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Systematic Prediction of New Ferroelectric Inorganic Materials in Point Group 6

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Abstract

A total of seven new families and sixteen structurally different inorganic materials with point group 6 are shown to satisfy the criteria presented previously by the present author [*Acta Cryst.* (1988), **B44**, 585–595] for predicting ferroelectricity. In case each prediction is experimentally verified, the 183 individual entries for point group 6 listed in the Inorganic Crystal Structure Database will result in over 80 new ferroelectrics, of which about 30 are rare-earth isomorphs. The total number of 'pure' ferroelectrics discovered through late 1988, as enumerated in Landolt–Börnstein [(1989), III/28*a*], is 201. Consideration of structures containing tetrahedral ions located on trigonal axes has led to a broadening of the normal symmetric double-well potential concept for displacive ferroelectrics to include asymmetric potential minima. Spontaneous polarization reversal in such cases may result neither in equal polarization magnitudes nor in equal coercive fields for the two states. Additional categories of ferroelectric substances considered include cryptoferroelectrics and also highly conductive ferroelectrics. Analysis of the database entries in space group $P6_3$ also results in the identification of over 20 structure determinations for which the assumption of polarity is probably incorrect.

Introduction

The principal structural requirement for a polar crystal to be considered as potentially ferroelectric is the presence in the unit cell of a maximum atomic displacement of about 1 Å along the polar direction from the corresponding position in which the resulting spontaneous polarization is zero (Abrahams, 1979, 1988). In addition, the largest atomic displacement from such a position must be significantly greater than about 0·1 Å or the r.m.s. amplitude of thermal displacement of that atom. Furthermore, the thermodynamic barrier to be overcome by each atom in reaching its location corresponding to zero spontaneous polarization must be less than the equivalent of an applied d.c. field that is sufficient to reverse the polarization sense but that does not exceed the dielectric strength of the material, with an estimated phase-transition temperature that does not exceed about 2000 K.

The phase-transition temperature (T_c) in a crystal satisfying the above criteria may be estimated by Abrahams, Kurtz & Jamieson's (1968) relationship, hereafter AKJ. In this, the square of the largest displacement (Δz in Å) along the polar direction from the zero spontaneous polarization position by the metal atom forming the shortest and least ionic bonds in the structure is found to be proportional to T_c:

$$T_c = (\mathscr{K}/2k)(\Delta z)^2\ \mathrm{K} \qquad (1)$$

where $\mathscr{K}$ is a force constant, k is Boltzmann's constant and $\mathscr{K}/2k \simeq 2{\cdot}0 \times 10^4\ \mathrm{K\ Å^{-2}}$.

The given structural criteria, together with the AKJ relationship, have now been systematically applied to all entries in the Inorganic Crystal

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Structure Database (ICSD) at the Fachinformationszentrum in Karlsruhe (see *Crystallographic Databases*, 1987) for space group *Pba*2 (Abrahams, 1989) and point group 6*mm* (Abrahams, 1988). Seven new inorganic materials in space group *Pba*2 were predicted to be ferroelectric, with two that have recently been confirmed experimentally. $Na_{13}Nb_{35}O_{94}$ was predicted to have $T_c = 340$ K, and a phase-transition temperature of 320 (10) K was found. $K_3Fe_5F_{15}$ was predicted to have $T_c = 535$ K and 490 (10) K was found.

Eight new families of compounds satisfy the structural criteria for ferroelectricity in point group 6*mm*, with eight additional materials recognized as potentially ferroelectric. Three other families of inorganic materials and four individual compounds, if they are not centrosymmetric rather than polar as published, have also been identified as possibly ferroelectric.

It may be noted that satisfaction of the structural requirements for ferroelectricity leads only to the identification of a material as being potentially ferroelectric. Experimental confirmation is always necessary in view of possible space-group misassignment, *cf.* for example Marsh & Herbstein (1988), and any other inadequacies in the underlying structural investigation upon which the present study depends.

The structural criteria outlined above have now been applied to the 183 separate entries for point group 6 to be found in the January 1989 release of ICSD, with results as presented below.

Reliability of phase-transition predictions and temperatures

The level of confidence to be placed on a structurally based prediction of ferroelectricity, as noted by Abrahams (1988), depends not only on the quality of the structural determination but also on the magnitudes of the atomic displacements. The confidence is highest for predictions based on a reliable determination in which all displacements are less than about 0·5 Å and the critical value as used in equation (1) is less than about 0·3 Å, while the basic criteria remain satisfied. It may also be noted that the values of Δz used in this paper are often a function of the choice of origin. The critical displacement should be an invariant function of structure that takes into full account the disposition of the associated polyhedral atoms. The confidence level decreases with increasing displacement magnitudes and expectation of error in the structural study.

It is pointed out that the force constant $\mathscr{K}$ in equation (1) is not a universal constant but is closely related to the nature of the surrounding atomic polyhedron and to the other atoms present in the crystal structure. In addition, errors in the atomic *z* coordinates for all cases considered below necessarily propagate error in the predicted value of T_c.

Extension of ferroelectric structure concept

The normal concept of a ferroelectric crystal considers the Gibbs free energy to vary with atomic displacement from the paraelectric state, at a temperature $T < T_c$ in the ferroelectric state, such that it forms a pair of symmetric minima corresponding to displacements with opposite sense for the spontaneous polarization, P_s. The magnitude of P_s is taken as identical at these minima.

Many crystals in point group 6 contain tetrahedral ions disposed about a trigonal axis. If such ions are rather rigid, *e.g.* SO_4^{2-}, PO_4^{3-}, SiO_4^{4-}, *etc.*, then it is improbable that the tetrahedron would become oppositely oriented in the course of polarization reversal as required in the case of symmetric potential minima. Such reorientation would entail atomic displacements greater than 1·5 Å. It is, however, notable that the polarization associated with such a BX_4^{x-} tetrahedron may be readily reversed in sense as the result of small changes in the two related tetrahedral angles, see Fig. 1. For $\alpha > 109{\cdot}47°$, *i.e.* $\beta < 109{\cdot}47°$, and the polarization direction taken as positive, then a change that results in $\alpha < 109{\cdot}47°$ will cause the direction to reverse and become negative. At $\alpha = 109{\cdot}47°$, the regular tetrahedron has zero net polarization. In the case of the formula unit ABX_4, if the cation A^{x+} is displaced along the polar **c** direction by Δz from the plane containing the effective negative point charge associated with the anion BX_4^{x-} (or from the plane midway between the negative charges), then the point-charge polarization sense depends on the sense of the displacement and is zero for $\Delta z = 0$. Small changes in α, β and Δz can

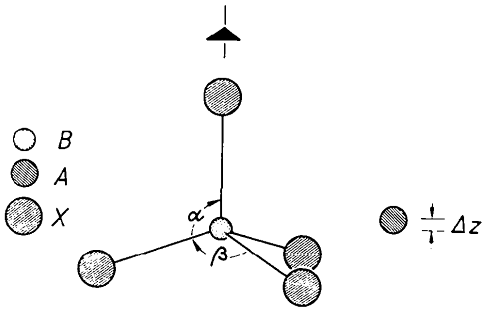

Fig. 1. Hypothetical structure of an ABX_4 asymmetric double-well potential ferroelectric with the BX_4^{x-} ion lying on a trigonal polar axis and the A^{x+} ion displaced Δz along the polar direction from the effective point charge on BX_4. For $\alpha > \beta$ and $\Delta z > 0$, the polarization P_s is positive along the trigonal-axis direction. For $\alpha = \beta$ and $\Delta z = 0$, $P_s = 0$ whereas for $\alpha < \beta$ and $\Delta z < 0$, P_s is negative. See text.

hence reverse P_s, passing through $P_s = 0$ with its resulting nonpolar atomic arrangement. The free energy of the latter is expected to be lower than either polar arrangement and to exhibit a single asymmetric potential minimum. Equation (1) is not expected to be applicable to such crystals. The thermally dependent changes in α, β magnitudes are anticipated to be comparable to those found in piezoelectric tetrahedral structures, such as zinc blende, under tensile stress.

The consequent possibility of ferroelectricity arising in crystals with tetrahedral ions pointing along the polar direction may hence be associated with asymmetric potential-minima states for the two P_s senses, *i.e.* the coercive field required to form a single domain of one sense may differ from that required for the opposite sense. A representation of the associated asymmetry in free energy as the A^{x+} ion is displaced from the paraelectric position with $\Delta z = 0$ at temperatures above and below the expected transition is given in Fig. 2. No change in entropy is expected at the transition.

A further extension of the traditional ferroelectric concept, which previously was confined to insulating crystals, is that the structural criteria may be satisfied by highly conductive crystals. Ferroelectic hysteresis and dielectric permittivity anomalies are unlikely to be long lived in such cases, although the associated atomic rearrangements may be fully comparable to those in insulating crystals.

Ferroelectric materials predicted in space group *P*6

The January 1989 release of ICSD contains a single entry in space group *P*6. The atomic coordinates for this material, if the choice of space group is correct, satisfy the structural criteria for ferroelectricity.

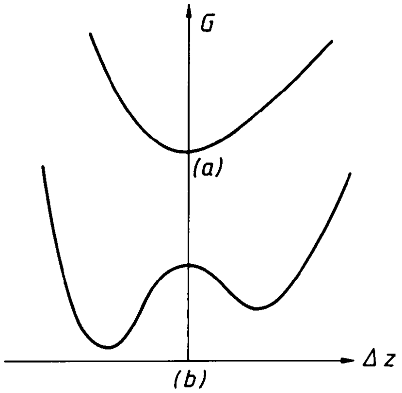

Fig. 2. Schematic representation of the asymmetry in free energy G *versus* atomic displacement such as Δz from a higher temperature special position for (*a*) the paraelectric state and (*b*) the ferroelectric state.

$K_2Ta_4F_4O_9$ *family*

The crystal structure of $K_2Ta_4F_4O_9$ was determined by Boukhari, Chaminade, Vlasse & Pouchard (1979) on the basis of 1077 independent diffractometrically measured reflections with $I > 3\sigma(I)$. The atomic coordinates given in Table 1*S** were refined from a model that assumed anisotropic thermal vibrations for the metal atoms and isotropic vibrations for the O,F atoms. Absorption corrections were not applied. The final value of $R = 0{\cdot}045$. The alternative choice of space group *P*6/*m* for this hexagonal tungsten-bronze-type structure was rejected by a variety of crystallographic tests although physical evidence in favor of the polar space group was not presented.

Examination of the polar displacements Δz in Table 1*S* from the paraelectric values with $z' = 0$ or $\frac{1}{2}$ reveals small but probably significant displacements for Ta and K with larger, more significant, displacements for most of the O,F atoms (no distinction between O and F was made in the analysis). Taking these displacements as physically significant, their magnitudes fall within the range required for structural polarization reversal, hence $K_2Ta_4F_4O_9$ may be predicted to be ferroelectric. Examination of Table 1*S* shows that the displacement by either Ta atom of 0·029 Å alone cannot lead to the paraelectric state but that the displacement of each O,F octahedron associated with a Ta atom must also be considered. The average displacement of the Ta(1) octahedron is −0·209 Å, that of the Ta(2) octahedron is −0·226 Å, hence the relative polar displacements required to achieve the hypothetical paraelectric state are 0·238 Å for Ta(1) and 0·197 Å for Ta(2). The e.s.d.'s associated with all O,F atoms are moderately large, hence the average relative Ta atomic displacement of 0·217 Å may be taken as representative, leading to a predicted (AKJ) Curie temperature T_c = 940 K. The uncertainty in T_c is necessarily large, of the order of 200 K.

Substitution of Na for K and Nb for Ta is possible (Boukhari *et al.*, 1979). In addition, $K_7Ta_{12}F_{11}O_{28}$ is said to be isostructural and to form solid solutions with $K_2Ta_4F_4O_9$.

Ferroelectrics predicted in space group $P6_1$

The January 1989 release of ICSD contains twelve entries under space group $P6_1$. Each of two pairs of entries refers to a different compound [one of which, $Ba(NO_2)_2.H_2O$, is described here and under space

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* Tables 1*S*–16*S* have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52643 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

group $P6_5$ as a nitrate rather than a nitrite], a third pair refers to two closely isomorphous organometallic compounds, and the remaining six entries refer to variants of the In_2Se_3 structure type. The ferroelectric criteria appear to be satisfied both by $Cs_2[Pt(CN)_4].H_2O$ and by the In_2Se_3 family.

$Cs_2[Pt(CN)_4].H_2O$

Two independent and nearly simultaneous determinations, by Johnson, Koch & Williams (1977) and Otto, Schulz, Thiemann, Yersin & Gliemann (1977), report atomic coordinates for $Cs_2[Pt(CN)_4].H_2O$. The former used 1348 neutron reflections with $F_o^2 > \sigma(F_o^2)$ to give $R = 0·074$ for a model with anisotropic thermal parameters for all atoms. The latter was based on 2210 X-ray reflections and gave $R = 0·068$ for a model with β_{ij} parameters for the three metal atoms and B parameters for the C and N atoms. The absorption corrections in the X-ray study were large. The two determinations are in general agreement although the results are given in different settings. The coordinates listed in Table 1 are those of Johnson *et al.* (1977), in view of their higher reliability.

It is apparent from Table 1 that the z coordinates of all atoms are either related in pairs by an approximate inversion or are close to zero. The z' values in Table 1 give these relationships explicitly. The x and y coordinates, however, are generally unrelated. $Cs_2[Pt(CN)_4].H_2O$ is hence not an ordinary ferroelectric but, since the coordinate set xyz' has zero spontaneous polarization, the weak P_s associated with the xyz set may be reversed in sense. The Δz atomic displacements required to reduce P_s to zero are small for the Cs and Pt atoms and are inappropriate for use in the AKJ relationship to estimate T_c. The 'hidden' nature of this ferroelectric atomic array, if P_s is indeed not zero at the temperature of the determination, suggests that it be referred to as a *cryptoferroelectric*. Further investigation that establishes definitively whether or not the material is polar would be appropriate.

Table 1. *Atomic coordinates* ($\times 10^4$) *for* $Cs_2[Pt(CN)_4].H_2O$ *at room temperature, hypothetical paraelectric* z' *coordinates and polar displacements*

$a = 9·709$ (4), $c = 19·343$ (8) Å.

	x	y	z	z'	Δz (Å)
Pt	−363 (2)	1304 (2)	0	0	0
C(1)	−942 (4)	3007 (4)	13 (3)	14·5	0·003
C(2)*	143 (4)	−449 (3)	−16 (3)	−14·5	−0·003
C(3)*	1888 (3)	2834 (3)	232 (2)	231	0·002
C(4)	−2611 (3)	−212 (3)	−230 (2)	−231	−0·002
N(1)	−1342 (3)	3952 (3)	21 (3)	22·5	0·003
N(2)*	433 (3)	−1469 (3)	−24 (2)	−22·5	−0·003
N(3)*	3208 (3)	3716 (3)	−370 (2)	370	0
N(4)	−3930 (3)	−1074 (3)	−370 (2)	−370	0
Cs(1)	−3412 (5)	−4215 (5)	−408 (3)	−402·5	−0·011
Cs(2)	−5613 (6)	841 (5)	397 (3)	402·5	0·011
O	2926 (5)	6685 (6)	4 (4)	0	0·008
H(1)	3993 (10)	7390 (10)	−138 (7)	−105·5	−0·063
H(2)	2883 (12)	5689 (10)	73 (7)	105·5	0·063

* Atomic numbering changed from that of Johnson *et al.* (1977) to place atoms related by $\pm z'$ together in the table.

In_2Se_3 *family*

The structure of the low-temperature form of In_2Se_3 was determined by Likforman, Carré & Hillel (1978), on the basis of 620 independent reflections that were corrected for absorption, and resulted in $R = 0·066$ for a model with variable β_{ij} parameters for each atom. The atomic coordinates are given in Table 2*S*, with a change in origin applied along the c axis. All resulting atomic displacements parallel to the polar direction from $z = 0$ are less than 0·56 Å, and hence satisfy the criteria for ferroelectricity. One In atom occupies a slightly distorted trigonal bipyramid, the other a distorted tetrahedron. The value of T_c from AKJ, based on Δz(In) = 0·269 Å (see Table 2*S*), is 1450 K. It is also possible that the distorted Se tetrahedron about In(2) gives rise to P_s reversal by displacements between asymmetric potential minima. A phase transition has been reported at about 920 K (Hahn & Frank, 1957).

$AlInS_3$ is isostructural with In_2Se_3; the structure reported by Schulte-Kellinghaus & Krämer (1979) has corresponding polar displacements by Al and In of 0·248 Å for the origin taken midway between these atoms along **c**. The resulting T_c = 1240 K, but see the *caveat* above. Although $AlInS_3$ is reported to generate second harmonics, no information is presently available concerning a high-temperature phase transition.

The structures of α-Ga_2S_3, $Mn_{0·23}Ga_{1·85}S_3$ and $GaInSe_3$ have also been reported in space group $P6_1$ (MRBUA 22 1549, MRBUA 17 293, IVNMA 23 854).* The unit-cell dimensions of each are very similar to those of In_2Se_3 and $AlInS_3$, as are the x,y atomic coordinates, but each compound is reported to have some z coordinates that are similar and others that are displaced by about $c/8$. Additional investigation of this family would be appropriate.

Ferroelectrics in space group $P6_5$

All seven entries in this space group are to various studies on $Ba(NO_2)_2.H_2O$, see also space group $P6_1$ above. This interesting pyroelectric crystal cannot be ferroelectric on the basis of its reported structure.

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* Coden-type references are given throughout this paper for most structure determinations cited but without giving their atomic coordinates, see *Checklist for Authors* (1985) regarding references taken from a database. ICSD omits the usual final check letter for the journal code, providing five letters only in each Coden.

Ferroelectrics in space groups $P6_2$ and $P6_4$

The sole entry in ICSD under space group No. 171 is to $SrS_2O_6.4H_2O$; the structure reported (ZEKGA 135 399) cannot lead to ferroelectricity.

No entries are given under space group No. 172.

Ferroelectric materials predicted in space group $P6_3$

The January 1989 release of ICSD contains 162 entries under space group No. 173, of which five publications cited were without atomic coordinates. The remaining 157 entries refer to 69 families or individual compounds, several of which have multiple entries. Nepheline, with 16 entries, is the most frequently referenced, followed by $LiIO_3$ and apatite with 12 entries each, and $KLiSO_4$ and cancrinite with 10 entries each. A number of additional materials also have multiple, but fewer, entries. The order in which the following materials are presented as potential ferroelectrics is without significance, and is largely parallel to their order of appearance in ICSD.

$Bi(Bi_2S_3)_9Br_3$

The atomic coordinates of $Bi(Bi_2S_3)_9Br_3$ in Table 3*S* are presented as reported by Mariolacos (1976) except for an origin shift along the polar axis to a position that results in equal polar displacements by Bi(1) and Bi(2). The structure determination was based on 1332 independent absorption-corrected structure factors with $I > 2\sigma(I)$ and a model in which anisotropic thermal parameters for each atom were varied in addition to the atomic positions to give a final $R = 0{\cdot}071$. The polar choice of space group was based entirely on the structural refinement, in the course of which the z coordinate of each Bi atom was in turn held constant. It is apparent from Table 3*S* that all seven atoms are within 0·25 Å of a paraelectric arrangement with $z = 0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$. Displacements by equal but opposite magnitudes from such an arrangement would exactly reverse the original spontaneous polarization sense. On the basis of the stated e.s.d.'s, all Δz values in Table 3*S* are highly significant. The largest $Bi(\Delta z)$ value results in $T_c = 915$ K for this black metallic material, from the AKJ relationship.

$K_9Na_{15}(AlSiO_4)_{18}(OH)_2(SO_4)_2(H_2O)_{6{\cdot}82}$

The atomic coordinates of this sulfate hydrocancrinite, determined by Klaska & Jarchow (1977), satisfy the structural requirements for ferroelectricity with all atoms except Na(3) displaced less than 0·5 Å from the paraelectric state in which $z = 0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$, see Table 4*S*. Furthermore, the dipolar contribution from each of the tetrahedral ions present may vanish at the temperature that the effective point charges similarly result in zero polarization, in accordance with the asymmetric double-well potential model discussed above. It is likely that water of hydration would be lost at temperatures much above 375 K, hence the phase transition to the paraelectric state would be detectable only if it were to occur at a temperature lower than the onset of dehydration.

Table 2. *Atomic coordinates* ($\times 10^4$) *of* $Cu_{20}Sn_6$, *hypothetical* z' *paraelectric coordinates and polar displacements*

$a = 7{\cdot}330\,(4)$, $c = 7{\cdot}864\,(5)$ Å.

	x	y	z	z'	Δz (Å)
Cu(1)	0	0	−223 (14)	0	0·175
Cu(2)	6667	3333	−900 (23)	−819	0·064
Cu(3)*	3333	6667	737 (17)	819	0·064
Cu(4)*	6472 (15)	−179 (11)	−845 (12)	−838	0·006
Cu(5)	3574 (13)	350 (10)	831 (12)	838	0·006
Cu(6)	6667	3333	2450 (26)	2500	0·039
Sn	6800 (3)	−200 (4)	2500	2500	0

* Cu(3) is the original Cu(4), and Cu(4) the original Cu(3), of Brandon *et al.* (1975).

$Cu_{20}Sn_6$

The structure of ζ-bronze $Cu_{20}Sn_6$ was determined by Brandon, Pearson & Tozer (1975) in space group $P6_3$ solely on the basis of diffraction studies. A total of 434 $I > 3\sigma(I)$ were used in least-squares refinement of a model in which isotropic thermal parameters were varied together with the appropriate positional parameters to give $R = 0{\cdot}082$ and the atomic coordinates in Table 2. The only atom in this model that is significantly displaced from locations corresponding to $P6_3/m$ is Cu(1). If this displacement, as well as those in which Cu(2) and Cu(3), also Cu(4) and Cu(5) exchange identity, is not an artefact then the AKJ relationship gives $T_c = 615$ K.

Nepheline

Sixteen entries for nepheline, $(K,Na)AlSiO_4$, appear in the January 1989 ICSD release under space group $P6_3$, of which six refer to Foreman & Peacor (1970) and three to Dollase & Thomas (1978). Minor variations in the composition of this mineral result in the same basic crystal structure (MIASA 22 569, AMMIA 57 1711, AMMIA 39 805, AMMIA 32 197, BUGMA 57 1182, BULMD 107 499). The determination by Foreman & Peacor (1970) is accepted as representative, since it was undertaken over a wide temperature range. Most nepheline studies note that the structure is close to being centrosymmetric, with space group $P6_3/m$. The atomic coordinates derived by Foreman & Peacor (1970) for nepheline at 281 and 672 K, of which each structure determination is based on about 490 independent reflections and a model with anisotropic temperature parameters that gave $R = 0{\cdot}053$ and 0·065 respectively, are presented in Table 3. It may be seen that the coordinates at 281 K are close to those expected in space group $P6_3/m$ and are generally closer still at 672 K. All investigators of nepheline report high parameter correlations, and it is hence likely that all e.s.d.'s obtained for this material by the method of least squares are underestimates. Comparable coordinates among investigations differ by as much as 15 e.s.d.'s. Compositional differences may also contribute to the reported variations.

Nepheline has been shown to be pyroelectric (Drozhdin, Novik, Gavrilova, Koptsik & Popova, 1975), hence the space group is polar and the structure meets the criteria for ferroelectricity. In addition, nepheline meets the conditions for asymmetric free-energy potential minima, see above. The AKJ relationship is hence not directly applicable. Although the lattice-parameter thermal dependence is reported as linear (Foreman & Peacor, 1970), a small discontinuity in both is observable at about 720 K. It may also be noted that the equivalent isotropic temperature factors exhibit a sharp change from an otherwise linear thermal dependence at 672 K, as is also the case with most of the averaged interatomic distances. Nepheline is hence a candidate for ferroelectric behavior, with a transition around 700 K. A wide uncertainty in T_c is expected, depending in part upon the sample composition.

Table 3. *Atomic coordinates* ($\times 10^4$) *for nepheline at* 281 K (*upper*) *and at* 672 K (*lower*), *hypothetical paraelectric z' coordinates and polar displacements*

$a = 9{\cdot}993\ (2)$, $c = 8{\cdot}374\ (3)$ Å.

	x	y	z*	z'	Δz (Å)
Na	4425 (3)	9968 (3)	2398 (17)	2500	0·106
	4432 (5)	9954 (5)	2457 (17)	2500	0·036
K	0	0	2351 (18)	2500	0·125
	0	0	2542 (28)	2500	−0·035
T(1)†	6667	3333	4347 (16)	4436	0·075
	6667	3333	4314 (14)	4429	0·096
T(2)†	6667	3333	476 (15)	564	0·074
	6667	3333	456 (13)	571	0·096
T(3)†	3343 (4)	934 (3)	5563	5632	0·058
	3329 (4)	967 (4)	5563	5634	0·059
T(4)†	3322 (4)	930 (4)	9299 (4)	9368	0·058
	3347 (4)	974 (4)	9296 (5)	9366	0·059
O(1)	7030 (59)	3337 (161)	2338 (82)	2500	0·136
	6895 (48)	3074 (50)	2671 (54)	2500	−0·143
O(2)	3185 (8)	283 (7)	7345 (25)	7500	0·130
	3183 (9)	342 (7)	7422 (21)	7500	0·065
O(3)‡	5210 (12)	1746 (12)	9838 (21)	9958	0·100
	5216 (13)	1753 (14)	9815 (20)	9918	0·086
O(4)‡	5134 (11)	1599 (12)	4921 (17)	5042	0·101
	5099 (10)	1656 (13)	4979 (29)	5082	0·086
O(5)‡	2888 (8)	2268 (9)	5589 (20)	5616	0·023
	2894 (12)	2322 (11)	5601 (17)	5618	0·014
O(6)‡	2639 (10)	2240 (11)	9358 (21)	9385	0·023
	2628 (12)	2194 (12)	9466 (19)	9483	0·014

* All z coordinates have been shifted 0·2466, relative to Foreman & Peacor's (1970) values, to midway between those of Na and K on the polar axis at 672 K.

† T(1) and T(4) were taken as primarily containing Al, and T(2) and T(3) as containing Si. Also, $z[T(1)] = \frac{1}{2} - z[T(2)]$ and $[T(3)] = \frac{1}{2} - z[T(4)]$ in the paraelectric state.

‡ $xyz[\mathrm{O}(3)] = x,y,\frac{1}{2} - z[\mathrm{O}(4)]$ and $xyz[\mathrm{O}(5)] = x,y,\frac{1}{2} - z[\mathrm{O}(6)]$ in the paraelectric state.

$NaSb_3F_{10}$

The atomic coordinates of $NaSb_3F_{10}$ at room temperature were determined by Fourcade, Mascherpa & Philippot (1975) on the basis of 589 reflections measured diffractometrically and corrected for absorption. Refinement of a model with variable anisotropic thermal parameters resulted in $R = 0{\cdot}049$. Translating the authors' origin by an arbitrary 0·220 along the 7·600 (3) Å polar axis to lie in a plane between the Sb and Na atoms, it is apparent that the transformed xyz coordinates in Table 5S are close to the paraelectric $x'y'z'$ values, where $z' = 0$, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ and $2\Delta x = x - x'$, $2\Delta y = y - y'$, $2\Delta z = z - z'$ are all relatively small. With Δz for Sb = 0·228 Å, the corresponding $T_c = 1040$ K from the AKJ relationship. The largest value of Δz is 0·912 Å for F(2), and falls within the expected range. It may be noted that placing the origin closer to Sb would increase Δz(Na) from the present 0·402 Å while reducing T_c.

$Ca_{10}(PO_4)_6S$ *family*

The apatite structure has been reported in space group $P6_3$ for several different compositions. The results obtained by Suitch, Taitai, Lacout & Young (1986) are taken as representative. These are based upon Rietveld analysis of the X-ray diffraction powder profile. For $Ca_{10}(PO_4)_6S$ at room temperature, the atomic coordinates presented in Table 4 were obtained. The three independent Ca atoms, together with S, P, O(1) and O(2), are within 0·15 Å of forming a nonpolar arrangement. Atoms O(3) and O(4) are related by $xyz = \bar{x}\bar{y}\bar{z} + \Delta$, where the polar component of the displacement Δ is only 0·038 Å. The displacements Δx, Δy are less than 0·4 Å, hence this apatite satisfies the structural criteria for ferroelectricity. Using the displacement of Ca(1) in the AKJ relationship gives $T_c = 470$ K. In case this and other apatites are more adequately described by an asymmetric double-well potential mode, due to the tetrahedral ions present, then this predicted value of T_c and the two that follow may be in substantial error.

Isomorphous apatites reported are $Sm_5(SiO_4)_3N$, with $T_c = 520$ K based on the largest Δz (BUFCA 98 214), $Sm_8Cr_2(SiO_4)_6N_2$ (BUFCA 99 203), $Ba_5[(Ge,C)(O,OH)_4]_3(OH)$ with $T_c = 480$ K (KRISA 20 644), $K_3Sn_2(SO_4)_3Cl$ and $K_3Sn_2(SO_4)_3Br$ (JCDTB 1973 1478), $Sr_6Ca_4(PO_4)_6F_2$ (ZSTKA 5 318), $Ba_5(CrO_4)_3(OH)$ (ZAACA 400 1) and $(Sr,Ca)_{10}(PO_4)_6F_2$ (KRISA 32 891). Closely related is $Cd_5(PO_4)_2(OH)$

Table 4. *Atomic coordinates* ($\times 10^4$) *for* $Ca_{10}(PO_4)_6S$ *at* ~300 K, *hypothetical paraelectric z′ coordinates and polar displacements*

$a = 9·4554$ (2), $c = 6·8405$ (2) Å.

	x	*y*	*z*	*z′*	*Δz* (Å)
Ca(1)	3333	6667	223 (19)	0	−0·153
Ca(2)	6667	3333	96 (2)	0	−0·066
Ca(3)	2459 (4)	−110 (5)	2500	2500	0
S	0	0	4846 (40)	5000	0·105
P	3968 (5)	3720 (5)	2441 (20)	2500	0·040
O(1)	3266 (10)	4852 (10)	2640 (38)	2500	0·096
O(2)	5841 (11)	4724 (11)	3061 (27)	2500	0·384
O(3)*	3848 (12)	2853 (14)	680 (25)	734	0·038
O(4)*	−3080 (16)	−2373 (17)	−789 (17)	−734	0·038

* O(3) and O(4) are related by an inversion center and a displacement $\Delta = \Delta x + \Delta y + \Delta z$, where $\Delta x = 0·363$, $\Delta y = 0·227$ and $\Delta z = 0·038$ Å.

which has a supercell based on that of hydroxyapatite (MJTOA 11 317) and has all atoms within 0·4 Å of a paraelectric arrangement.

It may be noted that a related group of apatite-type materials typified by $Ba_5(ReO_5)_3Cl$, crystallizing in space group $P6_3cm$, has previously been shown (Abrahams, 1988) to satisfy the structural criteria for ferroelectric behavior.

Table 5. *Atomic coordinates* ($\times 10^4$) *for* $K_3SbS_3(Sb_2O_3)_3$ *at* ~300 K, *hypothetical paraelectric z′ coordinates and polar displacements*

$a = 14·256$ (5), $c = 5·621$ (2) Å.

	x	*y*	*z**	*z′*	*Δz* (Å)
Sb(1)	3333	6667	589	0	−0·331
Sb(2)	3888 (1)	4035 (1)	−5592 (8)	5000	0·333
Sb(3)	1679 (1)	4505 (1)	−5584 (9)	5000	0·328
K	1817 (3)	2797 (3)	−570 (21)	0	0·320
S	3648 (5)	5322 (5)	−1047 (54)	0	0·589
O(1)	2287 (9)	3546 (9)	−5643 (47)	5000	0·361
O(2)	630 (15)	3571 (15)	1997 (30)	2479	0·271
O(3)	670 (17)	3616 (16)	−2961 (33)	−2479	0·271

* Origin translated 0·6911 along the polar axis to midway between *z* coordinates of Sb(1) and the pair Sb(2),Sb(3).

Table 6. *Atomic coordinates* ($\times 10^4$) *for* $Ca_3Si(OH)_6(CO_3)(SO_4).12H_2O$ (*thaumasite*) *at room temperature, hypothetical paraelectric z′ coordinates and polar displacements*

$a = 11·030$ (7), $c = 10·396$ (6) Å.

	x	*y*	*z*	*z′*	*Δz** (Å)
Ca	1949 (1)	9883 (1)	2513	2500	0·014
Si	0	0	26 (2)	0	0·027
C	3333	6667	4660 (6)	5000	0·353
S	3333	6667	9847 (2)	0	0·159
O(1)	3910 (2)	2282 (2)	2546 (4)	2500	0·048
O(2)	2618 (2)	4024 (2)	2521 (4)	2500	0·022
O(3)	29 (3)	3395 (3)	719 (4)†	695	0·025
O(4)	242 (4)	3485 (3)	4329 (4)†	4305	0·025
O(5)	2010 (3)	6229 (3)	4602 (3)†	4633	0·032
O(6)	1920 (3)	6227 (3)	337 (3)†	367	0·032
O(7)	1304 (3)	1245 (3)	1071 (3)†	1045	0·027
O(8)	1308 (3)	1250 (3)	3981 (3)†	3955	0·027
O(9)	3333	6667	8436 (4)	7500	0·973

* All values of *Δz* for the H atoms are less than 0·7 Å.

† O(3),O(4); O(5),O(6); and O(7),O(8) form related pairs of atoms with $x_1y_1z_1 = x_2,y_2,\frac{1}{2} - z_2 + \Delta$, where $\Delta x = x_1 - x_2$, $\Delta y = y_1 - y_2$, $\Delta z = z_1 - z_2$ and $\Delta = \Delta x + \Delta y + \Delta z$, all differences being less than about 0·3 Å.

$K_3SbS_3(Sb_2O_3)_3$

The atomic coordinates of $K_3SbS_3(Sb_2O_3)_3$ in Table 5 are as provided by Graf & Schaefer (1975) but with the origin translated 0·6911 along the *c* axis. The structure was refined on the basis of 2200 independent structure factors with a model in which anisotropic thermal parameters for Sb, K and S and isotropic thermal parameters for O were varied, giving a resulting $R = 0·090$. It may be seen from Table 5 that all atoms are close to $z = 0$ or $\frac{1}{2}$ except for O(2) and O(3) which are related by $x_iy_iz_i = x_jy_j\bar{z}_j + \Delta$. The latter relationship is applicable to all atoms in this structure at room temperature on reversing polarity, with no *Δz* displacement from the hypothetical paraelectric phase that is greater than 0·6 Å and $\langle Sb(\Delta z)\rangle = 0·331$ Å. The resulting $T_c = 2190$ K, from the AKJ relationship, is higher than the expected upper limit but is nevertheless possible. $K_3SbS_3(Sb_2O_3)_3$ is hence predicted to be most likely ferroelectric.

$Ca_3Si(OH)_6(CO_3)(SO_4).12H_2O$ (*thaumasite*)

At least five independent refinements of the structure of the mineral thaumasite have been reported. The results of the latest investigation by Effenberger, Kirfel, Will & Zobetz (1983) are used here, as both representative and more reliable than the earlier work (AMNGA 2 137, CHDDA 270 2151, KRISA 26 1215, ACBCA 27 594). A total of 3928 reflections were measured diffractometrically and symmetry-related values averaged to give $R_{\rm int} = 0·022$. The positional and isotropic thermal parameters of all ten independent H atoms were varied in the final refinement together with the positional and anisotropic thermal parameters for the heavier atoms and an isotropic extinction parameter, resulting in $R = 0·032$ for all 1425 unique reflections. All non-H-atom *z* coordinates in Table 6 are within 0·35 Å of the paraelectric values except for that of O(9) which is 0·97 Å distant. All associated H atoms are within 0·71 Å of the zero spontaneous polarization positions. Taking the S atom as the critical AKJ atom, then $T_c = 510$ K (but see also *Extension of ferroelectric structure concept* above, in view of the SO_4 tetrahedra located on trigonal axes). It is noted that, while the C, S and O(9) *z* coordinates reported are relatively far from their paraelectric *z′* values, the remaining atoms are within their r.m.s. amplitudes of vibration of these values. Confirmation of the polar properties expected in space group $P6_3$ for thaumasite would indicate that this mineral may exhibit interesting dielectric attributes, despite the likelihood that it may lose water at temperatures lower than T_c.

$Na_6(SiAlO_4)_6Ca_{1·5}(CO_3)_{1·5}.2H_2O$ (*cancrinite*)

Many refinements of cancrinite [$Na_8(AlSiO_4)_6(CO_3).2H_2O$] and its substitutional variants have been reported. The atomic coordinates of a carbonate-rich variant determined by Grundy & Hassan (1982) are typical and are presented in Table 6*S*, with the origin translated 0·02 along the polar axis to a plane between the Si and Al atoms. In addition to a normal structural study, these authors used high-resolution transmission electron microscopy to arrive at a description of the superstructure in terms of substitutions consistent with $P6_3$. They measured 1918 reflections with $F_o > 3\sigma(F_o)$, thereby obtaining 855 observed values after averaging ($R_{\rm int}$ not given). The final atomic coordinates correspond to $R = 0·028$ for anisotropic thermal parameters varied on each non-H atom. All z coordinates are within 0·5 Å of a paraelectric set with $z = 0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$. Those of Si and Al are about 0·11 Å, the Na and Na,Ca atoms are 0·49 and 0·34 Å respectively, and the C and O atoms are all less than about 0·4 Å from the paraelectric z positions. The AKJ relation is not directly applicable to cancrinite with its tetrahedral ions. However, if the space group reported here and in comparable determinations (ZEGKA 122 407, KRISA 26 63, KRISA 27 51, JCSIA 1970 1523, ACBCA 38 893, PIATA 1933 56, KRISA 31 874 and AMMIA 72 816) is correct, then cancrinite is likely to be an asymmetric double-well potential ferroelectric. As is the case with other hydrates, cancrinite may lose water at temperatures well below T_c. Vishnerite (CAMIA 20 239) is isostructural with cancrinite.

$BaZnGeO_4$ *family*

The structures of several (isostructural) aluminates and germanates have been determined, all derived from the high-tridymite framework, including $BaAl_2O_4$ (ZAACA 451 40), $BaFe_{1·5}Al_{0·5}O_4$ (ZAACA 448 135), $BaGe_2O_4$ (JINCA 35 3177) and $BaMn_{0·12}Al_{1·88}O_4$ (ZAACA 468 197). The results reported on $BaZnGeO_4$ by Iijima, Marumo & Takei (1982) (see also YGKSA 91 67) appear to be the most reliable and hence are used here. These authors measured 306 independent $F_o > 3\sigma|F_o|$, of which 140 were superlattice reflections. Refinement of their final model with anisotropic thermal parameters for all atoms and O(4) equally distributed over three different sites gave the coordinates listed in Table 7*S*, with $R = 0·0464$. The z values of all atoms except Ge and Zn are within 0·26 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ for which the resulting spontaneous polarization is zero, The z coordinates of Zn and Ge are each within 0·1 Å of $\pm z = 0·4489$. If the Zn and Ge atoms have equal effective point charges and their O-atom tetrahedra have zero dipoles, then the polarization within the unit cell would be zero for equal but opposite-sense Zn,Ge z values. Alternatively, if the Zn and Ge atoms are disordered, then their polarizations would cancel. The authors state that piezoelectricity in this phase has been detected, also that it undergoes a phase transition at 522 K (with another at 1108 K). They also give atomic coordinates at 1073 K that are essentially identical to those for the hypothetical paraelectric structure in Table 7*S*. The AKJ relationship is not directly applicable to tetrahedral-ion ferroelectrics, see above. However, $BaZnGeO_4$ and related family members may be regarded as attractive ferroelectric candidates with asymmetric double-well potential minima that should be investigated further.

$NaPO_3NH_3$

The structure of this material was refined by Cruickshank (1964) on the basis of 119 earlier estimates of $|F_o|$ (ACCRA 6 621) to give $R = 0·064$ and the atomic coordinates of Table 8*S*, assuming the H-atom position. The origin has been translated along the polar axis to the z value midway between that of Na and P. The largest polar non-H atomic displacement needed to reverse the spontaneous polarization is that of N, with a 0·44 Å displacement to the paraelectric position. Both the P and O atoms are displaced 0·19 Å from $z = \frac{1}{4}$, with Na similarly displaced from $z = 0$. If the potential barrier required to invert the pyramidal PO_3 ion can be overcome without exceeding the dielectric strength of the crystal, then Δz(P) results in $T_c = 720$ K from the AKJ relationship.

$La_6Mn_2Ga_2S_{14}$ *family*

The atomic coordinates of $La_6Mn_2Ga_2S_{14}$ were refined by Rodier, Guittard & Flahaut (1983) on the basis of 725 $I > 2\sigma(I)$ measured diffractometrically, with final $R = 0·033$, and are given in Table 9*S*. The origin has been translated 0·0280 along the polar axis to place the Ga and Mn z coordinates at an equal distance from the planes at $z = 0$ and $\frac{1}{4}$ respectively. All atomic z coordinates are within 0·4 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ and hence satisfy the structural criteria for ferroelectricity. The tetrahedrally coordinated Ga-atom displacement, for the origin chosen, corresponds to $T_c = 2050$ K; a choice closer to Ga (hence further from Mn) would readily reduce T_c to about 1000 K or less while retaining acceptable (but larger) displacements for all other atoms. However, this material is more likely to be described correctly as an asymmetric double-well potential ferroelectric. Investigation of the dielectric properties of this complex sulfide is hence of interest.

Other family members include $La_6Cu_2Si_2S_{14}$ (BUFCA 94 175), $R_6Mn_2Al_2S_{14}$ (R = La to Dy and Y) (CHDCA 270 488), $R_6Mn_2Ga_2S_{14}$ (R = La to Gd) (BSCFA 1972 2207), $La_6MnSi_2S_{14}$ (CHDCA 270 410) and $La_6Mn_2Fe_2S_{14}$ (JSSCB 49 51).

Tl_3PO_4 *family*

The crystal structure of this strongly second-harmonic generating material (CHDCA 276 1755) was remeasured and refined by Zalkin, Templeton, Eimerl & Velsko (1986) to $R = 0{\cdot}017$ for 241 independent averaged structure factors with $R_{\rm int} = 0{\cdot}035$. The unit cell contains Tl atoms in general positions, with z(Tl) taken as the origin (see Table 10*S*). P and O(1) lie on the trigonal axes and O(2) is in a general position. All PO_4^{3-} ions hence point toward $-\mathbf{c}$, with z(P) only 0·082 Å from $z = 0$. A displacement of 0·082 Å by the PO_4^{3-} ion would result in zero point-charge polarization, assuming an effective charge of $3-$ at the P atom. Similar small displacements by O(1) and O(2) would result in a net zero dipole by the anion. It is hence apparent that such displacements would result in a paraelectric state, without spontaneous polarization, and that close to this state the sign of the polarization could be readily reversed. Tl_3PO_4 may hence be regarded as a prototypic asymmetric double-well potential ferroelectric. It is thus not possible to estimate T_c in Tl_3PO_4 from the AKJ relationship but, since the crystal is strongly polar at 296 K, a transition above room temperature should be sought experimentally. It may be noted that the r.m.s. amplitudes of vibration for the PO_4^{3-}-group atoms, at about 0·15 Å, are comparable to or greater than the displacements necessary to form the hypothetical paraelectric structure. Tl_3AsO_4 is isomorphous with Tl_3PO_4 (NBSMA 25 37).

$LiKSO_4$ *family*

The structure determination of $LiKSO_4$ has recently been reported by five independent groups, with similar results. Those of Schulz, Zucker & Frech (1985) are taken as representative since they include the atomic coordinates at 293, 398 and 568 K; others may be found in PSSAB 83 K117, WLHPA 32 1196, KRISA 28 67, ACSCE 39 34 and ACSCE 40 1648. The coordinates at 293 K of Schulz *et al.* (1985) are presented in Table 11*S*, transposed for compatibility with the other sets. The structure consists of LiO_4 and SO_4 tetrahedra sharing O(1) and lying on the trigonal axes, with K^+ ions located on the hexagonal axes. The tetrahedra are hence oppositely oriented along the polar direction. Taking K^+ as defining the origin along the c axis, $z({\rm Li}) \simeq \bar{z}({\rm S})$; also, $z[{\rm O}(1)] \simeq \frac{1}{2}$ and $z[{\rm O}(2)] \simeq \frac{3}{4}$. Displacements less than about 0·3 Å convert these relationships to equalities. However, smaller displacements for the O atoms result in a zero dipole for the $[LiSO_4]^-$ complex as it is displaced further by the small polar translation (~0·1 Å) needed to produce a zero point-charge polarization with respect to K^+.

$LiKSO_4$ can hence form a nonpolar state in which the orientation of neither kind of tetrahedron changes from that in the initial ferroelectric state, nor from that in the reversed P_s state. As discussed above, the AKJ relationship is not directly applicable to such structures. However, several phase transitions have been reported in $LiKSO_4$, see references in Schulz *et al.* (1985). That at about 700 K is accompanied by anomalies in dielectric permittivity, resistivity and pyroelectric current, although reversal of the polarization direction by an applied electric field has not been reported. Further investigation may relate this or the subsequent transition at about 950 K, or an intermediate temperature, to a change from a ferroelectric asymmetric double-well to a single-well potential.

The $LiKSO_4$ family includes crystals with the general formula $M^{\rm I}M^{\rm II}BX_4$, where $M^{\rm I}$ is Li or Na and $M^{\rm II}$ is Na, K, Rb, Cs, NH_4 or N_2H_5. The BX_4 anion may be BeF_4, SO_4 or SiO_4. The atomic positions reported in $LiBeF_4$ (ACBCA 28 1383) and in $KAlSiO_4$, the mineral kalsilite (MIASA 35 588), are closely comparable to those in $LiKSO_4$ following transposition. Kalsilite is found to undergo a phase transition at 1125 K, possibly related to the predicted paraelectric state. Additional dielectric study of this family would be appropriate.

$Mo_6I_8Se_2$

The structure determination by Perrin & Sergent (1983) of $Mo_6I_8Se_2$ was based upon 308 independent reflections with $I > \sigma(I)$ and refined to give a final $R = 0{\cdot}179$ for the atomic coordinates listed in Table 7. It is apparent from this table that the atoms are either located close to $z = 0$ or $\frac{1}{4}$ (hence also to $z = \frac{1}{2}$ or $\frac{3}{4}$) or else form in pairs such that the x and y coordinates are related in value with z and $\sim\frac{1}{2} - z$ coordinates respectively. A paraelectric structure hence exists with z' coordinates as given in Table 7. All atomic displacements necessary to form the hypothetical paraelectric structure are less than 0·4 Å and hence satistfy the criteria for ferroelectricity, providing the space group is correctly assigned. In the latter case, the Mo atoms are critical with $\Delta z = 0{\cdot}148$ Å, resulting in T_c (AKJ) = 440 K. The high value of R and low precision of the determination make further investigation of $Mo_6I_8Se_2$ advisable.

Table 7. *Atomic coordinates* ($\times 10^3$) *for* $Mo_6I_8Se_2$ *at room temperature, hypothetical paraelectric z′ coordinates and polar displacements*

a = 16·265 (4), c = 12·316 (8) Å.

	x	y	z	z'	Δz (Å)
Se(1)	0	0	10 (9)	0	0·123
Se(2)	333	667	251 (10)	250	0·012
Se(3)	333	667	731 (10)	750	0·234
Mo(1)*	894 (3)	908 (3)	165 (3)	153	0·148
Mo(2)*	103 (3)	96 (3)	360 (3)	347	0·148
Mo(3)	239 (3)	584 (3)	419 (3)	420	0·012
Mo(4)	228 (3)	576 (3)	79 (3)	80	0·012
Mo(5)	437 (3)	744 (3)	584 (3)	596	0·148
Mo(6)	434 (3)	749 (3)	892 (3)	904	0·148
Se,I(1)*	197 (2)	172 (2)	167	155	0·148
Se,I(2)*†	27 (2)	200 (2)	358 (3)	345	0·148
Se,I(3)†	549 (2)	849 (2)	383 (3)	413	0·369
Se,I(4)†	592 (2)	885 (2)	57 (2)	87	0·369
Se,I(5)†	364 (2)	897 (2)	584 (3)	585	0·012
Se,I(6)†	374 (2)	880 (2)	913 (3)	915	0·012
I(1)	15 (2)	218 (2)	23 (2)	0	0·283
I(2)	532 (2)	621 (2)	247 (3)	250	0·037
I(3)	436 (2)	144 (2)	225 (2)	250	0·308

* Mo(1);Mo(2) are related by $xyz;\bar{x},\bar{y},\frac{1}{2}-z$ and Se,I(1);Se,I(2) by $xyz;y,y-x,\frac{1}{2}-z$.

† A fixed ratio of Se:I = 1:5 was assumed.

Table 8. *Atomic coordinates* ($\times 10^4$ *for* Tm, Si *and* $\times 10^3$ *for* Na, O) *for* $Na_3TmSi_2O_7$ *at room temperature, hypothetical paraelectric z′ coordinates and polar atomic displacements*

a = 9·387 (2), c = 13·717 (4) Å.

	x	y	z*	z'	Δz (Å)
Tm(1)	0	0	2519 (6)	2500	0·026
Tm(2)	6667	3333	185	0	0·254
Tm(3)	6667	3333	4815 (1)	5000	−0·254
Si(1)	3240 (7)	3506 (7)	1397 (4)	1411	−0·019
Si(2)	3309 (7)	3435 (7)	3576 (4)	3589	−0·018
Na(1)	0	0	495 (5)	500	−0·069
Na(2)	333	667	757 (2)	750	0·096
Na(3)	333	667	479 (1)	500	0·288
Na(4)	309 (1)	329 (1)	583 (1)	586	0·041
Na(5)	317 (2)	332 (2)	911 (1)	914	0·041
O(1)†	265 (3)	431 (3)	65 (2)	67	0·027
O(2)	276 (3)	451 (3)	430 (1)	433	0·041
O(3)	604 (4)	126 (4)	128 (2)	122	0·082
O(4)	616 (2)	127 (3)	384 (1)	378	0·082
O(5)	204 (3)	147 (3)	144 (1)	140	0·055
O(6)	188 (3)	153 (3)	364 (1)	360	0·055
O(7)	320 (1)	421 (1)	258 (4)	250	0·110

* Origin displaced 0·0185 along the polar direction to give equal-magnitude displacements by Tm(2) and Tm(3).

† The O atoms are numbered differently from those of Sebais *et al.* (1985).

Mn_4SiO_7

The structure of welinite, ideally $Mn^{IV}Mn_3^{II}SiO_7$ but with some substitution of W together with vacancies in the Mn^{4+} site and with Mg, W and corresponding vacancies in the Mn^{2+} site, was reported by Moore (1967). Based on 277 independent symmetry-averaged F_o measured on a manual diffractometer, with isotropic thermal parameters and site-occupancy factors as additional variables, the atomic coordinates in Table 12*S* were obtained with a final $R = 0·106$. An origin displacement of 0·024 along the polar axis, to midway between the z coordinates of Mn,W(1) and Si, results in all atoms having a location within 0·35 Å of $z = 0$, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$. The last positions correspond to zero spontaneous polarization. The displacement $\Delta z = 0·187$ Å for Si gives T_c (AKJ) = 700 K. Mn_4SiO_7 may, however, be closer to an asymmetric double-well potential than to an AKJ-type ferroelectric. All displacements appear to be highly significant, although no physical evidence has been presented that demonstrates the polar characteristics expected in space group $P6_3$.

$Sn_7Br_{10}S_2$

The structure of the tin chalcogenide halide $Sn_7Br_{10}S_2$ was determined by Valle, Donaldson, Grimes, Calogero, Russo & Smith (1984) on the basis of 296 independent reflections with $|F_o| > 2|F_c|$ that were uncorrected for absorption. The polar choice of space group, made on the basis of refinement behavior, gave the atomic coordinates in Table 13*S* and $R = 0·059$ for partial site occupancy by all atoms except Br(1). It may be noted that the origin used has been translated 0·0084 along the polar axis to the value midway between z[Sn(2)] and z[Sn(3)]. The z coordinate of each atom is close to $\frac{1}{4}$, the largest displacements being 0·147 Å for Sn(2) and Sn(3). The AKJ relation hence gives $T_c = 430$ K for this yellow prismatic material. Neither the e.s.d.'s for the atomic coordinates nor the thermal parameters were given, hence further investigation is necessary to confirm the space group; if correct, then this material satisfies the structural conditions for ferroelectricity.

$Na_3TmSi_2O_7$ *family*

The structure of $Na_3TmSi_2O_7$ was determined by Sebais, Pobedimskaya & Dimitrova (1985) on the basis of 1745 reflections, corrected for absorption ($F_{\rm min}$ not defined). Refinement in $P6_3$ gave a better fit than in $P6_3/m$ and led, with variable anisotropic thermal parameters, to $R = 0·055$ and the atomic coordinates in Table 8. Examination of this table shows that a displacement no greater than 0·3 Å results in zero spontaneous polarization, with Tm(2) and Tm(3) each displaced 0·254 Å in opposite senses from $z = 0$ and $\frac{1}{2}$ respectively. The only other atomic displacement significantly greater than 0·1 Å is that of 0·288 Å for Na(3). The AKJ relation gives T_c = 1290 K, although the Si_2O_7 groups present suggest the possibility that an asymmetric potential-minimum model may apply more appropriately. A confirmation of the polar properties of $Na_3TmSi_2O_7$ would indicate that this colorless crystal is indeed ferroelectric. The corresponding Y compound was

Table 9. *Atomic coordinates* (× 10^4) *of* $Ca_3Mn(SO_4)(CO_3)(OH)_6.12H_2O$ (*jouravskite*) *at room temperature, hypothetical paraelectric z′ coordinates and polar displacements*

a = 11·06 (3), c = 10·50 (3) Å.

	x	y	z*	z'	Δz (Å)
Mn	0	0	175 (80)	0	0·184
C	3333	6667	−260 (91)	0	0·273
S	3333	6667	5085 (12)	5000	0·089
Ca	24 (4)	2049 (3)	7676 (7)	7500	0·185
O(1)	3333	6667	3607 (89)	†	†
O(2)	1963 (18)	6289 (24)	−260 (24)	−376	0·122
O(3)	1937 (26)	5881 (25)	5493 (33)	5376	0·123
O(4)	45 (15)	1356 (17)	4059 (20)	3920	0·146
O(5)	1356 (17)	1355 (17)	6219 (24)	6080	0·146
O(6)	179 (19)	3452 (21)	9574 (23)	9343	0·243
O(7)	−141 (15)	3327 (18)	5888 (20)	5657	0·243
O(8)	2531 (16)	4037 (17)	7549 (24)	7456	0·098
O(9)	3987 (16)	2396 (17)	7637 (30)	7544	0·098

* Origin translated 0·0260 along the polar axis to give the same positive and negative displacements by Mn, C and S from $z' = 0$ or $\frac{1}{2}$.

† For $z' = \frac{1}{4}$, Δz = 1·162 Å; however, O(1) need be displaced along the trigonal axis only by the small distance necessary to reduce the dipole moment of the $S[O(1)][O(3)]_3$ tetrahedron to zero, see text.

previously shown to be centrosymmetric (PCMID 5 245), but the Tm diorthosilicate is stated to differ in symmetry. Other rare-earth compounds may also be expected to be isostructural with $Na_3TmSi_2O_7$.

$V_3P_5SiO_{19}$

The structure determination of $V_3P_5SiO_{19}$ by Leclaire, Chahboun, Groult & Raveau (1986), based on 2837 absorption-corrected reflections with $I > 3\sigma(I)$, led to the atomic coordinates presented in Table 14*S* with R = 0·047. The polar choice of space group was made on the basis that refinement was not possible in $P6_3/m$. It may be seen from the table, in which the origin has been translated 0·0202 along the polar axis to give equal P(1) and P(4) atomic displacements, that all atoms either have z coordinates within 0·36 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ or else form pairs with coordinates xyz and $x + \Delta x$, $y + \Delta y$, $\frac{1}{2} - z + \Delta z$. All values of Δx and Δy are less than 0·35 Å and the largest value of Δz is 0·18 Å [for the O(4),O(5) pair]. Taking phosphorus as the critical atom in this structure, then the AKJ relationship for Δz(P) = 0·157 Å gives T_c = 500 K. Investigation of this possible phase transition to a paraelectric phase would be appropriate.

$Ca_3MnSO_4(CO_3)(OH)_6.12H_2O$ (*jouravskite*)

The structure of jouravskite was determined by Granger & Protas (1969), using 739 independent microdensitometered film-recorded reflections. The polar space group was selected since $P6_3/m$ would require the tetrahedral sulfate ion to have an apical atom located on a mirror plane. Refinement with isotropic thermal parameters led to R = 0·16 and the atomic coordinates presented in Table 9. It is apparent from this table that Mn^{IV}, C, S and Ca are all within 0·3 Å of $z' = 0$, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$, which would result in zero spontaneous polarization if all effective charges were localized on these atoms. The planar $C[O(2)]_3^{2-}$ ionic displacement of 0·27 Å is the largest [note that $O(2)xyz = O(3)x,y,\frac{1}{2} - z + \Delta$ as assumed in Table 9 or, more likely, O(2)z is displaced to $z' = 0$ and O(3)z is displaced by about 0·09 Å as O(1) undergoes a comparable Δz displacement to form a geometrically regular SO_4 tetrahedron] with Δz = 0·184 Å for Mn within its octahedron of O atoms. The orientation of the dipoles associated with the water molecules in jouravskite at room temperature is undetermined and these may not cancel at any temperature. Furthermore, the SO_4 tetrahedra on the trigonal axes are indicative of asymmetric potential minima, see above. Nevertheless, jouravskite appears to be capable of ferroelectric behavior, with T_c (AKJ) at about 690 K, well above the temperature at which water of hydration is lost. Dielectric measurement below the water-loss temperature would be appropriate.

$TlLaO_3$ *family*

The structure of α-$TlLaO_3$, proposed by Jouini, Verbaere & Tournoux (1977) in space group $P6_3$ on the basis of electron and X-ray powder diffraction, has the coordinates given in Table 15*S* with R = 0·12 on the basis of 18 powder lines. The cations are displaced less than 1·7 e.s.d.'s from the corresponding positions in $P6_3/m$, and the O-atom positions were not refined. The La atom, in its O-atom octahedron, has a polar displacement from the centrosymmetric position that corresponds to T_c = 685 K. A phase change to cubic symmetry is reported at 810 K. La can be replaced by Nd, Sm, Eu and Gd. Further experimental investigation is necessary before the assumed polar properties of this family are accepted.

$Na_3SbSe_3(Sb_2O_3)_3[Sb(OH)_3]_{0.5}$

The structure of this hydrothermally grown complex was determined on the basis of 985 symmetry-independent $I \geq 2\sigma(I)$, corrected for absorption and refined to give R = 0·083 by Kluger & Pertlik (1985). The polar space group was chosen, rather than $P6_3/m$, in view of the refinement behavior. The resulting atomic coordinates, as given in Table 16*S*, have all z values within 0·55 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$. The largest Sb Δz value, for Sb(1) and Sb(2), is 0·300 Å which corresponds to T_c (AKJ) = 1800 K. Although this predicted ferroelectric–paraelectric phase-transition temperature is high, it is within the range of known values. It is noted that the atomic coordinates in Table 16*S* bear a close similarity to those in

Table 5, apart from the additional atoms Sb(4) and O(4).

Structures reported in space group $P6_3$ but probably nonpolar

Entries in space group $P6_3$ include a number of determinations in which the polar atomic coordinates differ from those in the postulated paraelectric position by less than the r.m.s. amplitudes of vibration. In most cases, physical evidence of polarity has not been presented and it is concluded that such determinations should either be reinvestigated in the nonpolar space group or else be regarded as unreliable. Thus $K_xV_xMo_{1-x}O_3$, with $x = 0{\cdot}13$ (JSSCB 8 189) and the origin translated 0·0324 along the c axis to midway between the K-atom and the shared V,Mo-atom z coordinates, has all resulting z coordinates less than 0·16 Å from 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$. With r.m.s. amplitudes ranging from 0·11 to 0·18 Å, the given atomic arrangement cannot be distinguished uniquely from one in $P6_3/m$.

Other crystal structure determinations reported in $P6_3$ but that are probably nonpolar follow: in $NaBF_3(OH)$ (CJCHA 48 405), all atoms have z coordinates within 0·1 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ or else are related in ij pairs by

$$x_iy_iz_i = x_j,y_j,\tfrac{1}{2} - z_j + 2\Delta_{ij} \qquad (2)$$

with Δz_{ij} less than 0·07 Å. The coordinates determined in $P6_3$ are hence, within a single r.m.s. amplitude of thermal vibration, equivalent to a corresponding set in $P6_3/m$. In $Fe_2[As(AsO_4)_3]$, all ith and jth atoms (ACBCA 35 1751) are similarly related in pairs by equation (2), either with Δz less than 0·1 Å or else with the z coordinate less than 0·1 Å from $\frac{1}{4}$ or $\frac{3}{4}$, an arrangement that does not differ significantly from one that is centrosymmetric. Each of the three independent atoms in β-Si_3N_4 (ACBCA 35 800) has a z coordinate within 0·04 Å of $\frac{1}{4}$, hence the structure is indistinguishable from one with all atoms in position 6(h) of space group $P6_3/m$.

The structure determination of $SrCa_2Yb_{10}O_{18}$ and isomorphous $SrCa_2Lu_{10}O_{18}$ (ZENBA 31 1064) also places all atoms in the 6(h) position of space group $P6_3/m$, except for Sr at $\frac{1}{3}\frac{2}{3}0$. Such an arrangement is paraelectric; however, if Sr is distributed over position 4(f), which is possible with $R = 0{\cdot}065$ for the Yb and 0·098 for the Lu compound, then all atom positions are consistent with $P6_3/m$. The mineral painite, $CaZrBAl_9O_{18}$, may be described (AMMIA 61 88) in $P6_3$ as having an arrangement in which ith and jth atoms are related in pairs by equation (2) with Δ_{ij} less than 0·01 Å; all other atoms not forming pairs have z_i less than 0·06 Å from the values 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$, thus corresponding to a paraelectric nonpolar structure. The sulfoiodide $Bi(Bi_2S_3)_9I_3$ structure was determined both in $P6_3/m$ and in $P6_3$ (NATWA 58 219) and the latter space group chosen on the basis of a private communication reporting the absence of inversion centers; nevertheless, no atom is further than 0·03 Å in the $P6_3$ model from the corresponding position in $P6_3/m$, hence the centrosymmetric structure is most probably correct at room temperature [see, however, isotypic $Bi(Bi_2S_3)_9Br_3$, with its highly significant polar atomic displacement, above].

Both BCl_3 (JCPSA 27 195) and BBr_3 (GCITA 77 361) structures have been reported in $P6_3$ but with z coordinates of zero for each atom rather than the more likely $\frac{1}{4}$ to be expected in positions 2(c) and 6(h) for $P6_3/m$. An origin displacement by $\frac{1}{4}$ along **c** leaves the atomic arrangement unchanged, hence $P6_3/m$ may be taken as the space group for both structures. The mineral gaudefroyite $Ca_4Mn_3(BO_4)_3(CO_3)$ has been reported (KRISA 20 152) in $P6_3$. An origin shift of 0·068 along the c-axis places the three independent cations and the B atom within 0·06 Å of $z = 0$, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$; the borate O atoms form pairs related by equation (2) with Δz_{ij} less than 0·02 Å. The CO_3^{2-} ion, however, is ~0·4 Å from $z = 0$, hence additional structural investigation of this mineral in space group $P6_3/m$ is indicated. The mineral zinckenite $Pb_6Sb_{14}S_{27}$ has been independently reported twice (ZEKGA 141 79, BUFCA 99 351) in $P6_3$. Following the application of an origin displacement of 0·014 along the c axis to the coordinates presented in the first report, all cations except for two sites partially occupied by Pb atoms have z coordinates within 0·1 Å of $\frac{1}{4}$ or $\frac{3}{4}$; the two sites are related by equation (2) with $\Delta_{ij} < 0{\cdot}1$ Å. Furthermore, all S atoms have z coordinates within 0·4 Å of $\frac{1}{4}$ or $\frac{3}{4}$ except for two that are related by z_i and $\bar{z}_j$ coordinates with $z_i - z_j < 0{\cdot}2$ Å. In the second report, all z coordinates are given as 0 or $\frac{1}{2}$ but clearly should be translated to $\frac{1}{4}$ to place each atom at x, y, $\frac{1}{4}$ in position 6(h) of $P6_3/m$. Further structural investigation of zinckenite is appropriate.

The structure of $KNd_9(SiO_4)_6O_2$, determined in $P6_3$ (DANKA 242 835), has all atoms with z coordinates no further than 0·13 Å from 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ except for the oxide O atom. If this atom were distributed over position 4(e) in $P6_3/m$, rather than 2(a) in $P6_3$, the arrangement would correspond to the centrosymmetric space group. It may be noted that this atom is reported to have an unusually large displacement amplitude along the c axis. Similarly, in $Na_6YSc(Si_2O_7)_2$, all atoms either have z coordinates within 0·04 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ or else are related in ith and jth atom pairs with coordinates $x_iy_iz_i = y_j,y_j - x_j,\bar{z}_j + \Delta_{ij}$ or $\bar{y}_j,x_j - y_j,\frac{1}{2} - z_j + \Delta_{ij}$ or $x_j,y_j,\frac{1}{2} - z_j + \Delta_{ij}$ with Δz_{ij} less than 0·08 Å (KRISA 25 708). The space group of this crystal is hence most likely $P6_3/m$. In the case of the apatite $Sr_5(CrO_4)_3Cl$ (ZNBAD 33 708), all atoms have z coordinates within 0·12 Å of 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$

except for two O atoms related by $x_iy_iz_i = \bar{x}_j\bar{y}_j\bar{z}_j + 2\Delta_{ij}$, with $\Delta_{ij} = 0{\cdot}19$ Å; $P6_3/m$ is hence the most likely choice of space group for this apatite. The atomic coordinates of $Tl_{0{\cdot}77}V_6S_8$ have been reported in $P6_3$ (JCOMA 105 L5) with z(Tl) = 0 and the z coordinate for each of the remaining three independent atoms within 0·03 Å of $\frac{1}{4}$; the symmetry is thus indistinguishable from that of $P6_3/m$.

$Pb_{0{\cdot}15}Nb_3S_4$ has also been reported in $P6_3$ (ACSCE 41 306), with z coordinates for Nb and the two independent S atoms less than 0·04 Å from $\frac{1}{4}$ and that of Pb within 3 e.s.d.'s of zero, hence the space group is most likely $P6_3/m$. Diffraction data for the isomorphous pair $K_3Sn_2(SO_4)Cl$ and $K_3Sn_2(SO_4)Br$ were refined in P_3 (JCDTB 1984 1301) to give atomic coordinates for both compounds that have z values less than about 0·1 Å from 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ except for the partially occupied Sn and K atoms and also two O atoms, which are related by equation (2) with values of Δz_{ij} that are similarly less than 0·1 Å. A remaining O atom (not the same in each compound) appears to be about 0·25 Å from $z = \frac{1}{4}$. The r.m.s. amplitudes of 0·1–0·3 Å hence indicate that further investigation of this isomorphous pair in $P6_3/m$ is appropriate. Rietveld-method refinement of the neutron powder diffraction data for $(Mn_{0{\cdot}7}Ca_{9{\cdot}3})(PO_4)_6F_2$, a substituted fluorapatite (ASBSD 41 173) in space group $P6_3$ results in atomic coordinates that differ only by about the r.m.s. amplitudes of vibration from those in the unsubstituted fluorapatite with space group $P6_3/m$; further study of this material is thus also indicated.

$Na_3Sc(SO_4)_3.5H_2O$ has atomic coordinates (DANKA 217 1073) obtained by refinement in $P6_3$ that are close to the positions of $P6_3/m$, with 'independent' ith and jth atoms related by equation (2) and with Δz_{ij} less than 0·04 Å for Na(1) and Na(2) and 0·15 Å for each of two O-atom pairs. No remaining z coordinate differs from that expected in $P6_3/m$ by as much as the overall r.m.s. atomic amplitude of vibration. A combined time-of-flight neutron and X-ray study of $K_{0{\cdot}26}WO_3$ presented a refinement in $P6_3$ (Schultz, Horiuchi & Krause, 1986), following an earlier report (MRBUA 14 1397) based upon space group $P6_322$. The resulting 'independent' O(1A) and O(1B) atoms are related by $x_iy_iz_i = y_j, y_j - x_j, \frac{1}{2} - z_j + \Delta_{ij}$, with $\Delta x = 0{\cdot}15$, $\Delta y = 0{\cdot}07$, $\Delta z = 0{\cdot}03$ Å and an r.m.s. amplitude of 0·09 Å. Atoms W and O(2) are within 0·19 Å of the special positions in $P6_3/m$ at $x,y,\frac{1}{4}$ and $\frac{1}{2}00$ respectively, with r.m.s. amplitudes of 0·06 and 0·20 Å, and K is at $00z$, with $\Delta z = 0{\cdot}40$ Å and r.m.s. amplitude of about 0·25 Å. Superlattice reflections were neglected. Further structural study is needed to describe this material more definitively.

The final material in ICSD under $P6_3$ that may be centrosymmetric is the mineral panunzite $(Na_{0{\cdot}283}K_{0{\cdot}717})AlSiO_4$, a natural tetrakalsilite, related to nepheline and to $LiKSO_4$ (see above). The structural refinement (NJMMA 1985 322) resulted in the location of all cations either within 0·1 Å of $z = \frac{1}{4}$ or $\frac{3}{4}$ or else related in Si,Al pairs by $x_iy_iz_i = y_j, y_j - x_j, \bar{z}_j + 2\Delta_{ij}$ with Δz_{ij} less than 0·03 Å. Similar relationships hold for the O atoms, with all Δz less than 0·17 Å. The r.m.s. amplitudes for the cations are about 0·1 Å, those for the O atoms are about 0·15 Å; hence, in the absence of physical evidence demonstrating polarity, tetrakalsilite may be regarded as nonpolar at room temperature.

Nonferroelectric materials in space group $P6_3$

Numerous entries in ICSD for space group $P6_3$ are for inorganic structure determinations with atomic arrangements that cannot become ferroelectric under relatively small atomic displacements, including $Fe(IO_3)_3$ (JSSCB 17 1), PI_3 (INOCA 15 780), $Na_3Mo_9PO_{31}(H_2O)_{15{\cdot}25}$ (ACAPC 32 439), $BrSn[Co(CO)_4]_3$ (JORCA 52 293), $Ba_{13}Al_{22}Si_{10}O_{66}$ (ZEKGA 135 437), $Na_3H_6Mo_9PO_{34}(H_2O)_{12}$ (ACAPC 28 217), $Te(OH)_6Na_2HPO_4.H_2O$ (ACBCA 35 1444), $LiIO_3$ (JCPSA 78 7343) and isomorphous $Mg(IO_3)_2$ (APYSI 27 710), amesite $[Mg_2Si_2O_5(OH)_4]$ (ACCRA 9 487), $AlH_2(IO_3)_5.6H_2O$ (ZEKRD 159 231), $Ba(ClO_4)_2.3H_2O$ (ZEKGA 114 200), SiC-II (ZEKGA 61 515), $(Mg_2SiO_4)_2[Mg(OH)_2]_3$ (AMMIA 64 593), $Zn(H_3O)PO_4$ (DANKA 236 597), kambaldite $[Na_2Ni_8(CO_3)_6(OH)_6.6H_2O]$ (AMMIA 70 423) and $KAlGeO_4$ (KRISA 31 883).

Note added in proof: A recent private communication from Dr I. D. Williams reporting that $K_3Sb_5O_{14}$ does not generate second harmonics establishes with high probability the presence of inversion centers in this material. In consequence $K_3Sb_5O_{14}$ cannot be ferroelectric, as predicted (Abrahams, 1989) for the space group $Pba2$ assignment.

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The Incommensurate Misfit Layer Structure of $(PbS)_{1\cdot14}NbS_2$, '$PbNbS_3$' and $(LaS)_{1\cdot14}NbS_2$, '$LaNbS_3$': an X-ray Diffraction Study

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Abstract

Single-crystal X-ray data of the mixed layer compound $La_{32}Nb_{28}S_{88}$ reported by Meerschaut, Rabu & Rouxel [*J. Solid State Chem.* (1989), **78**, 35–45] in an orthorhombic supercell, $a = 23\cdot216$, $b = 5\cdot806$, $c = 23\cdot031$ Å, space group *Bbcb*, were analyzed in terms of a composite crystal $(LaS)_{1\cdot14}NbS_2$, consisting of an LaS part with $a = 5\cdot828\,(1)$ ($\simeq 23\cdot216/4$), $b = 5\cdot799\,(1)$, $c = 11\cdot512\,(2)$ ($\simeq 23\cdot031/2$) Å, $Z = 4$, and an NbS_2 part with $a' = 3\cdot310\,(1)$ ($\simeq 23\cdot216/7$), $b' = 5\cdot793\,(2)$, $c' = 23\cdot043\,(9)$ Å, $Z = 4$. Refinements, performed in space group *Cm*2*a* for the LaS part, and in *Fm*2*m* for the NbS_2 part, converged to $R_F = 0\cdot048$ and $0\cdot087$, respectively. The relative origin of the two structural units was found from the common reflections $0kl$. Reflections not belonging to the LaS or NbS_2 part are weak; they are satellites due to the mutual modulation of the sublattices. Single-crystal X-ray diffraction of $(PbS)_{1\cdot14}NbS_2$ showed the compound to be isostructural with $(LaS)_{1\cdot14}NbS_2$ disregarding the disorder of the NbS_2 sublattice in $(PbS)_{1\cdot14}NbS_2$. The two misfit layer compounds are built of alternate double layers of LaS (PbS) with La and Pb in distorted square-pyramidal coordination by sulfur (as La and Pb in a slab of half the cell edge of NaCl-type LaS and PbS) and sandwiches of NbS_2

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