomic coordinates for the tetragonal phase, deposited in Table 2S,* show that Eu is displaced by 0.067 Å (e.s.d.'s are not given by Nocera *et al.*, 1980) from the body-centered position and that the axially disposed Cl1 atom is displaced by −0.146 Å from the face-centered position of *Pm3m*, with both displacements oriented parallel to the polar axis. The average displacement of Eu from the center of its Cl octahedron (the equatorially disposed Cl2 atom is not displaced from $0,\frac{1}{2},\frac{1}{2}$) is hence *ca* $0.067 + 0.146/2 = 0.140$ Å, for a Curie temperature predicted by (1) to be 390 K. An experimental investigation by Pugmire, Christen, Mirsky, Nielson & Abrahams (1996) reveals both a heat capacity and a dielectric permittivity anomaly at 382 K, confirming the prediction that $CsEuCl_3$ is the first ferroelectric halide perovskite. $CsSmCl_3$, reported by Meyer (1978) to be isostructural, is expected to be the second.

2.8. *$Nd_{0.33}TaO_3$*

This new polymorphic modification of $NdTa_3O_9$ investigated diffractometrically by Pushcharovskii, Yamnova, Bogdanova & Leonyuk (1986) is reported to contain ~0.74 Nd atoms at the Nd1 site and ~0.30 atoms at the Nd2 site, with a final value of $R = 0.067$ based on 329 independent reflections. If the Nd sites were equally occupied, then an origin shift of 0.0225 along the polar axis as presented in Table 3S* would make the atomic displacements of Nd1 and Nd2 from the special position at $z = \frac{1}{2}$ in *P4/mmm* equal but opposite in sign, with resulting polarizations at $z = \frac{1}{2}$ that exactly cancel. Assuming the given Nd site occupancies, an origin shift of 0.013 is necessary. The resulting polar displacement required for Ta and its octahedral center to occupy the plane at $z = 0$ is dependent on the mean value of z(octahedron). With $\langle z(\mathrm{O})\rangle = -0.010(32)$, $\Delta z \simeq 0.07(12)$ Å and the corresponding T_c from the AKJ relationship is only *ca* 100(700) K. However, Puschcharovski *et al.* (1986) report generation, presumably second harmonic, by the pale lilac transparent crystals, hence the material is indeed polar at room temperature and perovskitic $Nd_{0.33}TaO_3$ satisfies the structural criteria for ferroelectricity. Dielectric measurements now in progress reveal a phase transition at ~550 K.

2.9. *$Pb[Zr_{0.44}Ti_{0.44}Mn_{0.04}Ni_{0.04}Nb_{0.04}]O_3$*

The large piezoelectric coupling coefficient in ferroelectric PZT ($PbZr_xTi_{1-x}O_3$) and its various substituted products has resulted in their widespread use in the form of multilayer ceramic capacitors. The most common substituent is probably La (to give PLZT), with $T_c \simeq 600$ K for low La and equal Zr and Ti composition. Rietveld refinement of the powder X-ray diffraction pattern for the modified PZT with composition $Pb[Zr_{0.44}Ti_{0.44}Mn_{0.04}Ni_{0.04}Nb_{0.04}]O_3$ measured at room temperature by Ng & Cheary (1985) led to the atomic coordinates in Table 4S,* with $R_{\mathrm{wp}} = 0.163$, $R_B = 0.051$. The displacement Δz by the composite Zr, Ti, Mn, Ni and Nb atom from the mean center of its oxygen octahedron is ~0.244 Å, corresponding to a Curie temperature of 1190 (130) K from (1). No atomic displacement is larger than 0.27 Å, hence the material satisfies the criteria for ferroelectricity. The high calculated value of T_c for this substituted PZT suggests remeasurement be undertaken of the structure with higher accuracy and the Curie temperature determined for comparison of the predicted and experimental results.

2.10. *Other ferroelectric perovskites*

Other perovskites in space group *P4mm* that newly satisfy the structural criteria for ferroelectricity together with their predicted Curie temperatures are: $Pb_{0.640}La_{0.206}Ti_{0.949}O_{2.846}$ with $T_c \simeq 670$ K, $Pb_{0.634}La_{0.209}Ti_{0.948}O_{2.844}$ with $T_c \simeq 700$ K (CMCAA 36 17) and $Ba_{0.88}Ca_{0.12}TiO_3$ with $T_c \simeq 595$ K (PHYBE 174 112).

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* Lists of atomic coordinates have been deposited with the IUCr (Reference: AN0527). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1, England.

* See deposition footnote.

2.11. *Nonferroelectric perovskites*

The 1.99 Å displacement required by an Fe atom and that of 1.85 Å by Cl to achieve centrosymmetry in hematophanite, $Pb_4Fe_3O_8Cl$, a derivative of the perovskite structure (MNLMB 39 49), is too large to satisfy the structural criteria; hence, if the structural determination is correct ($R = 0.091$), this material cannot be ferroelectric.

Each of the two entries for $NaTaO_3$, the series of 14 entries on various substituted perovskites and an additional five entries on $NaNbO_3$ under *P*4*mm* list all atoms in these structures with locations at special positions in *P*4/*mmm*, hence, if correct, none can be polar.

2.12. *YBaCuFeO*$_{5+\delta}$ *family*

The atomic coordinates of $YBaCuFeO_{5+\delta}$, with $\delta < 0.1$, in Table 2 were first determined by Rietveld analysis of the neutron diffraction powder profile at room temperature by Er-Rakho, Michel, Lacorre & Raveau (1988), with $R = 0.081$. Several other structural studies have subsequently appeared. An X-ray diffraction single crystal structure refinement of $YBaCuFeO_{5+\delta}$ by Vaughey & Poeppelmeier (1991), based on space group *P*4*mm*, led to $R = 0.092$. A recent neutron diffraction powder profile redetermination between 320 and 500 K by Mombru, Christides, Lappas, Prassides, Pissas, Mitros & Niarchos (1994) also confirmed the polar space group, with $R_{wp} = 0.045$ at 450–500 K, as did the accompanying magnetic spin structure determination. A similar study by Caignaert, Mirebeau, Bourée, Ngyen, Ducouret, Greneche & Raveau (1995) reports the space group as *P*4/*mmm*. Isostructural $LuBaCuFeO_{5+\delta}$ reported in *P*4*mm* (JMMMD 104 571) is confirmed in PHYCE 192 35, where the Nd, Sm, Gd, Dy and Tm analogs are also reported. O-atom coordinates in the three determinations of $YBaCuFeO_{5+\delta}$ differ by as much as 0.5 Å. The family structure is perovskite-related, but with one O atom almost missing, resulting in square pyramidal rather than octahedral coordination about Cu and Fe.

The atomic arrangement in space group *P*4*mm* could transform to that of *P*4/*mmm* with no displacement greater than ~0.13 Å, see Table 2, if the Cu and Fe atoms are equally present at the two Wyckoff 1(*b*) sites. However, Er-Rakho *et al.* (1988) proposed a ratio of 62:38 for the two atoms at the 1(*b*) site with $z \approx 1/4$ and 38:62 at the site with $z \approx 3/4$. Vaughey & Poeppelmeier (1991) suggested no disorder, but placed Cu completely at the site with $z \approx 3/4$, because the more highly distorted pyramidal coordination there was consistent with the Jahn–Teller d^9 configuration. Mombru *et al.* (1994) place the Cu ion at $\frac{1}{2}, \frac{1}{2}, 0.262$. Mössbauer studies have suggested a single Fe site. Equal occupancy of the 1(*b*) sites corresponds to a ferroelectric structure, with predicted $T_c \simeq 340$ K for the atomic coordinates in Table 2. Variations in the value of δ and the prior thermal treatment may influence the range of reported results. Further crystallographic and physical investigation of this material is clearly appropriate in view of the controversy in the literature over the space group assignment and also in order to clarify the relationship of $YBaCuFeO_{5+\delta}$ to that of the high-T_c superconducting $YBa_2Cu_3O_{7-\delta}$ family.

Table 2. *Atomic coordinates of* $YBaCuFeO_{5+\delta}$ *at room temperature, hypothetical* z' *coordinates and polar* Δz *displacements in* Å

$a = 3.865\ (1), c = 7.6425\ (8)$ Å

	x	y	z†	z'	Δz‡
Ba	0	0	0	0	0
Y	0	0	0.4886 (3)	1/2	−0.087
Cu1, Fe1	1/2	1/2	0.2512 (5)	0.2682	−0.130
Cu2, Fe2	1/2	1/2	0.7161 (6)	0.7331	−0.130
O1	1/2	1/2	−0.0077 (23)	0	−0.059
O2	1/2	0	0.3105 (9)	0.3152	−0.036
O3	1/2	0	0.6802 (9)	0.6849	−0.036

† Origin translated 0.0226 to place Ba at origin. ‡ $\Delta z = (z† - z')c$.

3. New inorganic ferroelectrics predicted in space group *P*4*bm*

A total of 26 entries are listed under space group *P*4*bm*, of which seven are to fresnoite and six more are to members of the fresnoite family, a predicted new ferroelectric family, see below. The tungsten-bronze-type family has eight entries, four of which are to previously well known and three others to newly predicted ferroelectrics. In addition, there are two entries to the new possibly ferroelectric complex nitride *A*CrN (*A* = Nb, Ta) family, one to an early but incomplete structure determination of NH_4ClO_2, another to $K_2(NbO)_2(Si_4O_{12})$ and the most recent entry to $KBaCuV_2O_7Cl$, a material shown below to belong to the fresnoite family.

3.1. *Fresnoite family,* $A_2(BO)(C_2O_7)$ *(A = K, Rb,* NH_4*, Ba; B = Ti, V; C = P, Si, V)*

The mineral fresnoite, $Ba_2(TiO)(Si_2O_7)$, is isostructural with at least four other materials in space group *P*4*bm* and is hence taken as naming this family [see also $KBaCu(V_2O_7)Cl$ in §3.2]. The atomic coordinates of fresnoite presented in Table 3 are from Markgraf, Halliyal, Bhalla, Newnham & Prewitt (1985); other values found under *P*4*bm* for this mineral are given in ZEKGA 130 438, BUFCA 90 20, SCIEA 156 1361 and ASBSD 48 609. Coordinates for isostructural $K_2V_3O_8$; $Rb_2V_3O_8$; $(NH_4)_2V_3O_8$; and $K_2(VO)P_2O_7$ are given, respectively, in ACBCA 31 1794; ZAACA 613 63; ZNBSE 43 309 and JPCSA 45 581; and DANKA 250 350. The structure of $Ba_2(TiO)(Si_2O_7)$ was determined at 297

Table 3. *Atomic coordinates for fresnoite, $Ba_2TiSi_2O_8$ at 297 K, hypothetical z′ coordinates and polar Δz displacements in Å*

$a = 8.527\ (1), c = 5.2104\ (9)$ Å

	x	y	z†	z'	Δz‡
Ba	0.32701 (3)	0.82701 (3)	−0.0242	0	−0.126
Ti	0	0	0.5112 (5)	1/2	0.058
Si	0.1280 (2)	0.6280 (2)	0.4888 (8)	1/2	−0.058
O1	0	1/2	0.6051 (19)	1/2	0.548
O2	0.1259 (5)	0.6259 (5)	0.1809 (12)	0	0.943
O3§	0.0772 (8)	0.7924 (6)	0.6187 (11)	1/2	0.619
O4	0	0	0.1854 (20)	0	0.966

† Polar direction reversed to make all original z coordinates positive, with origin translated by −0.0242 to give equal but opposite displacements from the plane at $z = \frac{1}{2}$ for the Si and Ti atoms. ‡ $\Delta z = (z\dagger - z')c$. § Authors' xyz coordinates replaced by equivalent $\frac{1}{2} + y, \frac{1}{2} + x, z$.

and 573 K; the largest coordinate difference found between them was 0.02 (2) Å, for O4(z), hence only coordinates reported at 297 K are considered here. A total of 1176 reflections were measured, giving 579 independent values in a least-squares refinement that started with the coordinates of ZEKGA 130 438 and that led to a final $R = 0.035$, $wR = 0.040$. Refinement of dependent y parameters of the form $x, \frac{1}{2} + x, z$ for Ba, Si and O2, as suggested by the e.s.d.'s accompanying these parameters, may have introduced high correlations, but the coordinates in Table 3 are comparable to those reported earlier and the full set of Bijvoet reflection pairs allowed determination of the absolute structural configuration.

The arbitrary origin selected by Markgraf *et al.* (1985) has been replaced in Table 3 by one midway between Ti and Si along the polar axis. All resulting atomic displacements required for the transformation to space group $P4/mbm$, as given in column 6 of Table 3, are less than 1 Å, but have values that clearly exceed their r.m.s. thermal or static amplitudes (~0.1 Å); they hence satisfy the structural criteria for ferroelectricity (Abrahams, 1988). Fresnoite and its family members are thus predicted to be potential new ferroelectrics as O1 exchanges identity with O4, and O3 exchanges with O2 in course of polarization reversal.

The largest Δz displacements given in Table 3 for fresnoite may be reduced by a further origin shift of 0.42 Å along the polar axis to result in maximum displacements of 0.55 Å equally by Ba and O4. Such displacements by atoms as massive as Ba are likely only at high temperatures. The square pyramidal coordination about Ti and the tetrahedral coordination about Si does not lead to a reliable estimate of T_c for fresnoite (*cf.* Abrahams, 1990), since the force constant for neither arrangement is immediately applicable in the AKJ relationship. The displacements of Ti and Si from the average z coordinate of the O atoms forming each polyhedron are no larger than 0.11 Å, with a corresponding value for T_c based on (1) below room temperature but with a wide uncertainty.

It is notable that fresnoite exhibits a positive pyroelectric coefficient at 297 K that reaches a maximum at 435 K, thereafter decreasing rapidly at higher temperatures to become negative at 465 K (Markgraf *et al.*, 1985); a sharp peak in dielectric polarization and permittivity, also in frequency constant and coupling coefficient, has similarly been reported at ~435 K (Halliyal, Bhalla, Markgraf, Cross & Newnham, 1985). These changes are unlikely to be associated with the transition from ferroelectric to paraelectric both in view of Markgraf *et al.*'s (1985) structural results and Halliyal *et al.*'s (1985) finding that no significant changes in structure are observed to 670 K. Based on the displacements in Table 3, the transition is expected to take place at higher temperatures, possibly before melting.

3.2. *$KBaCu(V_2O_7)Cl$*

The atom coordinates in Table 5S* reported by Martin & Müller-Buschbaum (1994) were derived from the refinement of 508 diffractometric independent reflections, resulting in $R = 0.088$ for isotropic atomic displacements. Comparison with the atomic coordinates in Table 3 shows that $KBaCu(V_2O_7)Cl$ is isostructural with fresnoite ($\frac{1}{2} - x, x, z$ is equivalent to $x, \frac{1}{2} + x, z$), although this relationship had not been noted previously. The origin was obtained by minimizing $\Sigma\Delta z$ for the four heavier atoms; it may be seen that no atom is displaced more than 0.86 Å from a paraelectric arrangement. Cu^{2+} occupies a strongly distorted octahedral or square pyramidal arrangement of O and Cl atoms and is displaced 0.21 Å, whereas V^{5+} occupies a distorted O-atom tetrahedron with a displacement of 0.20 Å, from zero polarization. Pairs of tetrahedra share corner O atoms to form V_2O_7 groups, all V atoms having the same z coordinate. The average V—O distance is 1.715 Å, compared with 2.067 Å for Cu—O, Cl in the square-pyramidal coordination, hence the potential barrier associated with V is the most relevant in determining T_c. The Curie temperature estimated from (1) is ~800 K, but application of the AJK relation to tetrahedral ions is known to be of low reliability (Abrahams, 1990). The dielectric properties of $KBaCu(V_2O_7)Cl$ are presently under study.

3.3. *Tungsten-bronze-type family*

The nine tetragonal tungsten-bronze-type structures currently listed under space group $P4bm$ include the four well known ferroelectrics $Ba_xSr_{5-x}Nb_{10}O_{30}$ (with $x \simeq 1.25$ and 3.35), $Ba_6Ti_2Nb_8O_{30}$ and $K_{6-x-y}Li_{4+x}Nb_{10+x}O_{30}$ with $x \simeq 0.07$ and $y \simeq 0.23$ (JCPSA 48 5048, ACCRA 18 496, KRISA 29 1084,

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* See deposition footnote.

JCPSA 54 2355 and ACBCA 24 984), in addition to three others that are expected to be new ferroelectrics. The structures of $Ba_6CoNb_9O_{30}$, $Ba_6FeNb_9O_{30}$ and $Ba_{5.2}K_{0.8}U_{2.4}Nb_{7.6}O_{30}$ may be most directly related to that of $Ba_6Ti_2Nb_8O_{30}$. The resulting atomic displacements form the basis for predicting their ferroelectric Curie temperatures, the latter material being taken as typical of the three former.

The atomic coordinates of $Ba_6CoNb_9O_{30}$ were derived by Lehmann & Müller-Buschbaum (1981) on the basis of 767 independent reflections. The Ba atoms were refined with anisotropic displacement parameters; all other atoms being refined isotropically to give a final $R = 0.076$. The final coordinates may be found in Table 6S* without change in origin, since the weighted average deviation in z coordinate from its corresponding z' value is close to zero for all five independent O atoms. Nb1,Co occupies an octahedron of two O1 and four O3 atoms, Nb2 an octahedron of two O2, one O3, one O4 and two O5 atoms. The polar deviation of the disordered pair of Nb1 and Co atoms at the 2(*b*) Wyckoff position from its mean octahedral O-atom z coordinate is 0.231 Å but, since the latter is located 0.055 Å below $z = 1/2$ whereas the former is above this plane, the net Nb1,Co displacement required to achieve a paraelectric state is $0.231 - 0.055 = 0.176$ Å. The corresponding displacement for Nb2 is only 0.020 Å and, since it is so much smaller than that for Nb1,Co, it is not critical in determining T_c. Application of (1) to the Nb1,Co displacement gives $T_c = 620$ K. The uncertainty in atomic coordinates was not reported but, assuming a value not less than 2 in the final digits of z(O), the corresponding uncertainty in T_c is at least 55 K.

The ferroelectric Curie temperatures of isotypic $Ba_6FeNb_9O_{30}$ and $Ba_{5.2}K_{0.8}U_{2.4}Nb_{7.6}O_{30}$ may be similarly derived as 360 K for the former, based on the polar displacement of 0.134 Å for Nb1,Fe to reach a paraelectric state (MOCMB 117 1239), and 485 K for the latter, based on a displacement of 0.155 Å for Nb1,U1 (JCOMA 139 315). The uncertainty in T_c is estimated as about 100 K in both materials.

3.4. $K_2(NbO)_2(SiO_3)_4$

The $K_2(NbO)_2(SiO_3)_4$ atomic coordinates deposited in Table 7S* were determined and refined by Crosnier, Guyomard, Verbaere, Piffard & Tournoux (1992) to give $R = 0.021$. These coordinates allow the prediction that this material is a new ferroelectric. The structure contains chains of corner-sharing Nb1 (4 × O1, O3, O4) and Nb2 (4 × O2, O3, O4) octahedra along the polar axis and pairs of corner-sharing Si1 (2 × O1, O5, O6) and Si2 (2 × O2, O5, O7) tetrahedra. The choice of origin in Table 7S results in equal Δz displacements of 0.122 Å along the polar axis by each independent Nb and Si atom, and no more than 0.149 Å by any O atom, from the corresponding locations in space group *P*4/*mbm*. These displacements satisfy the structural criteria for ferroelectricity. An estimate of T_c may be made on the basis of the AKJ relationship and Table 7S, assuming the transition from the ferroelectric phase is, respectively, either to an antiferroelectric or to a paraelectric phase, as follows.

If the higher-temperature phase is antiferroelectric, then the atomic positions in this phase are fully represented by the z' coordinates in Table 7S.* The displacement of Nb1 or Nb2 from the plane at $z = 0.2483$ is $-0.122(2)$ Å, as shown in Table 7S; the Si1 and Si2 displacements are identical but of opposite sign. The corresponding $T_c = 298(10)$ K. However, if the transition is to a paraelectric phase in which no ion makes a contribution to the spontaneous polarization, then the z coordinates of both Nb and both Si ions must coincide with the mean z coordinate of their polyhedral O atoms. Taking Nb as forming stronger and less ionic bonds to O than tetrahedral Si, attention may be directed to Nb1 and Nb2.

The mean z coordinate for the O atoms in the Nb1 octahedron is 0.2561_3 requiring an additional displacement of 0.063 Å for a total $\Delta z = 0.185$ Å. Substitution in (1) gives $T_c = 690(60)$ K. Similarly, the mean z coordinate for the 4 × O2 + O3 + O4 atoms of the Nb2 octahedron is −0.2223, requiring an additional displacement of 0.212 Å for a total $\Delta z = 0.334$ Å; the corresponding $T_c = 2230(100)$ K. Since both sets of displacements are required to achieve the paraelectric phase, the higher estimate of T_c is expected to be closer to the phase transition temperature. The large difference between the two estimates is due primarily to the positions of O3 and O4, with their corresponding Nb1—O3 = 1.76 and Nb1—O4 = 2.32, Nb2—O3 = 2.28 and Nb2—O4 = 1.78 Å distances. The report by Crosnier, Guyomard, Verbaere, Piffard & Tournoux (1991) that $K_2(NbO)_2(SiO_3)_4$ generates second harmonics to temperatures at least as high as 1350 K, the upper limit of their equipment, indicates the high-temperature phase to be paraelectric. A more reliable measure of T_c in ferroelectric $K_2(NbO)_2(SiO_3)_4$ hence awaits dielectric investigation.

3.5. NbCrN family

The structure of NbCrN and isotypic $Ta_{1-x}Cr_{1+x}N$ was determined from the X-ray powder pattern, yielding $R_I \approx 0.075$ for the former (Ettmayer, 1971). The atomic coordinates in Table 8S* show that a choice of origin midway between the two independent Nb atoms results in a nonpolar atomic arrangement for the Nb and N atoms, whereas the two independent Cr

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* See deposition footnote.

* See deposition footnote.

atoms must be displaced 0.37 Å for the entire structure to become nonpolar. If this displacement is reliable, then NbCrN is ferroelectric with a high Curie temperature. Reinvestigation of the structure is necessary to confirm the apparent polar distortion. Ettmayer (1971) also reports an identical structure for $Ta_{0.8}Cr_{1.2}N$, with Ta and Cr distributed statistically over the Ta sites (*i.e.* those of Nb in Table 8S)* in the ratio 0.8:0.2.

3.6. NH_4ClO_2

An early study of NH_4ClO_2 (ZEKGA 76 431) was able to locate only the N and Cl atoms, at 000 and $\frac{1}{2}0\frac{1}{4}$, respectively. If the given space group assignment is confirmed and all independent atoms are satisfactorily located within it, then this chlorite may satisfy the criteria for ferroelectricity, although there is presently insufficient information for such a prediction.

4. Space groups $P4_2cm$ and $P4nc$

No entries appear in the June 1995 issue of the ICSD under space groups $P4_2cm$ or $P4nc$.

5. New inorganic ferroelectrics predicted in space group $P4_2nm$

A total of 14 entries are listed under space group $P4_2nm$ in the current release of the ICSD, of which two are to $K_2Zn_6O_7$, three are to S_4N_2 and two are to $(NH_3)_{10}Co_2O_2(NO_3)_5$. Only one material in this space group, S_4N_2, is predicted to be ferroelectric.

5.1. S_4N_2

Two entries with identical atomic coordinates are given for the structure of S_4N_2, one published by Chivers, Codding, Laidlaw, Liblong, Oakley & Trsic (1983), the other by three of the same authors in a preliminary communication: a third entry with comparable value coordinates was reported in JCDTB 1981 2188. All four independent atoms may be seen from Table 4 to lie within 0.45 Å of the plane at $z = 1/2$; occupation of this plane would result in a paraelectric structure. The structural criteria for ferroelectricity are hence satisfied by S_4N_2. Polarity reversal would necessarily be accompanied by inversion of the molecular half-chair conformation. The expected Curie temperature is so high, however, that it may not be practically attainable, although investigation of the dielectric properties of S_4N_2 may be of interest.

Table 4. *Atomic coordinates for S_4N_2 at room temperature, hypothetical z′ coordinates and polar Δz displacements in Å*

$a = 11.146\ (4), c = 3.773\ (1)$ Å

	x	y	z†	z'	Δz‡
S1	0.38869 (9)	0.38869	0.61889	1/2	0.499
S2	0.17863 (9)	0.17863	0.56408 (71)	1/2	0.242
S3	0.14505 (9)	0.34959 (9)	0.38110 (64)	1/2	−0.449
N1	0.25685 (30)	0.43082 (31)	0.55578 (133)	1/2	0.210

† Origin shifted 0.05595 along the polar axis. ‡ $\Delta z = (z\dagger - z')c$.

5.2. Space-group assignment

The following structures assigned to space group $P4_2nm$ may be in error and should be reinvestigated. That of $K_2Zn_6O_7$, determined diffractometrically by Wambach & Hoppe (1978) with a final $R = 0.085$, is reported to have both tetrahedral and planar triangular coordinated Zn atoms. The atomic coordinates in Table 9S* show that all atoms except O3 are located within 0.12 Å of planes with $z = 0$ or $1/2$, the corresponding positions in paraelectric space group $P4_2/mnm$. Since the average r.m.s. amplitude of atomic displacement is ~0.13 Å, O3 is the only atom in this structure with a displacement that is suggestive of ferroelectricity. The atomic coordinates in Table 9S are as listed by the ICSD, although the authors give $x(O2) = 0.106(1)$, $y(O2) = 0.196(1)$; symmetry, however, requires these two coordinates to be identical. This error, resulting in a short O1—O2 contact, other possible typographic errors in the atomic coordinates, the unusual coordination found for Zn and the approach to centrosymmetry, are together indicative of a need for further study.

The structure of $LiFe_2F_6$ has been determined by Fourquet, Le Samedi & Calage (1988) on the basis of diffractometer measurements. A good fit ($R < 0.05$) was obtained both in space groups $P4_2/mnm$ and $P\bar{4}n2$, but the best fit with final $R = 0.0208$ was found in $P4_2nm$. Bijvoet pairs of reflections were not measured, nor were physical tests made to detect inversion centers. Mössbauer analysis showed that the Fe^{2+} and Fe^{3+} ions are ordered. If, however, the Fe^{2+} and Li ions (at 0, 0, 0.3339 and 0, 0, −0.3336, respectively) are disordered, then no atom in the structure is further than 0.03 Å from centrosymmetry. A new structural study, or calorimetric and dielectric measurements, could resolve this choice between space groups.

It has been reported (ACBCA 27 1740) that refinement of previously measured powder data for β-uranium cannot resolve the choice between $P4_2nm$, $P4_2/mnm$ and $P\bar{4}n2$, although the ICSD entry is given under $P4_2nm$ in view of its slightly smaller (*i.e.* 0.24 compared with 0.28 for both alternative space groups) R

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* See deposition footnote.

* See deposition footnote.

value. No atomic displacement from a special position in $P4_2/mnm$ exceeds 0.2 Å, less than double the estimated r.m.s. atomic displacement amplitude, hence the latter space group is the more probable.

The structures of μ-hyperoxobis(pentamminecobalt(III)) nitrate, $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ (ACCRA 16 247, NATUA 190 714), and isostructural μ-amidobis(pentamminecobalt(III)) nitrate, $[(NH_3)_5CoNH_2Co(NH_3)_5](NO_3)_5$ (ACSAA 17 79), were refined in space group $P4_2nm$ using visually estimated film-recorded reflection intensities, each resulting in a final R of ~0.20. The atomic coordinates of neither material, however, differ significantly from those expected in space group $P4_2/mnm$.

The atomic coordinates of $Sr_4Tl_2O_7$ (ZAACA 396 113) differ by less than 0.05 Å from a centrosymmetric arrangement. The atomic coordinates of $Ca_{11}N_8$ (ACBCA 25 199), reported on the basis of a photographic study leading to $R = 0.13$, are nonpolar. The atomic coordinates of Ca_3Cd_2 were taken (JCOMA 50 275) as identical to those of Gd_3Al_2 (ACCRA 17 620) on the basis of the X-ray powder diffraction pattern. The z coordinates of the latter are within 0.1 Å of a nonpolar structure, if the origin is shifted 0.004 along the c axis. The structures of both should be reinvestigated. The atomic coordinates of $(Li_{0.32}H_{1.68})(TiTe)O_6$ are given (EJSCE 39 321) without values for the Li or H atoms. All remaining atoms, except for an independent Te, Ti atom sharing the same site at $00z$, satisfy the structural criteria for ferroelectricity. The exception results in the characterization of $(Li_{0.32}H_{1.68})(TiTe)O_6$ as pyroelectric but not ferroelectric.

6. New inorganic ferroelectrics predicted in space group *P4cc*

The seven entries in space group *P4cc* refer to four different materials; only one, $VOSe_2O_5$, is likely to be ferroelectric.

6.1. $VOSe_2O_5$

All atoms in oxovanadium(IV) diselenate(IV) reported by Meunier, Bertaud & Galy (1974) have z coordinate relationships that lead to a paraelectric arrangement following atomic displacements no greater than 0.71 Å, as may be seen in Table 10S.* The structure was determined on the basis of a photographic survey of single crystal intensities, with final $R = 0.157$. A piezoelectric test was positive. Cancellation of dipoles in the hypothetical paraelectric atomic arrangement shown in the table follows from the equal but opposite contributions by V1 and V2, O1 and O2, O5 and O6, and O7 and O8. The two largest atomic displacements, 0.71 Å by O3 and 0.62 Å by O4, together with the 0.40 Å displacements by Se1 and Se2 and that of 0.36 Å by V3, if achievable before melting or decomposition, are expected to result in an elevated Curie temperature; it is not possible to estimate the probability of polarity reversal at fields less than breakdown. However, the dielectric properties of this crystal are of interest, in view of these structural features, and are worthy of investigation.

Table 5. *Atomic coordinates for $BaGe_2As_2$ at room temperature, hypothetical z' coordinates and polar Δz displacements in Å*

$a = 7.618\ (5)$, $c = 8.500\ (5)$ Å

	x	y	z†	z'	Δz‡
Ba1	0	0	−0.0121	0	−0.103
Ba2	1/2	0	0.0121 (8)	0	0.103
Ge1	0.3351 (5)	1/2	0.8543 (8)	0.8798	−0.217
Ge2	1/2	0.1632 (5)	0.5947 (8)	0.6202	−0.217
As1	0.2290 (3)	0.2453 (4)	0.2437 (7)	0.2500	−0.054

† Origin shifted 0.0121 along polar axis. ‡ $\Delta z = (z^{\dagger} - z')c$.

6.2. $TaTe_4$ *family*

All remaining ICSD entries under space group *P4cc* are to the $TaTe_4$ family. The structure at room temperature is incommensurately modulated. It is shown in ASBSD 43 305 that the supercell has space group *P4/ncc*, the subcell *P4/mcc*, hence, ferroelectricity is not possible in this family.

7. New inorganic ferroelectrics predicted in space group $P4_2mc$

Two of the three entries under space group $P4_2mc$ are to isostructural $BaGe_2P_2$ and $BaGe_2As_2$, the third to $Mg(ClO_2)_2.6H_2O$. All three materials are either ferroelectric or else were assigned to an incorrect space group.

7.1. $BaGe_2As_2$ *family*

The atomic coordinates for $BaGe_2As_2$ presented in Table 5 were reported by Eisenmann & Schäfer (1981) on the basis of diffractometer measurement of 414 independent reflections leading to $R = 0.069$, but with the origin moved to midway between the independent Ba atoms. Examination shows that no atom is further than 0.22 Å from a centrosymmetric arrangement. The structural criteria for ferroelectricity are hence satisfied by $BaGe_2As_2$ and its family member $BaGe_2P_2$; although the Curie temperature cannot be estimated reliably from the displacements of atoms located within tetrahedra (Abrahams, 1990), a value of ~800 K is indicated by (1). The large magnitudes of U^2(Ba), reported in the range 0.73–1.08 Å^2 for the two materials and corre-

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* See deposition footnote.

sponding to r.m.s. amplitudes of ~1 Å for these massive atoms at room temperature, should be reinvestigated. Dielectric measurement is necessary to determine T_c.

7.2. $Mg(ClO_2)_2.6H_2O$

The atomic coordinates of magnesium chlorite hexahydrate were determined at 300 K (ACSCE 46 1755) on the basis of 313 unique reflections measured diffractometrically. The final value of R was 0.041 in space group $P4mc$, that in the alternative choice of space group $P4_2/nmc$ was 0.066 with a much larger value of wR; the former was hence chosen. However, no atom in the chosen space group is further than ~0.05 Å from a centrosymmetric arrangement. This distance is significantly less than the average r.m.s. atomic displacement amplitude of 0.22 Å. It is thermodynamically unlikely that a structure so close to paraelectric would remain ferroelectric, hence $Mg(ClO_2)_2.6H_2O$ should be reinvestigated.

8. New inorganic ferroelectrics predicted in space group $P4_2bc$

Two entries, one for $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$ and the other for $NaZn(OH)_3$, appear under this space group in the current release of the ICSD. $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$ (ACBCA 35 46) was flux-grown by analogy with the tetragonal tungsten-bronze crystals $K_{0.6}WO_3$ and $K_3Fe_5F_{15}$, see §3.3, both of which are ferroelectric. The structure was reported in space group $P4_2bc$, but, with all atomic displacements from positions corresponding to $P4_2/mbc$ uniformly less than 0.1 Å, is most likely to be centrosymmetric; it should hence be reinvestigated. $NaZn(OH)_3$ is predicted to be ferroelectric.

8.1. $NaZn(OH)_3$

The atomic coordinates of sodium trihydroxyzincate at 190 K presented in Table 11S* were determined by von Schnering, Nesper & Stoilova (1986) on the basis of 331 symmetry-independent reflections, with a final value of $R = 0.049$. The origin has been shifted 0.0293 to place the mean negative-charge center of the distorted tetrahedron of O atoms about Zn at $z = 0$. No atomic displacement from the hypothetical structure with z' coordinates in Table 11S is greater than 0.69 Å, hence the structural criteria for ferroelectricity are satisfied. A displacement of 0.16(2) Å by Zn^{2+} along the polar axis to achieve coincidence with the mean negative-charge plane of the distorted tetrahedron, together with the 0.01 Å displacement by Na^+, would result in zero dipole due to the ionic charges; that due to the H atoms also becomes zero at the z' locations. The ferroelectric–paraelectric transition resulting from these displacements probably corresponds to the phase transition expected, but not yet characterized, between the present structure at 190 K and that reported in space group $P4_2/mbc$ at 290 K (NATWA 48 665). The predicted value of $T_c \simeq 510(150)$ K from the AKJ relationship (1), based on this displacement, has a rather high uncertainty both in view of the Zn tetrahedral coordination (Abrahams, 1990) and the possibility of large parameter interactions caused by the polydomain study crystal, but is in agreement with experiment.

The principle that spontaneous polarization reversal in ferroelectric crystals is charge- rather than position-dependent is clearly illustrated by the structure of $NaZn(OH)_3$. Although the direction in which the apex of the ZnO_4 tetrahedron points along the polar axis remains unchanged on reversing P_s, the dipole sense of the tetrahedron and of the spontaneous polarization is determined primarily by the relative position of Zn^{2+} within the tetrahedral O_4 group.

9. New inorganic ferroelectrics predicted in space group $I4mm$

This space group, with 32 entries, has the second largest number of citations in the ICSD for point group $4mm$. Seven materials satisfy the structural criteria for ferroelectricity. The structures of 19 others corresponding to 22 entries have been examined and are not found to be candidates for ferroelectricity. The remaining two entries are most likely assigned to the wrong space group.

9.1. Sr_2SbMnO_6

Atomic positions in the perovskite Sr_2SbMnO_6 were reported by Politova, Kaleva, Danilenko, Chuprakov, Ivanov & Venevtsev (1990) on the basis of a Rietveld refinement of the powder diffraction pattern that led to a final $R_p = 0.072$. Examination of their coordinates in Table 12S,* in which the origin is shifted 0.242 along the polar axis to illustrate the compatibility of O1 and O2 in Wyckoff position 2(a) of space group $I4mm$ with the 4(e) position of space group $I4/mmm$, reveals that all atoms, except O3 with its displacement of ~0.18 Å, are within 0.06 Å of a centrosymmetric arrangement. The r.m.s. atomic amplitude of thermal or static displacement for O3 determined from the powder pattern is ~0.12 Å. Dielectric permittivity anomalies in several compositions within the $PbTiO_3$–Sr_2SbMnO_6 system are reported by Politova *et al.* (1990), with a transition in Sr_2SbMnO_6 to space group $Pm3m$ at ~725 K. The choice of space group at 293 K was based only on diffraction data; if correctly assigned, the polar

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* See deposition footnote.

* See deposition footnote.

displacement of O3 only in this material would satisfy the structural criteria for ferroelectricity, but a single crystal redetermination is necessary to predict a Curie temperature with confidence. Measurement of dielectric hysteresis would confirm the property.

9.2. KNa_2CuO_2

The atomic coordinates of KNa_2CuO_2 in Table 13S* were determined by Losert & Hoppe (1984) on the basis of 155 independent X-ray reflections measured diffractometrically, resulting in a final $R = 0.074$. Each atom within the linear CuO_2^{3+} ion is within 0.05 Å of the corresponding location in space group $I4/mmm$. The K and Na atoms, however, are 0.88 and 0.18 Å, respectively, from the special positions at $00\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{4}$ in the higher symmetry space group. It is notable that the CuO_2^{3+} ion becomes symmetric in the hypothetical paraelectric phase. The K^+ ion displacements required are large, but not improbable. Estimation of T_c in this unusual structure is not feasible at present. If the structure is correct, it clearly satisfies the polar displacement criteria for ferroelectricity. Investigation of the dielectric and other physical properties of KNa_2CuO_2 would be of interest.

9.3. $Na_{1.26}La_{0.913}Nb_2O_7.(H_2O)_{1.6}$

All atoms in this elongated unit cell (SSIOD 57 285), with $a = 3.891$ and $c = 25.7131$ Å, occupy the locations $00z$, or $0\frac{1}{2}z$ in $I4mm$ and are within 0.1 Å of the corresponding positions in space group $I4/mmm$, except O6, for which the displacement is ~1.0 Å. This atom may have been incorrectly placed in the X-ray powder diffraction profile Rietveld analysis, for which $R_{wp} = 0.112$, in view of the magnitude of its scattering relative to that of the La and two independent Nb atoms. It is noted that O6 is located within 2.4 Å of another O atom; further study is advisable.

9.4. $K_3InCl_6.(H_2O)_{1.5}$ and $K_3InBr_6.(H_2O)_{1.5}$

These two isostructural materials are represented by three entries in the ICSD under space group $I4mm$, of which two are for the hexachloroindate. The atomic coordinates in Table 14S* are taken from the refinement with 880 independent reflections measured diffractometrically by Knop, Cameron, Adhikesavalu, Vincent & Jenkins (1987) to give $R = 0.057$. A comparable study on the hexabromoindate has been reported by Lorriaux-Rubbens, Wignacourt, Drache & Wallart (1991) and an earlier report on the hexachloroindate is given in RICHD 2 207. It may be seen in Table 14S that all atoms in $K_3InCl_6.(H_2O)_{1.5}$ are within 0.35 Å of corresponding positions in space group $I4/mmm$. Eight pairs of atoms in Table 14S, with apparently arbitrary values of z', are related either by coordinates such as $0, 0, \pm z'$, $0, x, \pm z'$ or $x, x, \pm z'$, or by additional body-centering. The three ICSD entries identify the atoms at the Cl9 and O1 sites differently; however, the coordinate relationships in Table 14S between K7 and K6, also that between Cl9 and O1, suggest that each pair of sites has its own identical content. Both recent studies agree that not all atomic sites are fully occupied.

If the nonpolar relationships used above to derive the Δz values in Table 14S are applicable, then each of the three independent In atoms occupies a slightly distorted octahedron of Cl atoms (the In3 octahedron includes one O atom). In1 and In2 are within 0.02 Å of their mean octahedral z planes and In3 is 0.12 Å from its mean z plane; in each case, the mean plane is closer than the In atom to the special position in Table 14S and hence does not contribute to the effective Δz, which remain as given in the table. The largest Δz (0.21 Å) is that of In3 and corresponds to $T_c = 880(120)$ K. Decomposition caused by loss of water at temperatures well below T_c is likely, thereby preventing detection of the phase transition, but dielectric hysteresis may be measurable at room temperature.

9.5. $K_{1.1}(M_xSi_{2-x}O_4)$ family

The atomic coordinates of three tectosilicates isostructural with $K_{1.1}(M_xSi_{2-x}O_4)$, with M = Mg, Zn or Fe and $x \approx 0.5$, were reported by Dollase & Ross (1993) and have separate entries in the ICSD; those for M = Mg, determined from diffractometric measurements and resulting in $R = 0.042$, are listed in Table 15S.* The studies of M = Zn and Fe were based on Rietveld refinement of powder data. The origin for the coordinates in Table 15S has been shifted 0.0055 along the polar axis to place O1 and O2 equidistant, respectively, from the special planes in $I4/mmm$ at $z = 0$ and 1/4. Although O1 and O2 do not become symmetry-equivalent in the hypothetical paraelectric phase both atoms continue to occupy eightfold sites; the structure in Table 15S with z' coordinates is hence nonpolar. Δz (K1) $\simeq$ 0.21 Å with Δz for all other atoms less than ~0.04 Å. It is notable that while this structure satisfies the criteria for ferroelectricity on the basis of a single K^+ ion displacement, the substituted Si tetrahedron [with *ca* 2.3 Mg and 5.7 Si distributed over their 8(*c*) Wyckoff position] makes no contribution either to the polarity or to the spontaneous polarization. The force constant value in (1) is inapplicable to such structures. The tectosilicates with M = Zn or Fe are closely comparable. Dielectric investigation of the body-centered tetragonal tectosilicate structure would be of interest.

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* See deposition footnote.

* See deposition footnote.

9.6. *$Co(NH_3)_5NO_2.(NO_3)_2.(H_2O)_{0.25}$*

The structure pentamminenitrocobalt(III) bis(nitrate) 0.25-hydrate reported by Virovets, Boldyreva, Burleva, Dulepov & Podberezskaya (1994), on the basis of diffractometer measurements that led to a final $R = 0.037$, is partially disordered. Apart from the O atoms in the NO_3^- ion, all other atoms either occupy positions less than ~0.2 Å from a plane with $z = 0, 1/4$ or $1/2$, or else form pairs (N1 and N3, H1N2 and H2N2) that have an $x, y, \pm z$ relationship. The latter atomic arrangement would have zero spontaneous polarization and, in principle, an opposite polarization would be produced on changing the signs of all Δz. The N atom in the NO_3^- ion is less than 0.1 Å from the plane with $z = 1/4$ and the z coordinates of the O atoms are within 0.33 Å of satisfying the relationship x, y, z and $x, y, \frac{1}{2} - z$, and, hence, the criteria for ferroelectricity. However, the fourfold occupancy for O1*a* and eightfold occupancy for O2*a* prevent zero spontaneous polarization unless these atoms can occupy locations along the polar direction in which the displacement of O1*a* from $z = 0$ is double that of O2*a* from $z = 1/2$, but with opposite sense. Dielectric investigation of this material is necessary to show if polarization reversal is possible.

9.7. *Space-group assignment*

An origin shift of 0.05 Å places all five independent atoms in Ca_2Sb (ACBCA 31 427) within 0.1 Å of corresponding positions in space group *I*4/*mmm*. Similarly, all six independent atoms in Nd_2AlO_3N, as located by profile analysis of a neutron time-of-flight powder pattern (RVCMA 19 684), are within 0.1 Å of corresponding positions in space group *I*4/*mmm* if the atomic sites taken as occupied, respectively, by O2 and N are, instead, disordered with an equal occupation by both. It is notable that *B*(O2) is unusually small, whereas *B*(N) is large, as expected for cross sections that are too large for the former and too small for the latter. Reinvestigation of both structures is in order.

9.8. *Nonferroelectric entries*

The atomic positions determined in each of the following structures reported with space group *I*4*mm* fail to satisfy the structural criteria for ferroelectricity: $Cs_2V_5O_{13}$ (ACBCA 33 784), Na_6PbO_5 (ZAACA 368 160), the high-pressure phase of SnP (INOCA 9 335) or GeP or GeAs (JSSCB 1 143), B_5H_9 (ACCRA 5 260), NH_3BH_3 (JACSA 78 502), $LaIrSi_3$ (JCOMA 95 309 and MRBUA 19 115), Co(NCS)-$(NH_3)_5Cl_2$ (NKAKB 88 1151 and NPKZA 88 1151), isostructural $[OsNO(NH_3)_4Cl]Cl_2$, $[OsNO(NH_3)_4Br]Cl_2$, $[OsNO(NH_3)_4Br]Br_2$ and $[OsNO(NH_3)_4I]Cl_2$ (ZNOKA 35 1760), HCN at 193 K (ACCRA 4 330), two almost identical entries for $BaBi_2O_2I_2$, another for $BaBi_2O_2Br_2$ (CSRPB 27 397) and also $Na_5Co_2S_5$ (JCOMA 98 165).

10. New inorganic ferroelectrics predicted in space group *I*4*cm*

A total of ten entries is given in the ICSD under space group *I*4*cm*, of which $Pb_5Cr_3F_{19}$ was previously known to be ferroelectric. Two others, $Hg_2AlF_5.(H_2O)_2$ and $Rb_5Nb_3OF_{18}$, are predicted to be new ferroelectrics. Three structures are nonferroelectric and the atomic coordinates of four others should be reinvestigated in space group *I*4/*mcm*.

10.1. *$Hg_2AlF_5.(H_2O)_2$*

The atomic coordinates of $Hg_2AlF_5.(H_2O)_2$, determined from diffractometer measurements by Fourquet, Plet & de Pape (1981), are presented in Table 16S* with a shift along the polar axis to place the mean center of the AlF_6 octahedron at $z = 1/4$. The largest atomic displacement required to transform the structure to paraelectric in space group *I*4/*mcm* may be seen in the table to be 0.32 Å for the O atom, followed by 0.06 Å for the Hg and Al atoms; that of the F-atom octahedron does not differ significantly from zero. Since the authors report that second harmonics are generated by $Hg_2AlF_5.(H_2O)_2$, there can be no inversion centers in the structure and the nonzero displacements may be accepted as genuine; the material is hence structurally ferroelectric. The structure contains infinite chains of corner-sharing AlF_6 octahedra along the polar axis linked by hydrogen bonds to quasi-linear chains of $[H_2O\text{–}Hg\text{–}Hg\text{–}OH_2]^{2+}$ cations. It may be seen, from the table, that the principal contribution to the spontaneous polarization arises from these cations. Since the force constant used in (1) has not been determined for such an atomic arrangement, the corresponding Curie temperature for $Hg_2AlF_5.(H_2O)_2$ cannot be estimated reliably. As a hydrate, the structure is likely to be unstable above ~400 K. Dielectric investigation is expected to reveal ferroelectric hysteresis.

10.2. *$Pb_5Cr_3F_{19}$ and $Rb_5Nb_3OF_{18}$*

The ferroelectric properties inferred from the structure of $Pb_5Cr_3F_{19}$ at room temperature have been discussed by Abrahams, Albertsson, Svensson & Ravez (1990), who showed that the atomic displacements from the hypothetical paraelectric phase lead to a predicted $T_c = 635(30)$ K from (1). The experimental value $T_c = 555$ K is in satisfactory agreement with prediction.

The structure of $Rb_5Nb_3OF_{18}$ as given in the atomic coordinates of Table 17S* reported by Agulyanskii, Zavodnik, Kuznetsov, Sidorov, Stefanovich, Tsikaeva & Kalinnikov (1991), is closely related to that of

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* See deposition footnote.

ferroelectric $Pb_5Cr_3F_{19}$. One independent Nb atom occupies an isolated seven-cornered polyhedron of F atoms, the other a chain of corner-sharing NbO_2F_4 octahedra. Agulyanskii *et al.* (1991) measured 505 independent reflections diffractometrically, refining the structure to a final R value of 0.025. The origin shift in Table 17S places the independent Nb atoms at distances from planes with $z = 0, 1/4, 1/2$ or $3/4$ that are equal but of opposite sense. Table 17S shows that all atomic displacements from these planes in the postulated paraelectric phase are less than 0.6 Å, hence the crystal is structurally ferroelectric. It may be noted that $z'(F5) = 1 - z'(F2)$. The Δz displacement by Nb1, with respect to its polyhedral center, is 0.084 Å; Δz for Nb2, which occupies the string of octahedra along the polar axis (similar to those in $Pb_5Cr_3F_{19}$), is ~0.228 Å for an expected Curie temperature from (1) of ~1040 (180) K. Since the *difference* in Δz between z(Nb2) and its mean octahedral z(4F4, 2O) is 0.228 Å, a further change in origin will not affect its magnitude. Agulyanskii *et al.* (1991) observe a phase transition in the Raman spectra at ~600 K; Agulyanskii, Ravez, von der Mühll & Simon (1994) report that P_s becomes identically zero at 485 K, but that it increases rapidly at higher temperatures. Chemical decomposition sets in above 600 K. The transition in the latter temperature range is hence unlikely to be identified with T_c.

10.3. *Nonferroelectric structures*

Three further materials listed in the ICSD under space group *I4cm* are structurally nonferroelectric as presented. A brief report on Sr_5Si_3 (ZENBA 22 101) gives atomic coordinates for Sr1 and Sr2 that are identical, but that must be different in order to maintain the given stoichiometry; if the structure belongs to the Cr_5B_3-type, as stated, then it is centrosymmetric with space group *I4/mcm*. Alternatively, if Sr1 and Sr2 have a pseudomirror relationship normal to the c axis in the polar space group, then ferroelectricity is possible.

$URh_{1.6}As_{1.9}$ (JCOMA 143 113) forms a superstructure with subcell–supercell relationship; the subcell has stoichiometry URh_2As_2 in space group *P4/nmm*. In the supercell the U atoms are displaced less than 0.3 Å from positions compatible with *I4/mcm*; the Rh and As atoms form pairs related by the coordinates x_1, y_1, z_1 and x_2, y_2, z_2 separated by $d(x_1 - x_2, y_1 - y_2, z_1 + z_2 - \frac{1}{2}) < 0.5$ Å for all atoms except As3 which occupies an *I4/mcm* position. If the related Rh and As atoms are ordered, then acceptable atomic displacements could lead to nonpolarity and the crystal would be ferroelectric; if ordered, then the structure would be nonferroelectric. It is noted that the final value of $R = 0.089$ for diffractometer-measured intensities is rather large. The possibility of absorption and other errors associated with the U atom suggests the advisability of either a structural redetermination or an investigation of the dielectric properties of the material. The remaining material, $Zn_2(VO)(PO_4)_2$ (JSSCB 90 291), does not satisfy the structural criteria for ferroelectricity; resemblances to the fresnoite structure (see §3.1), however, suggest an investigation into the possibility of a phase transformation at higher temperatures.

10.4. *Space-group assignment*

The atomic coordinates reported for $AgTlI_2$ (BSCFA 1972 3028) completely satisfy space group *I4/mcm*. Those reported for Bi_2PdO_4 (ZENBA 31 1708), K_2SnTe_5 (MRBUA 18 383) and the low-temperature phase of K_3NO_3 (ZAACA, 502 153) are close to, and probably should be remeasured and refined in, *I4/mcm*.

11. New inorganic ferroelectrics predicted in space group $I4_1md$

Space group $I4_1md$ in the ICSD contains 12 entries. Assuming the space group reported for $AgYbS_2$ is indeed correct, then this material is predicted to be ferroelectric. It is thermodynamically more likely that $LiMo_8O_{10}$ and $ZnMo_8O_{10}$ are nonpolar than polar. LaPtSi and EuPtAs cannot be ferroelectric if they are fully ordered, as reported. None of the remaining eight structures is likely to be ferroelectric.

11.1. $AgYbS_2$

The atomic coordinates of $AgYbS_2$, estimated by Ballestracci (1966) from diffractometer powder intensities measured with Cr $K\alpha$ radiation, are given in Table 18S* with an origin shift of 0.02 along the c axis. The author chose the polar space group, rather than $I4_1/amd$, since the latter results in an unacceptably long (2.94 Å) Ag—S bond distance and a better fit ($R = 0.07$ rather than 0.17) was obtained with the former. Assuming the space group is indeed polar, the entire YbS_6 octahedron is displaced 0.24 Å from a zero spontaneous polarization location. $AgYbS_2$ in this case meets the structural criteria for ferroelectricity, with $T_c = 1150 (300)$ K. The author pointed out that a transition occurs at 'high temperature' to a NaCl structure, with $a = 5.491$ Å. Structural reinvestigation or dielectric measurements are needed for confirmation of ferroelectricity.

11.2. $LiMo_8O_{10}$ and $ZnMo_8O_{10}$

The coordinates of isomorphous $LiMo_8O_{10}$ and $ZnMo_8O_{10}$ were reported by Lii, McCarley, Kim & Jacobson (1986) on the basis of diffractometer

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* See deposition footnote.

measurement and structural refinement, with a final $R = 0.042$. An origin shift of 0.24804 to minimize the sum of the displacements of the four independent Mo atoms from positions corresponding to zero polarity leads to displacements no greater than 0.06 Å for any atom except Li, for which the displacement is 0.10 Å. The three atomic pairs Mo3 and Mo4, O2 and O3, and O4 and O5 become symmetry dependent in the nonpolar structure, all other atoms having $z = 1/4, 1/2$ or, for Li, 3/8. In the polar structure as given these relationships are only closely approached. With r.m.s. thermal or static displacements of ~0.5 Å for each Mo and ~0.7 Å for the O and Li atoms, it is thermodynamically unlikely that $LiMo_8O_{10}$ is polar at the measurement temperature. Although the nonpolar atomic arrangement does not correspond to space group $I4_1/amd$, further study may result in better refinement in another centrosymmetric space group.

11.3. *LaPtSi*

The structure of the ternary compound LaPtSi, as noted by Klep & Parthé (1982), is closely related to that of $ThSi_2$ in space group $I4_1/amd$. The independent Pt and Si sites were, however, shown to be ~98% ordered, despite their disposition 1.21 Å on either side of the mirror at $z = 0$, hence the structure is not expected to be ferroelectric. The ternary alloys *R*PtSi, with R = Ce, Pr, Nd, Sm and Gd, are isotypic, as is EuPtAs (ZAACA 543 49).

11.4. *Nonferroelectric structures*

Seven further structures are entered under $I4_1md$, Ga_2S_2Te (ACBCA 35 1046), NbAs (ACCRA 17 1077), $KC(NO_2)_3$ (ZSTKA 8 307), $NdD_{2.36}$ (JCOMA 95 323), $Cr(NH_3)_4F_2ClO_4$ (MOCMB 112 1359), CaPtAs (ZAACA 543 49) and Ga_2Se_2Te (PSSAB 107 7). None of these is predicted to be ferroelectric.

12. Inorganic ferroelectrics predicted in space group $I4_1cd$

Two of the ten ICSD entries in space group $I4_1cd$ satisfy the structural criteria for ferroelectricity. Four are to nonferroelectric $Li_2B_4O_7$ and the four remaining materials are also nonferroelectric.

12.1. *$SrNi_2(VO_4)_2$ family*

The atomic coordinates of $SrNi_2(VO_4)_2$ were refined by Wichmann & Müller-Buschbaum (1986) on the basis of diffractometer measurements leading to $R = 0.076$. These coordinates are deposited in Table 19S,* with a polar shift of 0.2294 that places the Ni atom at the origin, and show no displacement from locations corresponding to zero spontaneous polarization greater than 0.28 Å for any atom. The atomic arrangement hence satisfies the structural criteria for ferroelectricity. The Ni atom occupies an octahedron, the V atom a tetrahedron, both of which contain all four independent O atoms (with two O2 and two O3 atoms in the octahedron). The equatorial plane of the octahedron is at $z = 0.003$, the axial atoms at $z(O2) = -0.241$ and $z(O3) = 0.246$; the center of the octahedron is displaced only 0.03 (2) Å from Ni along the polar direction. The tetrahedral center is located at $z = -0.1215$, only 0.05 (2) Å from V along the polar axis. The corresponding value of T_c from these Δz displacements, based on the AJK relationship, is less than the diffraction measurement temperature, although the tetrahedral displacement may be critical. A higher accuracy structural redetermination of $SrNi_2(VO_4)_2$ using a single-domain study crystal would eliminate the possibility of higher parameter correlations [B(O1, O2 and O4) is reported $\gtrsim 1.0$ Å^2, whereas $B(O3) \simeq 0.2$ Å^2]; investigation of the dielectric properties is expected to result in $T_c > 300$ K.

The closely related $SrCo_2(VO_4)_2$ structure reported by Osterloh & Müller-Buschbaum (1994) exhibits comparable atomic displacements, for an origin shift of 0.2212. It is noted that $z(O2)$ appears to be in error, since its given coordinates place this atom only 0.20 Å from Co; replacement of $z(O2)$ by $z + \frac{1}{4}$ restores O2 to a position comparable to that in $SrNi_2(VO_4)_2$. With an average $z = -0.005$ for the oxygen octahedron around Co, a displacement of only 0.05 (1) Å would exhibit zero dipole. The tetrahedral center is located at $z = -0.1290$, only 0.01 (1) Å from V along the polar direction. The value of T_c corresponding to either of these displacements is very low, whereas T_c must be greater than ~300 K if the crystal is indeed ferroelectric. B(O) is reported to have a spread of values from 0.3 to 1.5 Å^2, similar to that noted above for $SrNi_2(VO_4)_2$, suggesting that redetermination with a single-domain study crystal might result in more accurate z coordinates. Dielectric measurement is necessary to determine T_c in the two known members of this family.

12.2. *Nonferroelectric entries*

Several relationships indicative of ferroelectricity may be noted among some but not all of the atomic coordinates reported for $Pr_8Sb_2S_{15}$ (KRISA 26 831), such as xyz and $\bar{y}x\bar{z}$, and those reported for $B_{10}H_{13}$ (JCDTB 1980 790), such as xyz and $xy\bar{z}$. Neither they, nor the remaining entries for $Li_2B_4O_7$, $Zr(Mo_2O_7)(OH)_2(H_2O)_2$ and $Be(BH_4)_2$, are likely to be ferroelectric.

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* See deposition footnote.

Table 6. *Distribution of ferroelectric and nonferroelectric materials crystallizing in point group 4mm*

ITC space group number	Space group	No. of ICSD entries	No. of different materials	No. of predicted ferroelectrics	No. known previously
99	*P4mm*	93	36	18	3*
100	*P4bm*	26	16	15	4
101	$P4_2cm$	-	-	-	-
102	$P4_2nm$	14	10	1	-
103	*P4cc*	7	4	1	-
104	*P4nc*	-	-	-	-
105	$P4_2mc$	3	3	2	-
106	$P4_2bc$	2	2	1	-
107	*I4mm*	32	28	7†	-
108	*I4cm*	10	10	3	1
109	$I4_1md$	12	12	1†	-
110	$I4_1cd$	10	7	2	-
Totals	12	209	128	51†	8

* Counting only compositions indentical to those listed under this space group in the ICSD. † One or more predictions may be in error due to space group misassignment.

13. Summary of results in point group 4*mm*

The distribution of the 128 different materials, the new ferroelectrics that have been structurally predicted and the previously established ferroelectrics, corresponding to the 209 individual entries in the ICSD in the 12 space groups of point group 4*mm*, is presented in Table 6. These entries lead to a total of 51 materials that have structures meeting the criteria for ferroelectricity; of these, only eight were previously known to be ferroelectric. Space groups *P4mm* and *P4bm* contain 60% of the newly predicted and nearly 90% of the previously known ferroelectrics, with *I4mm* providing the next most abundant space group for new ferroelectrics. A total of ~40% of inorganic materials reported in point group 4*mm* are predicted to be ferroelectric. By comparison, ~64% of inorganic materials reported in point group 6 (Abrahams, 1990) and ~61% of those reported in point group 6*mm* (Abrahams, 1988) are predicted to be ferroelectric.

The results obtained above suggest that the present set of 201 'pure' (*i.e.* excluding mixed crystal) ferroelectrics discovered through late 1988 and available for technological application, as enumerated in Landoldt-Börnstein (1989), will be greatly expanded as the entries in the ICSD for each polar space group are investigated and the resulting predictions based on structural criteria experimentally verified.

Access to the ICSD has been through the NRC Scientific Numeric Database Service in Ottawa, with visualization of the structures performed by use of Dowty's (1994) *ATOMS* program. It is a pleasure to thank Professor H. H. Schulz for correspondence concerning $K_2[Pt(CN)_4]X_{0.3}.3H_2O$ and Professor O. Knop for kindly providing a copy of his deposited atomic coordinates presently redeposited as Table 14S. Support of this work by the National Science Foundation (DMR-9310461) is gratefully acknowledged.

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