

Systematic prediction of new ferroelectrics in space group $P3$

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The current release of the Inorganic Crystal Structure Database contains a total of 57 entries under space group $P3$ that correspond to 50 different materials. There are 21 structures reported with this space group that satisfy the criteria for ferroelectricity, at a confidence level that depends on the reliability of the underlying structural determination. One ferroelectric discovered earlier is also listed. In addition, the database contains 19 entries that probably should be assigned to a centrosymmetric space group, seven that are polar but probably not ferroelectric and two that are without atomic coordinates. Seven entries are either duplicates or present additional structural studies of the same material. Structures in space group $P3$ identified as potentially new ferroelectrics include $\text{LiAsCu}_{0.93}$, Na_2UF_6 , BiTeI , BaGe_4O_9 , $\alpha\text{-UMo}_2\text{O}_8$, Cu_2SiS_3 , $\text{Co}(\text{IO}_3)_2$, $\text{Sr}_7\text{Al}_{12}\text{O}_{25}$, KSn_2F_5 , YbIn_2S_4 , $\text{Na}_5\text{CrF}_2(\text{PO}_4)_2$, $\text{Sn}(\text{ClO}_2)_2(\text{ClO}_4)_6$, Eu_3BWO_9 , $\text{Li}(\text{H}_2\text{O})_4\text{-B}(\text{OH})_4\cdot 2\text{H}_2\text{O}$, $\text{Mn}_3\text{V}_{1/2}(\text{SiO}_4)\text{O}(\text{OH})_2$, $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$, $\text{Na}_{6.9(2)}[\text{Al}_{5.6(1)}\text{Si}_{6.4(1)}\text{O}_{24}](\text{S}_2\text{O}_3)_{1.0(1)}\cdot 2\text{H}_2\text{O}$, $\text{BaCa}_2\text{In}_6\text{O}_{12}$, $\text{Ni}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$, $\text{Sr}_4\text{Cr}_3\text{O}_9$ and $\text{Cu}_5\text{O}_2(\text{VO}_4)_2\cdot \text{CuCl}_2$.

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1. Introduction

1.1. Previous systematic predictions of new ferroelectrics

All structures entered under space group $Pba2$, in addition to those under point groups 6, $6mm$, 4 and $4mm$ in the edition of the Inorganic Crystal Structure Database (ICSD) that was then current, see Bergerhoff *et al.* (1983), have been examined in recent years in the light of the criteria described in §1.3 to determine which of these, if any, might be new ferroelectrics. The 20 entries under space group $Pba2$ were initially chosen as a test case (Abrahams, 1989) for the efficacy of these criteria since they included the familiar ferroelectrics $\text{Gd}_2(\text{MoO}_4)_3$ and $\text{Tb}_2(\text{MoO}_4)_3$ in addition to antiferroelectric PbZrO_3 . Excluding the latter three, also three others for which the atomic coordinates were undetermined, ten candidate materials remained for examination. Of these, $\text{Na}_{13}\text{Nb}_{35}\text{O}_{94}$ (340 K), $\text{K}_3\text{Fe}_5\text{F}_{15}$ (535 K), $\text{Mo}_{17}\text{O}_{47}$ (1750 K), $\text{Bi}_3\text{Nb}_{17}\text{O}_{47}$ (500 K), $\text{Ba}_{15}\text{Pr}_{38}\text{Ti}_{72}\text{O}_{216}$ (650 K), $\text{K}_3\text{Sb}_5\text{O}_{14}$ (340 K) and $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ (~300 K) satisfied the criteria and were predicted to be ferroelectric; their estimated Curie temperatures, T_c , are given in parentheses. The study noted that the validity of each prediction rested upon the quality of the underlying structural determination. Subsequent measurement confirmed the first two predictions, see §1.2; the other five have not yet been subjected to experiment.

Following the successful demonstration of the method, application to point group $6mm$ resulted in the prediction of over 40 new ferroelectrics (Abrahams, 1988). Point group 6 led to 50 or more additional predictions (Abrahams, 1990), point

group $4mm$ to another 50 or more (Abrahams, 1996) and point group 4 to a further 30 or more predictions (Abrahams, 1999). The inclusion of isostructural family members introduces uncertainty into these totals. New entries subsequently listed by ICSD in each point group mentioned have not yet been examined, although the three new entries appearing under space group $Pba2$ in the 1995 edition have been analyzed, with one predicted to be a new ferroelectric, see §1.2 (Abrahams *et al.*, 1996). This was followed by the further reexamination of the current entries in $Pba2$ by Kroumova *et al.* (2000), who found the well known ferroelectric $Ba_2NaNb_5O_{15}$ with a recently reassigned space group as an additional candidate.

1.2. Experimental verification of predictions

Among the ferroelectrics predicted in space group $Pba2$ that have been shown to exhibit the expected dielectric and calorimetric properties are $Na_{13}Nb_{35}O_{94}$, with predicted $T_c = 340$ (175) K and experimental $T_c = 323$ (11) K (Abrahams *et al.*, 1989); and $K_3Fe_5F_{15}$, with predicted $T_c = 535$ (200) K and experimental $T_c = 495$ (10) K (Ravez *et al.*, 1989). Relationships among the atomic coordinates of $K_3Fe_5F_{15}$ also led to the 1989 prediction that it was ferroelastic, as confirmed optically by Ravez *et al.* (1989). The new ferroelectric predicted from the 1995 entries in $Pba2$ is $[(NH_2)_2C(NHNH_3)]ZrF_6$, a material shown by Bauer *et al.* (2000) to exhibit dielectric hysteresis at $T < T_c$, but not at $T \geq T_c$ for $T_c = 383$ (1) K. Uncertainties given here and later in predicted Curie temperatures are a function only of the reported uncertainties in the atomic coordinates.

Ferroelectrics predicted in point group $4mm$ and confirmed experimentally include $Ba_6CoNb_9O_{30}$ and $Ba_6FeNb_9O_{30}$, both in space group $P4bm$; predicted $T_c = 1060$ (520) K for the former, with an experimental value of 660 (11) K. The predicted value of T_c is 270 (220) K for the latter, whereas the experimental value is $T_c = 583$ (5) K (Foster, Brown *et al.*, 1997). The prediction of ferroelectricity in the mineral fersnoite with reported space group $P4bm$, for which an estimate of T_c could not be made, was verified by Foster, Arbogast *et al.* (1999) with experimental $T_c = 810$ (5) K; recent optical studies reveal the point group at room temperature to be $mm2$ (Asahi *et al.*, 2000). The semiconductor Sr_2SbMnO_6 is found to be a new ferroelectric in space group $I4mm$, with predicted $T_c = 450$ (175) K and experimental $T_c = 432$ (20) K (Foster, Nielson *et al.*, 1997). A series of predicted ferroelectrics in point groups 6, $6mm$ and 4 have been prepared and measurements are presently in progress in the undergraduate laboratories of Southern Oregon University.

1.3. Criteria used for prediction of ferroelectricity

The criteria used to determine if a structure reported in a polar space group is likely to be ferroelectric have been presented previously, *e.g.* Abrahams (1999). Briefly, they require:

(a) that the i th atom in the unit cell forming the shortest and least ionic bonds undergoes no displacement $\Delta z_i \gtrsim 1 \text{ \AA}$, where $\Delta z_i = (z_i - z_{p_s=0})c$, along the polar direction between

the location reported at $(xyz)_i$ and that at which the resulting spontaneous polarization $P_s = 0$;

(b) that the largest $\Delta z_i \gtrsim 0.1 \text{ \AA}$ or the r.m.s. thermal or static displacement u of that i th atom (see also Abrahams, 1988).

The predicted Curie temperature T_c is related to Δz_i by (1), see Abrahams *et al.* (1968)

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

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.

1.4. Experimental procedures in polar structure determination

Reports of structural determinations in polar space groups often omit the presentation of definitive evidence in support of the choice made. Examination of the atomic coordinates in all structures entered under space group $P3$ in the 99/1 edition of the ICSD indicates that over 35% may suffer from space group misassignment, based on differences between the reported and corresponding centrosymmetric atomic arrangement, see §4. Marsh's (1995) advice to authors that a centrosymmetric, rather than a noncentrosymmetric, description should be accepted if 'adequate' agreement is obtained between observed and calculated intensities could well be applied more generally. In case assignment to a polar point group is contemplated, the application of no less than three of the 15 different diffraction-based procedures together with two or more of the seven physical measurements considered by Abrahams *et al.* (1998) would result in a space-group choice of higher reliability.

1.5. Ferroelectric-to-paraelectric phase transitions

The prediction of a new ferroelectric, followed by experimental verification, implies a phase transition at T_c from the ferroelectric to a higher temperature nonpolar phase, unless T_c exceeds the decomposition or melting temperature. Each new phase transition offers the possibility of detailed structural studies in the thermal regime that includes T_c . Much new information concerning the atomic movements leading to these phase transitions may be anticipated from high-quality structural measurements in this regime. Among the results expected is the enhancement of our present insight into the nature of phase transitions that are traditionally described by Landau's (1965) theory.

1.6. Overview of results reported in space group $P3$

Space group $P3$ offers a total of 57 entries in the 99/1 edition of the ICSD, following transfer to $P\bar{3}$ of an entry listed under $P3$ in the 98/2 edition. The 21 candidates for ferroelectric behavior presented in §2 under space group $P3$, together with the 54 entries listed under space group $P3_1$, the seven under $P3_2$ and the 114 under $R3$, would have resulted in an unwieldy

Table 1

Atomic positions for Na_2UF_6 at room temperature with hypothetical z' coordinates, polar and thermal/static displacements in Å.

$$a = 6.112 (2), c = 7.240 (2) \text{ \AA}; \Delta z = (z^* - z')c, \text{ with } z^* = z - 0.0014.$$

	Wyckoff positions $P3, P\bar{3}$	x	y	z^*	z'	Δz	$u(z)$
U1	1(<i>b</i>) 2(<i>d</i>)	1/3	2/3	0.8593	0.8593	0	0.07
U2	1(<i>c</i>)	2/3	1/3	0.1408 (1)	-0.8592	0	0.04
Na1	1(<i>a</i>), 1(<i>a</i>)	0	0	0.033 (3)	0	0.24	0.14
Na2	1(<i>a</i>), 1(<i>b</i>)	0	0	0.512 (4)	1/2	0.09	0.15
Na3	1(<i>b</i>) 2(<i>d</i>)	1/3	2/3	0.415 (2)	0.396	0.14	0.08
Na4	1(<i>c</i>)	2/3	1/3	0.623 (2)	0.604	0.14	0.09
F1	3(<i>d</i>) 6(<i>g</i>)	0.317 (2)	0.919 (2)	0.110 (2)	0.103	0.05	0.08
F4	3(<i>d</i>)	0.699 (4)	0.080 (3)	0.904 (2)	0.897	0.05	0.11
F2	3(<i>d</i>) 6(<i>g</i>)	0.716 (2)	0.091 (2)	0.345 (2)	0.353	-0.06	0.11
F3	3(<i>d</i>)	0.092 (3)	0.395 (3)	0.637 (3)	0.645	-0.06	0.12

analysis if all were combined under point group 3. An analysis of the latter entries will hence be presented separately. §3 contains the only previously known ferroelectric in $P3$, §4 presents 19 structures that probably have been misassigned to space group $P3$, §5 covers seven polar structures that probably are polar, but unlikely to be ferroelectric, and §6 notes two entries for which atomic coordinates were not determined.

The order in which entries are reported follows that of the ICSD within this space group. Unless noted otherwise, all intensity measurements were made by the use of an automatic diffractometer.

2. New inorganic ferroelectrics predicted in space group $P3$

2.1. $\text{LiAsCu}_{0.93}$

The structures of $\text{LiAsCu}_{0.93}$ and isostructural $\text{Li}_{1.25}\text{GeZn}$ were reported by Schönemann & Schuster (1977), the former having been refined to $R = 0.167$ based on 507 independent reflections, the latter to $R = 0.12$ based on 251 strong reflections. Table 1S¹ contains the experimental atomic coordinates of $\text{LiAsCu}_{0.93}$, following an origin displacement of -0.025 along c to minimize $\Sigma\Delta z$ for the independent atoms, the hypothetical coordinates z' in space group $P\bar{3}$, and the corresponding Wyckoff positions in both $P3$ and $P\bar{3}$. Assuming the As1 and Cu2 sites (with atomic numbers 33 and 29, respectively) are identically occupied, as supported by $B(\text{As1}) = 1.03 (12)$ and $B(\text{Cu2}) = 0.65 (14) \text{ \AA}^2$, then the maximum value of $\Delta z(\text{Cu2}) = 0.36 \text{ \AA}$ is consistent with the criteria of §1.3 for ferroelectricity. If the structure is essentially correct, this displacement suggests an elevated Curie temperature T_c . However, Sportouch *et al.* (1995) recently reported $\text{Li}_{1.25}\text{GeZn}$, or more likely LiGeZn , as forming in space group

¹ Tables 1S–22S have been deposited. Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR0096). Services for accessing these data are described at the back of the journal.

$P\bar{6}m2$, a noncentrosymmetric space group with nonpolar c axis but very nearly the same unit cell as that of Schönemann & Schuster (1977). A single phase with composition $\text{Li}_{1.25}\text{GeZn}$ or LiGeZn , but two phases with composition Li_2GeZn , have been reported [ZAACA 506 133].² Confidence in the prediction of ferroelectricity in isostructural $\text{LiAsCu}_{0.93}$ may hence be reduced until the material is reinvestigated.

2.2. Na_2UF_6

The atomic arrangement in Na_2UF_6 with space group $P3$ was reported by Cousson *et al.* (1979) following initial refinement in $P\bar{3}$ that terminated at $R = 0.098$; refinement in the polar space group with $1504 F^2_{\text{meas}} > 3\sigma(F^2_{\text{meas}})$ reduced R to 0.056. The atomic coordinates thereby obtained are presented in Table 1, following an origin shift of -0.0014 along the polar axis to midway between independent U atoms. Table 1 shows that Na1,

Na3 and Na4 are the only atoms with $\Delta z > u(z)$ at 0.24, 0.14 and 0.14 Å, respectively; all remaining atoms are close to the corresponding Wyckoff locations in space group $P\bar{3}$. If the three largest Δz magnitudes indeed differ significantly from zero (each is ~ 10 times its given standard uncertainty), then Na_2UF_6 satisfies the structural criteria for ferroelectricity; if not, then the space group is probably misassigned.

2.3. BiTeI

SbSI and several isostructural compounds form a well known ferroelectric family (Mitsui & Nakamura, 1990), generally crystallizing in space group $Pna2_1$ with a transition at T_c to $Pnam$ and typical lattice constants $a \simeq 8.2$, $b \simeq 10.4$, $c \simeq 4.1 \text{ \AA}$. By contrast, BiTeI was reported in $P3$ with $a = 4.346 (3)$, $c = 6.835 (4) \text{ \AA}$ and a phase transition at 743 K (Tomokiyo *et al.*, 1977). The structure was refined by Keramidas *et al.* (1993) to $R = 0.075$ on the basis of 1924 independent I_{obs} , with atomic coordinates as in Table 2(*a*) following an origin shift of 0.045 to equalize each $|\Delta z|$ at $\sim 0.31 \text{ \AA}$. A transition from space group $P3$ to $P\bar{3}$ can occur only if the contents of Wyckoff positions 1(*b*) and 1(*c*) are identical at T_c . With atomic number $Z = 52$ for Te and 53 for I, X-ray scattering by each is almost equal. The closest Te–Te and I–I distances are indistinguishable at 4.34 Å, with Bi–I 3.05, Bi–Te 3.88 Å. Bi thus occupies a distorted octahedron of three Te and three I atoms and is displaced 0.62 Å from its center.

A subsequent powder profile investigation by Shevelkov *et al.* (1995), unaware of the 1993 single-crystal study, chose the polar space group $P3m1$ for refinement and obtained $R_f =$

² 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; the final entry in the coden is the number of the first page.

Table 2

Atomic positions for BiTeI at room temperature with hypothetical z' coordinates and polar displacements in Å.

For (a) $a = 4.346$ (3), $c = 6.835$ (4) Å and $\Delta z = (z^* - z')c$, with $z^* = z + 0.045$; for (b) $a = 4.3392$ (1), $c = 6.854$ (1) Å and $\Delta z = (z^* - z')c$, with $z^* = z + 0.0188$.

	Wyckoff positions	x	y	z^*	z'	Δz
(a) In $P3, P\bar{3}$						
Bi	1(a), 1(a)	0	0	0.046 (4)	0	0.314
Te	1(c)	2/3	1/3	0.611 (4)	0.656	-0.308
	2(d)					
I	1(b)	1/3	2/3	0.299 (4)	0.344	-0.308
(b) In $P3m1, P\bar{3}m1$						
Bi	1(a), 1(a)	0	0	0.0188	0	0.133
Te	1(c)	2/3	1/3	0.7116 (2)	0.7209	-0.066
	2(d)					
I	1(b)	1/3	2/3	0.2698 (2)	0.2791	-0.066

0.054 for the coordinates in Table 2(b), after an origin shift of 0.0188 to minimize the total $\Sigma\Delta z$. The closest Te–Te distance is then 3.93 Å, that of I–I is 4.34 Å, with Bi–I 3.04, Bi–Te 3.27 Å; Bi continues to occupy a distorted octahedron of three Te and three I atoms and is displaced 0.193 Å from its center.

The atomic arrangements in Tables 2(a) and (b) are almost identical except for $z(\text{Te})$, which differs by a relative 0.90 Å between the two studies. Both models satisfy the structural criteria for ferroelectricity, with $0.12 < u < 0.16$ Å, the former giving a predicted $T_c > 7000$ K, the latter $T_c \simeq 745$ K in close agreement with a transition temperature of ~ 743 K determined on the basis of differential thermal analysis by Tomoiyo *et al.* (1977).

2.4. BaGe₄O₉

The structure of BaGe₄O₉ was first determined in space group $P3$ by Robbins *et al.* (1966) from densitometrically measured photographic data, the weakest reflections being estimated visually. Refinement based on 327 F_{obs} and 435 F_{unobs} led to $R = 0.068$, with final atomic coordinates as in Table 2(a)S. Each atom is seen to be related to a Wyckoff position in space group $P321$, with corresponding Δz displacement no larger than 0.84 Å (for the O5, O9 pair). The structure of BaGe₄O₉ was redetermined in space group $P321$ [DANKA 181 595] and later refined by Shashkov *et al.* (1985) using 1040 $F_{\text{obs}} > 3\sigma(F_{\text{obs}})$; the latter also studied isostructural PbGe₄O₉. The 1966 work was not referenced in either paper. Eliminating 114 reflections with $(\sin \theta)/\lambda < 0.35$ Å⁻¹ to reduce extinction and absorption, Shashkov *et al.* (1985) reported a final $R = 0.027$, $wR = 0.036$ for the atomic coordinates in Table 2(b)S. Comparable coordinates in the two tables are clearly related, with the largest total $\Delta(xyz) = 2.01$ Å between the position of O8 determined in space group $P3$ and that of O5 as determined with a name change in $P321$. Notably, however, the criteria for ferroelectricity in Table 2(a)S are satisfied, considering $0 < u < 0.20$ Å.

Further structural investigation or physical measurement is necessary to confirm the existence or otherwise of a polar BaGe₄O₉ phase at room temperature, in view of the

comparable nonpolar phase reported at room temperature and the need for improved intensity data in the earlier study. If a stable polar phase is confirmed, then it may be predicted to be ferroelectric.

2.5. α -UMo₂O₈

The structure of the high-temperature α -UMo₂O₈ phase was determined by Serezhkin *et al.* (1974) on the basis of 544 photographically recorded reflections that, on refinement, gave $R = 0.085$. The atomic coordinates, with origin shifted 0.016 along c to minimize $\Sigma\Delta z$ (U, Mo), are presented in Table 3S. All z coordinates, except for the O1, O13 and O3, O16 pairs, are seen to differ by 0.22 Å or less from the corresponding values in space group $P\bar{3}$; atoms in these two pairs differ by 0.30 and 0.47 Å, respectively. Many independent z coordinates were assigned fixed values with uncertainties that were not evaluated. The four independent Mo atoms in the structure occupy MoO₄ tetrahedra with $\langle d_{\text{Mo-O}} \rangle = 1.790$ Å, three independent U atoms occupy UO₆ octahedra with $\langle d_{\text{U-O}} \rangle = 2.256$ Å and two other independent U atoms occupy UO₉-centered trigonal prisms with $\langle d_{\text{U-O}} \rangle = 2.389$ Å. All varied O(z) uncertainties are given as 0.01 Å, hence, if reliable, α -UMo₂O₈ satisfies the structural criteria for ferroelectricity with $u(\text{U, Mo}) \simeq 0.1$ Å. The claim that α -UMo₂O₈ is piezoelectric lends support to the prediction.

2.6. Cu₂SiS₃

The high-temperature form of Cu₂SiS₃ was reported [ANCPA 1965 243] on the basis of 20 visually estimated powder diffraction lines, in space group $P3$, as having a structural resemblance to wurtzite. A later single-crystal redetermination by Parthé & Garin (1971) identified the space group as $Cmc2_1$, but without substantial change in the earlier atomic coordinates and with normal SiS₄ and CuS₄ tetrahedra; refinement led to $R = 0.068$. With an origin shift of 0.300 along c to minimize $\Sigma\Delta z$ in the latter space group, the $z(\text{Cu})$ and $z(\text{Si})$ coordinates in Table 4S are distant 0.36 and 0.30 Å, respectively, from $\frac{1}{4}$, with $z(\text{S1})$ and $z(\text{S2})$ distant -0.36 and -0.31 Å, respectively, from $\frac{3}{4}$, the corresponding z coordinates in space group $Cmcm$. Cu₂SiS₃ is hence a candidate for ferroelectric behavior, although it is unlikely that either the SiS₄ or CuS₄ tetrahedra could conform to the geometry required by the z' coordinates even momentarily. With two Si–S1 distances of 2.079 Å, one Si–S2 of 2.198 Å and the other Si–S2, parallel to the polar direction, of 2.293 Å the Si atom is 0.06 Å from $z = 0.123$, the value at which the net polarization of the tetrahedron becomes zero. By contrast, the Cu atom is not displaced from its tetrahedral charge center. A displacement of 0.06 Å by Si would result in $\Delta z(\text{Si}) = \Delta z(\text{Cu})$. The large polarization associated with displacements of the magnitude given in Table 4S would result in wall formation between domains of opposite polarization; the elimination of such walls at higher temperatures is likely to provide an energy minimum. Observation of temperature-dependent domain walls in single crystals of Cu₂SiS₃ could hence be a direct indicator of ferroelectricity in this material.

Table 3

Atomic positions for $\text{Co}(\text{IO}_3)_2$ at room temperature with hypothetical z' coordinates and polar displacements in Å.

$$a = 10.9597 (1), c = 5.0774 (1) \text{ \AA}; \Delta z = (z^* - z')c, \text{ with } z^* = z - 0.0241.$$

	Wyckoff position <i>P3, P321</i>	<i>x</i>	<i>y</i>	<i>z</i> *	<i>z</i> '	Δz
Co1	1(<i>a</i>), 1(<i>b</i>)	0	0	0.5475 (9)	1/2	0.241
Co2†	3(<i>d</i>), 3(<i>e</i>)	0.5057 (3)	0.9967 (3)	0.0517 (9)	0	0.263
Co3	3(<i>d</i>), 3(<i>f</i>)	0.5019	0.9971 (7)	0.5352 (16)	1/2	0.179
I1	1(<i>c</i>), 1(<i>e</i>)	2/3	1/3	−0.0241	0	−0.122
I2	1(<i>b</i>), 1(<i>d</i>)	1/3	2/3	0.4596(6)	1/2	−0.205
I3	3(<i>d</i>), 3(<i>j</i>)	0.6763 (1)	0.8319 (2)	0.9625 (5)	0	−0.190
I4	3(<i>d</i>), 3(<i>k</i>)	0.8223 (1)	0.6568 (1)	0.4675 (4)	1/2	−0.165
O1	3(<i>d</i>)	0.827 (1)	0.377 (1)	0.799 (3)	0.757	0.21
	6(<i>g</i>)					
O2	3(<i>d</i>)	0.468 (1)	0.819 (1)	0.285 (3)	0.243	0.21
O3	3(<i>d</i>)	0.951 (1)	0.821 (1)	0.318 (2)	0.274	0.22
	6(<i>g</i>)					
O7	3(<i>d</i>)	0.824 (1)	0.857 (1)	0.771 (2)	0.727	0.22
O4	3(<i>d</i>)	0.860 (2)	0.540 (1)	0.273 (3)	0.236	0.19
	6(<i>g</i>)					
O6	3(<i>d</i>)	0.640 (1)	0.958 (1)	0.802 (3)	0.765	0.19
O5	3(<i>d</i>)	0.672 (1)	0.632 (1)	0.279 (3)	0.235	0.22
	6(<i>g</i>)					
O8	3(<i>d</i>)	0.543 (1)	0.674 (1)	0.810 (3)	0.766	0.22

† The Co2 and Co3 locations are 67 (1) and 36 (2)%, respectively, occupied in the polar phase, see §2.7.

2.7. $\text{Co}(\text{IO}_3)_2$

$\text{Co}(\text{IO}_3)_2$ was shown to be pyroelectric, with $p_3 = 51 (5) \mu\text{C m}^{-2} \text{K}^{-1}$, by Svensson *et al.* (1981) who refined the structure on the basis of 1825 independent F_{meas} to $R = 0.0502$, $wR = 0.0697$ with atomic coordinates as in Table 3, following an origin displacement of -0.0241 to minimize $\Sigma\Delta z(\text{Co}, \text{I})$. Only two of each Wyckoff 3(*d*) position are occupied by Co2 and Co3, thereby eliminating Co2–Co3 contacts of $\sim c/2$ (*i.e.* $\sim 2.54 \text{ \AA}$) along the polar axis. All atoms are less than 0.27 \AA , along the polar direction, from corresponding locations in space group $P321$. Atom I2 is -0.205 \AA from Wyckoff position 1(*d*), atom I3 is -0.190 \AA from position 3(*j*), and the two other I atoms are displaced by lesser distances. With $0.07 \geq u^{33} \geq 0.20 \text{ \AA}$, the criteria of §1.3 for ferroelectricity are hence satisfied. The four independent I atoms form trigonal pyramidal IO_3^- ions, the I atom in each pointing with the same sense as that of the positive pyroelectric polarization. Three normal I–O bonds with average length 1.805 \AA and three others with average length 2.772 \AA formed by the I atom lone electron pair complete each distorted IO_6 octahedron. The atomic displacements associated with the less ionic I–O bonds may be taken as determining the Curie temperature, see §1.3. The lone pair introduces considerable uncertainty into estimates of the effective octahedral charge center; taking the largest $\Delta z(\text{I})$ in Table 3 as an approximate measure of the total displacement for use in (1), I2 gives $T_c = 840 (17) \text{ K}$. Since decomposition has been reported at 693 K (Nassau *et al.*, 1973), dielectric hysteresis measurement at lower temperatures is necessary to verify the prediction unless T_c is found experimentally to be less than 693 K .

2.8. $\text{Sr}_7\text{Al}_{12}\text{O}_{25}$

The structure of $\text{Sr}_7\text{Al}_{12}\text{O}_{25}$, with 12 independent Sr, 12 independent Al and 30 independent O atoms, was reported by Nevskii *et al.* (1978, 1979). Refinement based on 1460 independent F_{obs}^2 gave $R = 0.06$ for the atomic coordinates in Table 5S, in which the origin is shifted -0.0058 along **c** to minimize $\Sigma\Delta(\text{Sr})$. The 1978 reference was entered twice in the ICSD under $P3$, the 1979 reference additionally reporting identical coordinates. Eight each of the 12 Sr and 12 Al atoms have z coordinates within 0.4 \AA , and eight of the 30 O atoms are within 0.5 \AA , of the corresponding positions in space group $P321$. All remaining atoms form pairs with coordinate relationships such as (x, y, z) and $\sim(y, \bar{x}, \frac{1}{2} - z)$ that are not derived from space group $P321$; the largest difference in z coordinate is 0.10 \AA for the metal atom pair Sr3, Sr4 and 0.30 \AA for the oxygen atom pair O9, O12. Such displacements would result in zero polarization and hence satisfy the criteria for ferroelectricity, since the average $u \simeq 0.07 \text{ \AA}$; however, the absence of a supergroup together with the presence of nonstandard symmetry relationships among many atom pairs may be indicative of problems with the structure solution. Nevertheless, the possibility of polarization reversal warrants dielectric investigation.

2.9. KSn_2F_5

The room-temperature structure of KSn_2F_5 was solved by Vilminot *et al.* (1983) and refined with 731 independent reflections having $\sigma(I)/I < 0.3$ to $R = 0.036$, $wR = 0.044$, see also [RVCMA 17 3976]. The final atomic coordinates are given in Table 6S, the origin having been displaced -0.3417 along **c** to a location midway between the two independent Sn atoms. The structure consists of two symmetry-independent distorted SnF_5 tetragonal pyramids, with $\langle d_{\text{Sn-F}} \rangle = 2.264 \text{ \AA}$; an alternative description is of distorted octahedra with the Sn out of plane and its electron lone pair completing the coordination. The F1, F5 and F8 sites about Sn2 are reported to have occupancies of 63, 94 and 27%, respectively, with all other sites fully occupied. K1 and K3 are each ten-coordinated, with $\langle d_{\text{K-F}} \rangle = 2.881 \text{ \AA}$; K2 is eight-coordinated with $\langle d_{\text{K-F}} \rangle = 2.729 \text{ \AA}$. Table 6S shows the atomic pairs Sn1, Sn2; K2, K3; F2, F8 and F6, F7 to be related by Wyckoff positions 6(*g*) or 2(*d*) in space group $P\bar{3}$, with K1 in Wyckoff position 1(*a*) for both $P3$ and $P\bar{3}$. Polarization due to the remaining atomic pairs F1, F3 and F4, F5 vanishes on displacements of $\sim 0.05 \text{ \AA}$ or less. The only Δz magnitudes greater than 0.1 \AA are those of K1 at $0.215 (12)$ and K2, K3 at $0.124 (15) \text{ \AA}$; these uncertainties reflect only the structural estimate. With $u^{33} \simeq 0.19 \text{ \AA}$ for K, the structure satisfies the criteria for ferroelectricity, if it is correct. The incomplete octahedral coordination does not allow reliable estimation of T_c ; however, Vilminot *et al.* (1983) report a first-order phase transition in KSn_2F_5 at 428 K , also the ionic conductivity at $\sim 300 \text{ K}$ as $5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

2.10. YbIn_2S_4

The structure of YbIn_2S_4 , isostructural with PbCr_2S_4 , SrCr_2S_4 , BaCr_2S_4 , EuCr_2S_4 , SrCr_2Se_4 and EuCr_2Se_4 , was

Table 4

Atomic positions for Eu_3BWO_9 at room temperature with hypothetical z' coordinates and polar displacements in Å.

$$a = 8.580 (2), c = 5.410 (2) \text{ \AA}; \Delta z = (z^* - z')c, \text{ with } z^* = z - 0.2695.$$

	Wyckoff position $P3, P\bar{6}$	x	y	z^*	z'	Δz
W1	1(<i>b</i>), 1(<i>c</i>)	1/3	2/3	-0.0195	0	-0.107
W2	1(<i>a</i>), 1(<i>b</i>)	0	0	0.4798 (3)	1/2	-0.107
Eu1	3(<i>d</i>), 3(<i>j</i>)	0.3078 (1)	0.0584 (1)	0.0197 (3)	0	0.108
Eu2	3(<i>d</i>), 3(<i>k</i>)	0.0257 (1)	-0.3905 (1)	0.5201 (3)	1/2	-0.108
O1	3(<i>d</i>)	0.185 (2)	-0.529 (2)	-0.245 (2)	-0.222	-0.13
	6(<i>l</i>)					
O5	3(<i>d</i>)	0.463 (2)	-0.398 (2)	0.198 (2)	0.222	-0.13
O2	3(<i>d</i>)	-0.201 (2)	-0.052 (2)	0.262 (3)	0.291	-0.15
	6(<i>g</i>)					
O3	3(<i>d</i>)	-0.061 (2)	-0.195 (2)	-0.319 (2)	-0.291	-0.15
O4	3(<i>d</i>)	0.795 (2)	0.284 (2)	0.383 (3)	0.269	0.62
	6(<i>g</i>)					
O6	3(<i>d</i>)	0.614 (2)	0.153 (2)	-0.154 (3)	-0.269	0.62
B1	1(<i>c</i>)	2/3	1/3	0.366 (7)	0.273	0.49
	2(<i>h</i>)					
B2	1(<i>c</i>)	2/3	1/3	-0.18 (1)	-0.273	0.49

reported in space group $P3$ by Amirov *et al.* (1984) and refined to $R = 0.098$ using 2015 independent $F^2(hkl) > 2\sigma(F^2)$ in a model with anisotropic displacement parameters, see Table 7S. Both Yb4 and Yb6 sites, only 1.999 Å apart, are reported to be 50% occupied. The structure consists of distorted InS_6 octahedra linked by shared S atoms to distorted trigonal YbS_6 prisms. All Yb atoms and 11 of the 12 independent S atoms have $\Delta z \lesssim 0.12$ Å with respect to the corresponding Wyckoff positions in space group $P321$. The six independent In atoms, however, are related in three pairs corresponding to Wyckoff position 6(*g*), except that one atom in each pair is shifted by $c/2$ so that instead of equivalent positions such as x,y,z and y,x,\bar{z} , for example, relationships exist such as x,y,z and $y,x,\frac{1}{2} - z$; their largest displacement is then $\Delta z(\text{In}1, \text{In}4) = 0.43$ Å. In this case, with $u \lesssim 0.08$ Å for all atoms, the structural criteria for ferroelectricity are satisfied. The low accuracy of two $z(\text{In})$ and many $z(\text{S})$ coordinates, the magnitude of the largest Δz and the presence of incompletely occupied sites suggest that further structural study may be advisable in addition to dielectric investigation.

2.11. $\text{Na}_5\text{CrF}_2(\text{PO}_4)_2$

The structure of $\text{Na}_5\text{CrF}_2(\text{PO}_4)_2$ was determined by Nagorny *et al.* (1990) on the basis of 1101 reflections with $F_{\text{meas}} \geq 3\sigma(F_{\text{meas}})$ and refined by block-diagonal least-squares using unpublished anisotropic displacement parameters to give $R = 0.045$ for the atomic coordinates in Table 8S. The Cr atom occupies a distorted octahedron of four O and two F atoms, the nine independent Na atoms occupy $\text{O}_6 - {}_n\text{F}_n$ octahedra with $n = 0-3$, and the two independent P atoms occupy O tetrahedra, all of which are strongly distorted. Table 8S shows that the unique Cr, seven Na and four O atoms are within 0.54 Å of corresponding locations in nonpolar space group $P312$. All remaining atoms form pairs, within 0.07 Å, that have z coordinates of opposite sign and equal magnitude.

These pairs, however, are unrelated by space group $P312$, although the atomic coordinates of the P1,Na1 pair, also the P2,Na2 pair, are close to Wyckoff 6(*l*) positions. If the given structure of $\text{Na}_5\text{CrF}_2(\text{PO}_4)_2$ is confirmed, then the magnitude $\Delta z(\text{Na}5) = 0.54$ Å and three other smaller $\Delta z > 0.25$ Å appear to satisfy the criteria for ferroelectricity in §1.3, although comparison with the unpublished r.m.s. thermal/static atomic displacements cannot be made.

2.12. $\text{SnCl}_8\text{O}_{28}$

The structure of the tin complex $\text{Sn}(\text{ClO}_2)_2(\text{ClO}_4)_6$ at 213 K was solved by Fourati *et al.* (1990) using 1530 independent $I_{\text{meas}} > 3\sigma(I_{\text{meas}})$ from crystals that were both hygroscopic and twinned; refinement gave $R = 0.139$. Refinement-package tests of the diffraction data indicated noncentrosymmetry, although the authors noted the possible influence that twinning may have on this result; they also noted that specimen limitations led to an 'admittedly poor crystal structure determination'. The final atomic coordinates are presented in Table 9S, with an origin shift of 0.119 along \mathbf{c} to minimize $\Sigma \Delta z(\text{Sn})$. Each of the three independent Sn atoms occupies an octahedron of O atoms with $\langle d_{\text{Sn-O}} \rangle = 2.041$ Å and atoms Cl1–Cl6 occupy somewhat distorted tetrahedra of O atoms with $\langle d_{\text{Cl-O}} \rangle = 1.425$ Å and angles that range from 89 to 137°. The chloryl Cl7, Cl8 and associated O atoms appear disordered. Table 9S shows that all resolved atoms occupy locations that result in $\Delta z \lesssim 0.6$ Å with respect to the corresponding Wyckoff positions in space group $P312$, except for O25 in the Cl8 chloryl cation; three O atoms remained undetected, one of which together with O25 may satisfy Wyckoff position 6(*l*). If the space group choice is correct, then the structure satisfies the criteria for ferroelectricity, although the amplitudes $u_{\text{max}}(\text{Sn}) = 0.30$, $u_{\text{max}}(\text{Cl}) = 0.42$ and $u_{\text{max}}(\text{O}) = 0.36$ Å are unusually large.

2.13. Eu_3BWO_9

The structures of Eu_3BWO_9 and La_3BWO_9 were reported by Gokhman *et al.* (1994); with corresponding unit-cell dimensions that differ less than 3.5%, the space group of Eu_3BWO_9 is given as $P3$, that of La_3BWO_9 as $P6_3$. The former was solved on the basis of 855 independent reflections with $I_{\text{meas}} > 2\sigma(I_{\text{meas}})$ and refined to $R = 0.065$, $wR = 0.077$ with anisotropic displacement parameters for the W and Eu atoms and isotropic parameters for the O and B atoms. The atomic coordinates are presented in Table 4, with an origin shift of 0.2695 along the polar axis to minimize $\Delta z(\text{W}, \text{Eu})$. Pairs of atoms related by the 6_3 axis in La_3BWO_9 retain a vestigial z to $\frac{1}{2} + z$ relationship in the Eu_3BWO_9 structure. The Eu atoms, eight-coordinated by O, form trigonal dodecahedra sharing edges with octahedral WO_6 groups. All atomic positions are related to a set of corresponding locations in space group $P\bar{6}$, hence, with $\Delta z_{\text{max}} = 0.49$ (5) Å for the two B atoms and $0.5 < u < 0.14$ Å, the structure satisfies the criteria in §1.3 for ferroelectricity. The WO_6 octahedra, which are most likely critical in determining T_c , have $\Delta z(\text{W}1) = 0.127$ (20), $\Delta z(\text{W}2) = 0.154$ (20) Å on taking the displacements of the octahedral centers into account; $\Delta z(\text{W}2)$ gives $T_c = 475$ (130) K from (1).

This result is consistent with the observation by Gokhman *et al.* (1994) that no transition is observed calorimetrically below a decomposition temperature of ~ 1775 K only if the corrected displacement $\Delta z(\text{W})$ is larger by about a factor 2, or the uncertainty in its atomic coordinates is larger by about a factor 3, than the values derived from Table 4.

2.14. $\text{Li}(\text{H}_2\text{O})_4\text{B}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$

The structure of $\text{Li}(\text{H}_2\text{O})_4\text{B}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, determined by Touboul *et al.* (1995) on the basis of 539 independent averaged $I_{\text{meas}} > 3\sigma(I_{\text{meas}})$, led to the coordinates in Table 10S after an origin shift of -0.0035 to make $\Sigma \Delta z(\text{O}) = 0$ for the six 'heavy' O atoms. Anisotropic displacement parameters were used for O, B and Li with isotropic parameters for H, resulting in $R = 0.026$, $wR = 0.028$. Both B and Li atoms form rather regular tetrahedra, with $\langle d_{\text{B-OH}} \rangle = 1.472$ and $\langle d_{\text{Li-OH}_2} \rangle = 1.934$ Å, linked by hydrogen bonds. All atoms form pairs, with coordinates displaced less than 0.25 Å for O and 0.45 Å for H, at corresponding Wyckoff positions in space group $P321$ except for B, Li, H1 and H8; the B and Li atoms in positions 1(c) and 1(b) of space group $P3$ are similarly related to position 2(d) in space group $P321$, the H1 atom to position 1(b) and H8 to 3(e) in $P321$. With $0.16 < u < 0.20$ Å for atoms other than H, the structure satisfies the criteria for ferroelectricity provided the B and Li atoms become equivalent in the paraelectric phase, *i.e.* have equal occupancy over the 2(d) position. An ordered interchange of B with Li atoms, or a disordered occupancy by both of Wyckoff position 2(d) in $P321$, is unlikely. However, the close approach to the supergroup-subgroup relation indicated by the structural arrangement of Table 10S satisfies the criteria of §1.3. It is noted that although the $\text{B}(\text{OH})_4$ group has a formal charge of -1 , $\text{Li}(\text{H}_2\text{O})_4$ a charge of $+1$, charge transfer may occur through connecting hydrogen bonds. The crystals grow from aqueous solution and are reported by Touboul *et al.* (1995) to lose two H_2O molecules of hydration at 333 K and the remaining four at 393 K. Dielectric measurement below 333 K would show if $\text{Li}(\text{H}_2\text{O})_4 \cdot \text{B}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ is indeed a new ferroelectric.

2.15. $\text{Mn}_3\text{V}_{1/2}(\text{SiO}_4)\text{O}(\text{OH})_2$

Solution and structural refinement of the very rare mineral franciscanite by Pertlik (1986), on the basis of 723 independent reflections with $F_{\text{meas}} > 2\sigma(F_{\text{meas}})$, gave $R = 0.060$, $wR = 0.049$; the positions of the four independent H atoms, however, remained undetermined. The resulting atomic coordinates, presented in Table 5 with an origin displacement of 0.0388 along **c** to minimize $\Sigma \Delta z(\text{Mn}, \text{Si}, \text{V})$, show that all metal atoms are within 0.20 Å, the O atoms within 0.4 Å, of corresponding locations in space group $P\bar{6}$. With $0.03 < u < 0.19$ Å along the polar axis, the Δz magnitudes in Table 5 satisfy the structural criteria for ferroelectricity. The Mn and V atoms in $\text{Mn}_3\text{V}_{1/2}(\text{SiO}_4)\text{O}(\text{OH})_2$ are octahedrally coordinated by oxygen, with $\Delta z(\text{Mn1}, \text{Mn2}) \simeq 0.19$, $\Delta z(\text{V2}) \simeq 0.14$ and $\Delta z(\text{V1}) \simeq 0$ Å. The $\Delta z(\text{Mn})$ displacements are taken as determining the Curie temperature in (1), since they are larger than $\Delta z(\text{V})$ and the Mn–O and V–O bonds are of

Table 5

Atomic positions for $\text{Mn}_3\text{V}_{1/2}(\text{SiO}_4)\text{O}(\text{OH})_2$ at room temperature with hypothetical z' coordinates and polar displacements in Å.

$$a = 8.1518(3), c = 4.8091(2) \text{ \AA}; \Delta z = (z^* - z')c, \text{ with } z^* = z + 0.0388.$$

	Wyckoff position $P3, P\bar{6}$	x	y	z^*	z'	Δz
Mn1	3(d), 3(j)	0.5848 (3)	0.8916 (3)	0.0388	0	0.186
Mn2	3(d), 3(k)	0.4090 (3)	0.1151 (3)	0.5382 (6)	1/2	0.184
Si1	1(b), 1(d)	1/3	2/3	0.473 (2)	1/2	-0.130
Si2	1(c), 1(e)	2/3	1/3	-0.021 (2)	0	-0.101
V1†	1(a), 1(a)	0	0	-0.001 (2)	0	-0.001
V2	1(a), 1(b)	0	0	0.471 (3)	1/2	-0.139
O1	3(d)	0.789 (1)	0.836 (1)	-0.180 (3)	-0.242	0.298
	6(l)					
O2	3(d)	0.214 (1)	0.163 (1)	0.304 (2)	0.242	0.298
O3	3(d)	0.367 (1)	0.868 (1)	0.333 (2)	0.249	0.404
	6(l)					
O4	3(d)	0.628 (1)	0.132 (1)	-0.164 (2)	-0.249	0.404
O5	1(b)	1/3	2/3	-0.177 (4)	-0.242	0.310
	2(h)					
O6	1(c)	2/3	1/3	0.306 (3)	0.242	0.310

† The V1 site in the polar phase is reported as 63 (1)%, the V2 site as 36 (1)%, occupied by V.

comparable length and ionicity, giving $T_c = 725$ (65) K. The uncertain significance of the relative displacement of ~ 0.17 (5) Å by the MnO_6 octahedral center leads to its neglect, but may substantially increase the uncertainty in the estimate of T_c . The smaller values of $\Delta z(\text{Si})$ in their distorted tetrahedra of O atoms (the O–Si–O angles range from 104 to 114°) are not expected to have a major rôle in determining T_c .

2.16. $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$

The mineral jaffeite, $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$, was reported by Yamnova *et al.* (1993) to have a structure similar to that of synthetic hydrated tricalcium silicate [DANKA 219 340]. The atomic coordinates for the latter were the starting values in a refinement, based on 871 independent nonzero reflections, that revealed the H-atom positions and led to a final $R = 0.030$. The resulting atomic coordinates presented in Table 11S, following an origin shift of 0.0084 to minimize $\Sigma \Delta z(\text{Ca}, \text{Si})$, correspond to columns of edge-sharing CaO_6 octahedra along the *c* axis that form channels occupied by Si_2O_7 groups. All displacements shown in Table 11S, with the exception of $\Delta z(\text{O1}) = \Delta z(\text{O2}) = 0.86$ Å, are less than 0.25 Å from related locations in space group $P\bar{6}$. It is notable that O1 or O2, in Wyckoff position 2(h), form the apex in each of all four independent SiO_4 tetrahedra with unique Si–O1 and Si–O2 distances that are either unusually long (~ 1.74 Å) or short (~ 1.56 Å). The average of 1.63 Å for all other $d_{\text{Si-O}}$ (each tetrahedron contains three identical Si–O distances formed either with O3, O4, O5 or O6) compares well with Shannon's (1976) value of 1.61 Å. Apart from O1 and O2, only five other atoms have $\Delta z \geq 0.09$ Å; with $0.03 < u < 0.20$ Å, the latter displacements may not be significant. Satisfaction of the structural criteria for ferroelectricity by the present results is hence open to doubt which may be resolved by dielectric measurement or structural reinvestigation.

2.17. $\text{Na}_{6.9}[\text{Al}_{5.6}\text{Si}_{6.4}\text{O}_{24}](\text{S}_2\text{O}_3) \cdot 2\text{H}_2\text{O}$

The atomic arrangement in thiosulfate cancrinite, $\text{Na}_{6.9(2)}[\text{Al}_{5.6(1)}\text{Si}_{6.4(1)}\text{O}_{24}](\text{S}_2\text{O}_3)_{1.0(1)} \cdot 2\text{H}_2\text{O}$, prepared by hydrothermal synthesis, was determined in space group $P3$ by Lindner *et al.* (1995). The refined atomic coordinates, based on 1098 independent reflections, are presented in Table 12S with an origin shift of 0.0041 along \mathbf{c} to minimize $\Sigma\Delta z(\text{Al}, \text{Si}, \text{Na})$ and led to $R = 0.0352$ for all observed reflections. In addition to axial twinning along $[001]$, the thiosulfate anions and the H_2O molecules are reported to exhibit orientational disorder. Table 12S shows that all atoms form pairs located within 1 Å of corresponding $2(c)$, $2(d)$ or $6(g)$ Wyckoff positions in space group $P\bar{3}$. The largest pairs of displacements $\Delta z(\text{O5}, \text{O6}) = 0.87$ and $\Delta z(\text{O7}, \text{O8}) = 0.97$ Å are near the expected upper limit for potential ferroelectrics, but otherwise satisfy the structural criteria for ferroelectricity; the next largest is $\Delta z(\text{Na1}, \text{Na2}) = 0.55$ Å. The partial occupancies, together with the values $0.19 < u < 0.25$ Å reported for all disordered atoms, and also the apparently fixed position for S1 (given without the stated uncertainty in the z coordinate) in addition to that of Al1 as the origin, should be reinvestigated. It may be noted that the mineral cancrinite, $\text{Na}_6[\text{AlSiO}_4]_6\text{Ca}_{1.5}(\text{CO}_3)_{1.5} \cdot 2\text{H}_2\text{O}$ crystallizing in space group $P6_3$, has previously been reported to satisfy the criteria for ferroelectricity (Abrahams, 1990). The force constants in (1), see §1.3, for the tetrahedral SiO_4 and AlO_4 groups in thiosulfate cancrinite are unknown, hence T_c cannot be estimated; however, the approach of several Δz to 1 Å is indicative of a high value, well above that at which water of hydration would be lost. Dielectric investigation at room temperature may confirm the presence of ferroelectricity.

2.18. $\text{Ba}_{0.85}\text{Ca}_{2.15}\text{In}_6\text{O}_{12}$

The original structure of $\text{BaCa}_2\text{In}_6\text{O}_{12}$ reported in $P6_3/m$ [ZAACA 563 11] was shown by Baldinozzi *et al.* (1996) to form a compositionally incommensurate modulated structure in $P3(1/3, 1/3, \gamma)$ associated with disorder of the Ba and Ca atoms; the average chemical formula was given as $\text{Ba}_{0.85}\text{Ca}_{2.15}\text{In}_6\text{O}_{12}$. Following electron microscopy, X-ray (Cu $K\beta$) and neutron (N , $\lambda = 1.2765$ Å) powder patterns were measured and refined simultaneously. The average structure was refined in space group $P6_3/m$ to give $R_{\text{wp}} = 0.1267$ (X-ray), 0.0764 (N); $R_I = 0.0519$ (X-ray), 0.0801 (N), although resulting U^{33} values as high as 0.105 Å² are reported for the unique Ba atom. Atomic coordinates refined by the use of four-dimensional formalism within the modulated structure are presented in Table 13S, with an origin shift of 0.0183 to minimize metal atom Δz displacements, giving $R_{\text{wp}} = 0.0805$ (X-ray), 0.0482 (N); $R_I = 0.0498$ (X-ray), 0.0542 (N) and $0.06 < u < 0.08$ Å for all atoms. Table 13S shows $\Delta z(\text{Ba}/\text{Ca}) = 0.15$ Å to be the largest displacement; this site is reported to be occupied by 31% Ba and 10% Ca within a distorted octahedron of O atoms. Force constants associated with Ba^{2+} or Ca^{2+} ion displacements are not generally determinative of ferroelectric Curie temperatures, see §1.3; however, if this 0.15 Å displacement is verifiable and proves to be the origin of ferro-

electric ordering in this modulated structure, then T_c may be estimated from (1) as 440 (100) K. The remaining $0.053 < \Delta z < 0.077$ Å atomic displacements, including Ba1, have $\Delta z \leq u$ and are hence unlikely to contribute to a ferroelectric state.

2.19. $\text{Ni}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$

The structure of the mineral bottinoite, $\text{Ni}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$, was determined by Bonazzi & Mazzi (1996) using both a natural and a synthetic crystal specimen for the measurements. The atomic coordinates of the latter were refined by the use of 4269 independent $I_{\text{meas}} > 0$ to the values listed in Table 14S, with final $R = 0.046$; the origin has been shifted 0.0337 along \mathbf{c} to minimize $\Sigma\Delta z$ for the eight independent Sb and two Ni atoms. The refined coordinates for the natural sample are closely comparable. The structure consists of layers of isolated NiO_6 and SbO_6 octahedra, parallel to (001) and joined by hydrogen bonds, connected by other hydrogen bonds to similar layers of octahedra which are separated by the distance $c/2$. Examination of Table 14S shows no atom is further than 0.40 Å from a corresponding location in space group $P\bar{3}$. All O atoms, both independent Ni and two independent Sb atoms form pairs close to Wyckoff position $6(g)$ in space group $P\bar{3}$, while four independent Sb atoms form pairs close to the position $2(d)$, with one Sb remaining in $1(a)$ and the other in $1(b)$. Since $0.07 < u < 0.19$ Å, the structural criteria for ferroelectricity are satisfied. The largest $\Delta z(\text{Ni})$ or $\Delta z(\text{Sb})$ magnitude, allowing for the mean displacement of each octahedral center, is that of Sb1 at 0.330 Å, which corresponds to $T_c \simeq 2180$ (200) K. The temperature at which water is lost was not stated but is probably less than ~ 450 K. Investigation of possible dielectric hysteresis is hence feasible only at lower temperatures.

2.20. $\text{Sr}_4\text{Cr}_3\text{O}_9$

The previously unknown material $\text{Sr}_4\text{Cr}_3\text{O}_9$ was prepared and its structure reported by Cuno & Müller-Buschbaum (1989). Refinement using 311 independent $F_{\text{meas}} > 6\sigma(F_{\text{meas}})$ led to $R = 0.094$ for the atomic coordinates in Table 6, in which the origin has been shifted -0.019 along the polar axis to minimize $\Sigma\Delta z(\text{Sr}, \text{Cr})$. Each of the nine independent Cr atoms occupies a face-sharing octahedron, with three different Cr repeating along each independent trigonal axis to produce three independent sets of chains. All Cr sites are necessarily populated, on average, by both Cr^{3+} and Cr^{4+} ions, leading to the possibility of interesting but unreported conductivity properties.

Although the determination appears to be essentially correct, several atoms may have refined to false minima as the octahedral $d_{\text{Cr4}-\text{O3}} = 2.62$ Å is unusually long (Shannon's, 1976, radii give $d_{\text{Cr}-\text{O}} = 1.97$ Å); the O3 atom also participates in the shortest (1.68 Å) reported Cr—O distance. Further, all Cr atoms except Cr4 and Cr6 have z coordinates within 0.15 Å of their mean octahedral z value, whereas these two are unexpectedly offset from their centers by 0.49 and 0.42 Å, respectively.

Table 6

Atomic positions for $\text{Sr}_4\text{Cr}_3\text{O}_9$ with hypothetical z' coordinates and polar displacements in Å.

$$a = 9.618 (1), c = 7.874 (2) \text{ \AA}; \Delta z = (z^* - z')c, \text{ with } z^* = z - 0.019.$$

	Wyckoff position <i>P3, P321</i>	<i>x</i>	<i>y</i>	z^*	z'	Δz
Sr1	3(<i>d</i>), 3(<i>e</i>)	0.343 (1)	0.035 (1)	−0.019	0	−0.15
Sr2	3(<i>d</i>)	0.638 (1)	−0.011 (1)	−0.225 (1)	−0.224	−0.01
	6(<i>g</i>)					
Sr4	3(<i>d</i>)	0.638 (1)	0.003 (1)	0.223 (1)	0.224	−0.01
Sr3	3(<i>d</i>), 3(<i>f</i>)	0.367 (1)	0.026 (1)	0.518 (1)	1/2	0.14
Cr1	1(<i>a</i>)	0	0	−0.165 (2)	−0.167	0.02
	2(<i>c</i>)					
Cr2	1(<i>a</i>)	0	0	0.168 (2)	0.167	0.01
Cr3	1(<i>a</i>), 1(<i>b</i>)	0	0	0.481 (2)	1/2	−0.15
Cr4	1(<i>b</i>)	1/3	2/3	0.027 (2)	−0.031	0.46
	2(<i>c</i>)					
Cr7	1(<i>c</i>)	2/3	1/3	0.089 (2)	0.031	0.46
Cr5	1(<i>b</i>)	1/3	2/3	0.326 (2)	0.291	0.28
	2(<i>c</i>)					
Cr9	1(<i>c</i>)	2/3	1/3	−0.256 (2)	−0.291	0.28
Cr6	1(<i>b</i>)	1/3	2/3	−0.341 (2)	−0.365	0.19
	2(<i>c</i>)					
Cr8	1(<i>c</i>)	2/3	1/3	0.389 (2)	0.365	0.19
O1	3(<i>d</i>)	0.852 (1)	0.328 (2)	0.258 (2)	0.252	0.05
	6(<i>g</i>)					
O3	3(<i>d</i>)	0.489 (2)	0.666 (2)	−0.246 (2)	−0.252	0.05
O2	3(<i>d</i>), 3(<i>e</i>)	0.957 (2)	0.826 (2)	0.016 (2)	0	0.13
O4	3(<i>d</i>)	0.899 (2)	0.839 (2)	−0.320 (2)	−0.321	0.01
	6(<i>g</i>)					
O7	3(<i>d</i>)	0.010 (2)	0.167 (2)	0.322 (2)	0.321	0.01
O5	3(<i>d</i>)	0.358 (2)	0.528 (2)	0.457 (2)	0.452	0.04
	6(<i>g</i>)					
O6	3(<i>d</i>)	0.487 (2)	0.317 (2)	−0.447 (1)	−0.452	0.04
O8	3(<i>d</i>)	0.487 (2)	0.673 (2)	0.176 (2)	0.139	0.29
	6(<i>g</i>)					
O9	3(<i>d</i>)	0.808 (2)	0.443 (2)	−0.102 (2)	−0.139	0.29

The largest atomic displacement along the polar axis from a corresponding location in space group *P321* is 0.46 Å by Cr4 and Cr7, with nine other atoms having $\Delta z \geq 0.14$ Å, see Table 6. Since these Δz values exceed the range $0.06 < u < 0.14$ Å the reported structure satisfies the criteria for ferroelectricity. If $z(\text{Cr4})$ is correct, then $T_c \simeq 4230$ (230) K based on (1); if partly in error, the next largest Δz , for Cr5 and Cr9, gives $T_c \simeq 1570$ (180) K. Both estimated Curie temperatures are very high, as are their uncertainties. The latter T_c is well below the preparation temperature. Confirmation of ferroelectricity must await dielectric measurement or structural remeasurement.

2.21. $\text{Cu}_5\text{O}_2(\text{VO}_4)_2 \cdot \text{CuCl}_2$

The structure of the mineral averievite, with the general composition $\text{Cu}_5\text{O}_2(\text{VO}_4)_2 \cdot n\text{MX}$, has been reported for the adduct $\text{MX} = \text{CuCl}_2$ by Starova *et al.* (1997) in space group *P3*. The structure was refined using 318 independent $I_{\text{meas}} > 3\sigma(I_{\text{meas}})$ to give $R = 0.052$ for the atomic coordinates in Table 15S, in which the origin is shifted 0.2242 along the polar axis to minimize $\Sigma \Delta z(\text{Cu}, \text{V})$. Charge balance is maintained by an occupancy determined as 69% at the Cu4 site and 32% at the Cu5 site. The coordinates of atom O6 in the Wyckoff position 3(*d*) were omitted from the original report. Three Cu are six-

coordinated by O atoms with $\langle d_{\text{Cu-O}} \rangle = 1.98$ Å, Cu4 and Cu5 each have two Cl neighbors at $\langle d_{\text{Cu-Cl}} \rangle = 2.10$ Å, and both V atoms are five-coordinated by O atoms with $\langle d_{\text{V-O}} \rangle = 1.66$ Å. For comparison, Shannon's (1976) radii give $d_{\text{Cu-O}} \simeq 2.13$, $d_{\text{V-O}} \simeq 1.85$ and $d_{\text{Cu-Cl}} \simeq 2.38$ Å. Assuming the unlisted O6 atom is in Wyckoff position 3(*d*) near 0.8, 0.6, $\frac{3}{4}$, as in Table 15S, then O6 and O5 satisfy Wyckoff position 6(*l*) in space group *P312* within $\Delta z = 0.04$ Å. If, in addition, Cu1 and V2 are related through Wyckoff position 2(*g*), with Cu3 and V1 related through 2(*i*), then $\Delta z(\text{Cu1}, \text{V2}) = 0.135$ and $\Delta z(\text{Cu3}, \text{V1}) = 0.145$ Å. Such a transposition may be possible through an appropriate exchange of chemical identity or atom misidentification. It is notable that $u(\text{V1}, \text{V2}) = 0.09, 0.06$ Å for $Z(\text{V}) = 23$, whereas $u(\text{Cu1}, \text{Cu3}) = 0.13, 0.15$ Å for $Z(\text{Cu}) = 29$. The only displacement in Table 15S larger than $\Delta z(\text{O3}) = 0.27$ (7) Å is $\Delta z(\text{O2})$ at 0.53 (5) Å. The present model may hence satisfy the structural criteria for ferroelectricity. Structural redetermination could clarify all atom identifications; dielectric investigation may also be of interest.

3. Known ferroelectrics in *P3*

The only ferroelectric known previously in space group *P3* was $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, with $P_s = 0.05 \text{ C m}^{-2}$ and $T_c = 450$ K, as reported by Iwasaki *et al.* (1971). The structure contains three independent sets of GeO_4 tetrahedra and nine sets of PbO_n polyhedra [FEROA 9 1]. All atoms are close to corresponding locations in space group $P\bar{6}$, the largest Pb and Ge polar displacements being 0.159 and 0.053 Å, respectively, with no $\Delta z(\text{O})$ displacement greater than 0.09 Å, except for $\Delta z(\text{O6}) = 0.35$ Å. Taking $\Delta z(\text{Pb6}) = 0.159$ Å as the displacement that determines the Curie temperature, and neglecting the polarization contribution from its distorted pentagonal pyramid, then $T_c = 506$ (140) K from (1), in agreement with the experimental result above. The given uncertainty in T_c is based only on $\sigma z(\text{Pb6}) = 0.021$ Å.

4. Incorrect or dubious structures in *P3*

[ZNBAD 33 1554] has shown that an earlier report of S_6 as crystallizing in space group *P3* [ZSTKA 3 559] is incorrect and that instead S_6 forms in $R\bar{3}$.

The structure of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ was determined in space group *P3* and refined with 22 positional parameters to $R = 0.058$ [DANKA 255 1099]. The resulting atomic coordinates of all metal atoms, after an origin shift of 0.0331 to minimize $\Sigma \Delta z$, are within 0.17 Å of locations that satisfy the space group $P\bar{6}$; the six O atoms are not related by this space group, but are within 0.02 Å of locations resulting in zero polarization. The same intensity data were subsequently rerefined with 10 positional parameters to $R = 0.079$ in space group *P321* [DANKA 260 1363]. Several coordinates are closely comparable, others change widely between the two models. Since the polar structure is not derived from a supergroup and the subsequent rerefined model is nonpolar, the former choice is assumed to be in error. $\text{Ba}_3\text{Fe}_2\text{Ge}_4\text{O}_{14}$, isostructural with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$, is hence also likely to belong to space group *P321*.

Early X-ray powder determinations [KNSFA 5 42; ZEKGA 74 67] of the BiI_3 family (the former of CrBr_3 ; the latter of AsI_3 , PI_3 and CrBr_3) reported their formation in space group $P3$, but it was found later [ZEKGA 123 67] that BiI_3 and isostructural SbI_3 form in $R\bar{3}$.

The mineral scholzite transforms to the phase β - $\text{CaZn}_2(\text{PO}_4)_2$ on dehydration and heating to 1175 K; a model deduced in space group $P3$ from high-temperature powder data [ACBCA 28 322] lacked six O atoms in $3(d)$, but all other coordinates satisfy space group $P\bar{3}$; this entry was transferred in the 99/1 edition of ICSD to space group $P\bar{3}$.

The atomic coordinates of β - Fe_2O_3 , reported by an early electron diffraction study [PRLAA 241 1] in space group $P3$, include eight independent Fe atoms forming two pairs in Wyckoff position $2(c)$, a third pair in position $2(d)$ and a fourth pair in position $6(g)$ of space group $P\bar{3}$. Two of the six independent O atoms have atomic coordinates $z = 0$ or $\frac{1}{2}$, the remainder form pairs with z and \bar{z} coordinates, to give an exactly nonpolar array. In addition, all Fe–O distances are approximately 2.64 Å except for two at 1.88 Å, whereas a length of 1.9–2.0 Å is expected.

The structure of β - $\text{Na}_2\text{S}_2\text{O}_3$, in the sequence $\gamma | > 715\text{--}660 \text{ K} | Im\bar{3}m (229) | Z = 2 | - | \text{powder pattern; } \beta | 660 \text{ to } \sim 600 \text{ K} | P3 (143) | Z = 3 | - | \text{powder pattern; } \alpha | < \sim 600 \text{ K} | P2/c (14) | Z = 4 | \text{non-ferroic} | \text{stable at ambient temperature [using the recommended nomenclature of Tolédano } et al. (1998)], \text{ was determined from the powder pattern on the basis of space group } P3 \text{ and reported with atomic coordinates to the nearest } 0.01 \text{ [ZNBAD 34 957]. The } z \text{ coordinates differ from values corresponding to space group } P\bar{3} \text{ by no more than } 0.04 \text{ (0.22 \AA)} \text{ for four pairs of atoms, by } 0.01 \text{ for three other pairs and by zero for all other atoms. Within the low structural accuracy of the determination, these differences may be without significance and the structure is hence likely to be nonpolar.}$

The atomic coordinates for Ni_2H , determined by electron diffraction from a powder [KRISA 23 724], are centrosymmetric if the origin is placed midway between $z(\text{Ni}1)$ and $z(\text{Ni}2)$, and correspond to space group $P\bar{3}$.

The structure of $\text{AsTe}_{0.5}\text{O}_2$ was refined to $R = 0.054$ on the basis of 206 independent reflections [ZEKRD 205 27]. An origin shift of -0.163 along the polar axis places all four independent atoms no further than 0.03 Å from Wyckoff positions $1(c)$ for As, $1(f)$ for Te and $2(g)$ for O1, O2 of space group $P312$.

The structure of the Li_6TaO_6 moiety of Li_7TaO_6 has been reported in space group $R\bar{3}$, the occupancy of the remaining Li atom at $00z$ in Wyckoff position $6(c)$ of this space group refining to 50% [ZAACA 620 659]; with anisotropic thermal parameters and 381 independent reflections, the final $R = 0.020$. Consideration of the Li-atom lattice energy favored reduction of the space group to $P3$. However, all coordinates are listed in xyz , $\bar{x}\bar{y}\bar{z}$ pairs, as required by the nonpolar space group $R\bar{3}$.

The structure of Li_2FeS_2 was independently determined nearly simultaneously by two studies, each finding a unit cell of identical dimensions. The first report [JPSOA 20 4271], which

noted that location of the Li atoms was ‘rather difficult’, refined the structure with 34 variables in space group $P3$ to give $R = 0.056$ for $286 I_{\text{meas}} \geq 3\sigma(I_{\text{meas}})$. Following an origin shift of -0.0358 to equalize $\Delta z(\text{Fe}1, \text{Fe}2)$, the largest displacement of any atom from its equivalent location in nonpolar space group $P321$ became $\Delta z(\text{Li}1) = 0.50 (6) \text{ \AA}$, with all other $\Delta z \leq 0.26 \text{ \AA}$. Such an arrangement satisfies the criteria for ferroelectricity; however, the presence of three S atoms at distances of 1.31–1.40 Å from each Fe atom is indicative of structural error. The second investigation [PRBMD 37 3699] refined the structure in space group $P\bar{3}m1$ with 9 variables to give $R = 0.043$ for $283 I_{\text{meas}} \geq 2.5\sigma(I_{\text{meas}})$; the resulting normal centrosymmetric arrangement is the more likely structure of the two.

The structure of the mineral olgite, with approximate composition $\text{Na}_{2.2}(\text{Sr}_{1.3}\text{Ba}_{0.5})[\text{PO}_4]_{1.8}$, was determined by Sokolova *et al.* (1984) and refined to $R = 0.066$ based on a variable occupation of the three metal atom sites $M1, M2, M3$; Sr and Ba were reported present in a ratio of $\sim 3:2$ in two sites, with Na and Sr in the third site at a ratio of $\sim 4:1$, see Table 16S. The P1, O1 and O3 sites were also reported partially occupied. The origin in Table 16S has been displaced 0.0083 to minimize $\Sigma \Delta z(M_i, \text{Na})$, with $i = 3$; the table indicates the maximum polar atomic displacement to be 0.06 Å. Since $0.08 \leq u \leq 0.17 \text{ \AA}$, the structure is in conformity with space group $P321$ if the latter symmetry is satisfied by the actual occupancy of the six variable sites. Unambiguous space-group determination depends upon the results of further diffraction and physical measurement tests, see Abrahams *et al.* (1998); until these have been applied, the nonpolar space group may be assumed.

The structure of $\text{LaNb}_7\text{O}_{19}$ was reported by Hofmann & Gruehn (1991) in space group $P3$ and refined to $R = 0.044$, $wR = 0.042$; $\text{CeNb}_7\text{O}_{19}$ is said to be isostructural. The atomic coordinates are listed in Table 17S, with an origin shift of -0.1533 along the polar axis to midway between the two independent La atoms. It may be seen therein that all eight independent metals and the ten O atoms occupying general Wyckoff $3(d)$ positions are displaced from corresponding locations in space group $P\bar{6}$ by less than 0.05 Å; the remaining eight O atoms in $1(a)$ or $1(c)$ positions form pairs located at $00z$ and $2/3, 1/3, \bar{z}'$ with $z - z' < 0.005 \text{ \AA}$. It may be noted, however, that 12 O atoms have been located within 2.45 Å of at least two other O atoms, hence some positions may be in error. With $0.06 < u < 0.14 \text{ \AA}$ the present barely polar arrangement is thermodynamically unlikely to be stable.

MnSb_2O_6 has been subjected to three structural determinations. Both an X-ray powder study in space group $P321$ [JSSCB 66 171] and a single-crystal X-ray study in space group $P3$ by Vincent *et al.* (1987) were made at room temperature and published the same year. The third was a neutron diffraction powder study 2 years later at 14 and at 298 K, in space group $P321$ [JSSCB 79 263]. Although the single-crystal study resulted in $wR = 0.018$ for 980 independent $F_{\text{meas}} > 2\sigma(F_{\text{meas}})$, all atoms are close to the locations reported in space group $P321$, see Table 18S. Since $\Delta z \leq 0.010 \text{ \AA}$ for all atoms, with corresponding values of u^{33} that range from 0.05 to

0.08 Å, the MnSb_2O_6 structure is most likely to be nonpolar, as found in the two powder studies.

The structure of the mineral wadeite, $\text{K}_2\text{ZrSi}_3\text{O}_9$, initially reported [AMMIA 40 775] in space group $P6_3/m$, was found [KRISA 22 59] to have four forbidden 000 l reflections with $l \neq 2n$. Following refinement of the original data first in $P6_3/m$, then in $P3$ as a subgroup of $P\bar{6}$ to a final $R = 0.030$, the authors noted that five O atoms only deviate significantly from the corresponding centrosymmetric atomic coordinates, the largest being $\Delta z(\text{O}2) = 0.13$ (5) Å. The significance of these deviations, which led to the space group choice of $P3$, may not be high however since $\Delta z \lesssim u^{33}$ for each atom. In addition, all uncertainties are inevitably likely to be underestimated. Such a polar structure is most probably less stable thermodynamically than the corresponding nonpolar structure, see Abrahams *et al.* (1998), hence in the absence of physical measurement to the contrary, $\text{K}_2\text{ZrSi}_3\text{O}_9$ may be assumed to be nonpolar.

The 1-T polytype of the mineral berborite structure, $\text{Be}_2\text{BO}_3(\text{OH})(\text{H}_2\text{O})$, was reported by Guiseppetti *et al.* (1990) and refined in space group $P3$ using 267 independent reflections with $I_{\text{meas}} \geq 2\sigma(I_{\text{meas}})$ to a final value of $R = 0.014$. No atomic displacement from corresponding locations in the nonpolar space group $P321$, however, is greater than 0.035 Å (for OH1 and OH2), see Table 19S; with $u(\text{OH}1)$ and $u(\text{OH}2)$ each ~ 0.14 Å, the nonpolar choice is hence more likely.

The structure of $\beta\text{-C}_3\text{N}_4$ predicted by a pseudopotential total energy technique is similar to that of $\beta\text{-Si}_3\text{N}_4$ in space group $P3$ [SCIEA 271 53]; the only departures from centrosymmetry for the two C and four N atoms, however, are $\Delta x(\text{C}1, \text{C}2) = 0.002$ Å and $\Delta y(\text{N}3, \text{N}4) = 0.009$ Å, results which are consistent with space group $P\bar{3}$.

The structure of the mineral bechererite, $\text{Zn}_7\text{Cu}(\text{OH})_{13}\text{SiO}(\text{OH})_3\text{SO}_4$, was first reported in space group $P\bar{3}$ [AMMIA 81 244]. A year later, however, Hoffmann *et al.* (1997) reported it in space group $P3$. Following an origin shift of -0.0011 to minimize $\Delta z(\text{Zn}/\text{Cu})$, see Table 20S, the only atoms in the latter determination with $\Delta z > 0.1$ Å are O1 and O2 in Wyckoff positions 1(*b*) and 1(*c*), each with $\Delta z = 0.24$ Å ($u = 0.15$ Å), and H3 and H4 each in general positions with $\Delta z = 0.30$ Å (u not determined). The O1 atom forms part both of the SO_4 tetrahedron and one Zn/CuO_6 octahedron, the O2 atom forms part both of the SiO_4 tetrahedron and the other Zn/CuO_6 octahedron, the tetrahedra becoming equivalent in the centrosymmetric space group. The bond lengths $d_{\text{Si}-\text{O}2} = 1.692$ Å and $d_{\text{Zn}/\text{Cu}1-\text{O}1} = 2.47$ Å of Hoffmann *et al.* (1997), on comparison with Shannon's (1976) values of 1.64 and 1.94 Å, respectively, indicate the single variable coordinate in O1 and also that in O2 may be of low reliability. A polar choice of space group that depends on these two O atom displacements is hence unlikely to be valid.

The atomic coordinates reported by Wulff & Müller-Buschbaum (1998) for $\text{LaTe}_{0.75}\text{Ti}_{1.25}\text{O}_6$ refined equally well both in space group $P3$ and in $P321$ to the same $R = 0.047$, $wR = 0.063$. However, a shift of -0.0023 along the c axis for the coordinates in $P3$, see Table 21S, shows that the La atom in Wyckoff position 1(*a*), the Te/Ti1 atom in 1(*c*), Ti2 in 1(*b*) and

the two O atoms each in position 3(*d*) are all within 0.02 Å of the corresponding positions 1(*a*), 1(*f*), 1(*d*) and 6(*l*), respectively, in space group $P312$. Since all Δz displacements associated with $P3$ have $\Delta z < u$, with $0.08 < u < 0.15$ Å, this model is expected to be less stable than that determined in $P321$.

5. Nonferroelectric but polar structures in $P3$

Two of the three independent molecules in the polar structure of $\text{Ir}_4(\text{CO})_{12}$ are reported to be disordered [INOCA 17 3528], with resulting approximate inversion symmetry. The polar arrangement of the remaining molecule, however, does not satisfy the criteria for ferroelectricity.

The structural coordinates of the mineral simpsonite, $\text{Al}_4\text{Ta}_3\text{O}_{13}(\text{OH})$, determined by Ercit *et al.* (1992) to $R = 0.053$ and presented in Table 22S, are not significantly different from those reported in a previous study [DANKA 147 683]. Table 22S shows that $\Delta z \leq 0.26$ Å for all O atoms as well as the Al2 atom. However, for Ta and Al1 to satisfy Wyckoff position 6(*g*) in space group $P\bar{3}$, $z(\text{Ta})$ and $z(\text{Al}1)$ must be displaced respectively to $z' \simeq \mp 0.248$, implying not only $\Delta z \simeq 1.12$ Å, but also equal occupancy of the 6(*g*) site by each atom. The chance that such large displacements could occur over the required path is small, since TaO_6 and AlO_6 octahedra share corners; $\text{Al}_4\text{Ta}_3\text{O}_{13}(\text{OH})$ is hence most likely polar, but not ferroelectric. An alternative possibility may be considered if half-occupancy of the Ta and Al1 planes at $z' = 0$ and $\frac{1}{2}$, respectively, can be realized in space group $P\bar{3}$; this model would lead to satisfaction of the structural criteria for ferroelectricity in $P3$. A final choice requires structural re-determination or dielectric measurement.

Most atomic coordinates reported for $\text{CdNi}_2\text{Cl}_6(\text{H}_2\text{O})_{12}$ [ACBCA 38 234] satisfy the structural criteria for ferroelectricity, following an origin shift of -0.0160 along \mathbf{c} to equalize the displacements of the two independent Cd atoms. The large displacement of two atoms, however, at $\Delta z(\text{Ni}2) = -1.24$ and $\Delta z(\text{Ni}3) = -1.10$ Å are more consistent with a polar but nonferroelectric structure.

The displacements from nonpolarity by the $(\text{NH}_4)_6\text{Sb}_4\text{F}_{12}(\text{SO}_4)_3$ structure [KRISA 26 488, ACSCE 44 1342] are sufficiently large that the criteria for ferroelectricity cannot be satisfied.

The structure of InSiTe_3 [CRAME 314 1151] is clearly polar but nonferroelectric.

The structure of the mineral cappelenite, $\text{Ba}(\text{Y,R-E})_6[\text{Si}_3\text{B}_6\text{O}_{24}]\text{F}_2$ with RE $\simeq 3\%$ La_2O_3 , 1.3% CeO_2 and 0.8% ThO_2 , as reconstituted from a metamict state by heating for two weeks at 1000 K in air, has been reported [AMMIA 69 190]. Although many pairs of atomic coordinates exhibit pseudosymmetric relationships, they are unable to satisfy the structural criteria for polarization reversal.

The mineral metavoltine, with idealized composition $\text{K}_2\text{Na}_6\text{Fe}^{2+}(\text{Fe}^{3+})_6(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$ and Fe^{2+} site occupied by $\sim 30\%$ Cu and $\sim 10\%$ Zn, was reported in space group $P3$ [MPMTA 23 155]. The final structure was derived partly by refinement of visually estimated photographic intensities and

partly by model building. Assuming the structure is essentially correct, it is polar but nonferroelectric.

6. Entries with missing or no atomic coordinates in P3

The powder pattern for the serpentine mineral $\text{Mg}_3\text{Ge}_2\text{O}_5(\text{OH})_4$ has been reported in P3 [CAMIA 14 314], but with undetermined atomic coordinates.

The space group of the mineral jagoite, $\text{Pb}_{24}\text{Fe}_8\text{Si}_{27}\text{O}_{84}\text{Cl}_8$, has been reported as in P3, but without atomic coordinates [AMNGA 2 315]. A later and superseding structural report places jagoite in space group $P\bar{6}2c$ [AMMIA 66 852].

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