

became lower and the deformation density decreased at the Pd nucleus and increased at the Cl nucleus. However, the charge asphericity due to the $4d$ electrons is not altered drastically. The change in deformation density based on (3) and (4) may be due to a tendency for $|F_o^a|$'s to be slightly larger than $|F_c^a|$'s for the high-order reflections, and to the different sign of $\Delta f^a(\text{Mo } K\alpha)$ for Pd and Cl atoms. The error in anomalous-dispersion correction along with the error in scale factor makes the deformation density in the vicinity of the nuclear position of heavy atoms unreliable.

The present study revealed that the very small valence/core electron ratio and large anomalous-dispersion effect of the heavy-metal atoms are not serious problems because the $4d$ electrons are distributed outside the high-density inner-core region and give sharp deformation density.

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Structurally Based Prediction of Ferroelectricity in Inorganic Materials with Point Group $6mm$

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Abstract

Ferroelectricity may be predicted in any pyroelectric crystal that has atomic displacements along the polar axis no greater than about 1 Å from the paraelectric position and in which the largest such displacement is greater than about 0.1 Å. The square of the largest atomic displacement associated with the atoms that form the strongest and least ionic bonds in the structure is proportional to the temperature at which the ferroelectric phase transforms to the paraelectric phase. A systematic approach to ferroelectric prediction, based on these structural principles, is now feasible with the availability of the Inorganic Crystal Structure Database (ICSD) in Karlsruhe. Ferroelectric crystals are generally important technologically more for their optoelectronic properties than for their reversible spontaneous polarization. Two new families of com-

pounds satisfy the structural criteria for ferroelectricity in space group $P6_3cm$ and six families satisfy them in $P6_3mc$; in addition, eight other compounds crystallizing in point group $6mm$ are possibly ferroelectric. Three other families and four additional compounds may be ferroelectric or alternatively may be centrosymmetric. A further thirteen compounds are unambiguously structurally nonpolar. No material reported by ICSD as crystallizing in either space group $P6mm$ or $P6cc$ is predicted to be ferroelectric.

Introduction

The study of relationships between the crystal structure of a material and its macroscopic properties is central to the field designated by *Acta Crystallographica* (Editorial, 1982) as structural science.

Among materials in which such relationships are strikingly evident are polar crystals with a spontaneous polarization that may be reversed in sense by the application of an electric field, *i.e.* ferroelectric crystals. The first ferroelectric crystal discovered was Rochelle salt (Valasek, 1921); the second was potassium dihydrogen phosphate (KDP), reported by Busch & Scherrer (1935); and the third (excluding other members of the KDP family) was BaTiO_3 (von Hippel, Breckenridge, de Bretteville, Brownlow, Chesley, Oster, Tisza & Westphal, 1944). The number of single-component ferroelectrics subsequently discovered increased at the nearly linear rate of about five annually, for a total of 150 in 1978 (Landolt-Börnstein, 1981). A much larger number of solid solutions of mixed ferroelectrics is known.

Polarization reversibility is generally not the property of greatest technological importance in most ferroelectrics but rather it is their associated optoelectronic properties that make them valuable. In the case of lithium niobate, for example, it has been estimated that total sales of this ferroelectric in the form of modulator, filter, switch and similar devices may reach the billion dollar level by the year 2000. However, the large current market for multilayer ceramic BaTiO_3 capacitors depends on the property of polarization reversal in the process of poling the ceramic. The discovery of new ferroelectrics in the past has depended largely on careful dielectric measurement made on numerous pyroelectric crystals selected by a variety of guidelines; see Jona & Shirane (1962). This procedure was more successful in discovering new members of existing families than new ferroelectric families.

Application of the structural basis for ferroelectricity (Abrahams & Keve, 1971) led to the successful prediction of this property in SrAlF_5 (Abrahams, Ravez, Simon & Chaminade, 1981) and in $\text{Pb}_3(\text{MF}_6)_2$ with $M = \text{Ti, V, Cr, Fe}$ and Ga (Abrahams, Ravez, Canouet, Grannec & Loiacono, 1984) on the basis of atomic coordinates previously determined respectively in SrAlF_5 and in $\text{Sr}_3(\text{FeF}_6)_2$ for unrelated reasons.

A systematic predictive approach, on the basis of published atomic coordinates for inorganic materials, became possible with the availability of the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983) as maintained on-line by STN International® (Scientific & Technical Information Network, Columbus, Ohio). The results of this approach for inorganic crystal structures determined in point group $6mm$ are presented below.

Optoelectronic properties of ferroelectric crystals

The principal electrooptic effects observed in polar crystals are the linear Pockels and the quadratic Kerr effects resulting from the application of external electric

fields (*cf.* Burfoot & Taylor, 1979). Nonlinear optical effects, with their numerous device applications, are also basically electrooptic in origin and depend upon a controlled variability in the refractive index. In the general case, nonlinear optical phenomena involve the mixing of two or more optical waves and arise from the use of very high intensity light sources such as may be obtained with lasers. High-frequency, large-amplitude, internal electric fields on the order of GV m^{-1} can develop within some dielectric media on illumination by an appropriate laser light source.

A particular nonlinear optical effect of considerable device value is the generation of second harmonics, in which the propagating high-intensity fundamental wave excites a driven polarization wave in the crystal at twice the fundamental frequency. This bound polarization wave radiates a free second-harmonic wave. Energy is converted from the fundamental to the free wave so long as the bound and free waves are in phase. Since the bound wave is locked to the fundamental wave at a velocity ω corresponding to the refractive index n_ω , and the free wave to a velocity 2ω corresponding to $n_{2\omega}$, then the intensity of the second harmonic is a maximum if $n_\omega = n_{2\omega}$. The required phase matching is usually accomplished by varying the optical birefringence, either by appropriate reorientation of the crystal or by changing its temperature. A d.c. electric field or mechanical stress has also been used to achieve exact phase matching. Other nonlinear optical effects include photochromism, photorefraction and photoluminescence (see also Lines & Glass, 1977).

Nonlinear optical effects have been widely used in the field of optical communications, as with optical signals that are switched by means of electrooptic waveguides fabricated in single crystals of ferroelectric LiNbO_3 . Light propagating in a waveguide produced by a titanium strip diffused into a single-crystal substrate, to increase the refractive index, is coupled into a neighboring waveguide by applying a small electric field thereby switching the light signal. Since field strength and switch length are inversely proportional to the electrooptic coefficients, materials with high coefficients are desirable. The enhanced phase-matching ability of ferroelectrics and their generally higher nonlinear dielectric susceptibilities, as compared with other piezoelectric crystals, has resulted in many of the most promising nonlinear optic materials being ferroelectric crystals.

Structural criteria for predicting ferroelectricity in point group $6mm$

A crystal structure determined in point group $6mm$ may be considered as potentially ferroelectric if no atom in the unit cell is displaced along the hexagonal direction by more than about 1 \AA from the location in which the resulting spontaneous polarization would be zero (*cf.*

Abrahams, 1979). Furthermore, the largest such atomic displacement must be greater than about 0.1 Å. Structure determinations in point group $6mm$ for which all atomic displacements from the paraelectric state (*i.e.* with zero spontaneous polarization) are found to be less than about 0.1 Å should be reexamined in point group $6/mmm$ or in other space groups since displacement magnitudes from higher symmetry positions that are comparable to or smaller than the r.m.s. thermal amplitudes may well be unstable.

Taking each atomic displacement from the published location at xyz to the paraelectric location at $x'y'z'$ as Δx , Δy , Δz , with the most likely paraelectric symmetry elements so positioned as to minimize these displacements, and considering only the Δz component (in Å) along the hexagonal axis, then the relationship derived by Abrahams, Kurtz & Jamieson (1968):

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

may be used to predict the phase-transition temperature T_c , where \mathcal{N} is a force constant, k is Boltzmann's constant and $\mathcal{N}/2k \approx 2.0 \times 10^4 \text{ K Å}^{-2}$. The largest value of Δz associated with the metal atom that forms the shortest and least ionic bonds in the structure is used in (1).

The predicted value of T_c in SrAlF_5 (Abrahams *et al.*, 1981) for example, as given by (1), was 685 K and the experimental value was subsequently determined as 695 K. In reviewing the range of ferroelectric–paraelectric phase-transition temperatures predicted in the following sections by use of (1), it may be noted that the lowest T_c must always exceed the diffraction measurement temperature leading to Δz and that, although an upper limit on T_c has not necessarily yet been reached, maximum values of T_c are most likely to exceed the well-established 1483 K measured for LiNbO_3 and even possibly the 1773 K reported for $\text{La}_2\text{Ti}_2\text{O}_7$ (Landolt–Börnstein, 1981).

The melting or decomposition temperature of most ferroelectric crystals is higher than the corresponding value of T_c although this is not a necessary condition. Furthermore, as T_c increases, the electric field required at room temperature to overcome the coercive field needed to reverse the polarization direction also increases. Very high fields may cause electrical breakdown in the crystal. The variation of Gibbs free energy with atomic displacement from the paraelectric state in a ferroelectric crystal at $T < T_c$ is considered to result in the formation of a pair of symmetrical minima, corresponding to displacements of opposite sense; see for example Lines & Glass (1977). These minima are separated by a potential barrier that is proportional in height to the coercive field. As T approaches T_c , the barrier decreases until either the two minima coalesce to form a single minimum centered at T_c or the local potential of critical atoms or ions in the crystal

(corresponding to kT per degree of freedom) exceeds the barrier at T_c .

It is emphasized that materials with published atomic coordinates in point group $6mm$ that satisfy the criteria above should be considered only as potentially ferroelectric until the property has been confirmed by experiment, since each specific prediction rests not only on the accuracy of the corresponding structural determination but also on the potential barrier associated with the largest atomic displacements required to achieve zero spontaneous polarization.

Systematic search for new ferroelectrics using the Karlsruhe ICSD database

The recent on-line availability of the Inorganic Crystal Structure Database (ICSD) at the Fachinformationszentrum in Karlsruhe, Federal Republic of Germany (see *Crystallographic Databases*, 1987) allows the atomic coordinates of nearly all but the most recent inorganic crystal structure determinations to be readily accessible to any investigator with a personal or equivalent computer. In its current release dated March 1987, ICSD contains over 26 000 entries of which 6047 are related to noncentrosymmetric space groups and 2703 to polar space groups. It should be noted that multiple entries may present different determinations of the same crystal structure but without cross reference and that not all entries are associated with a complete set of atomic coordinates. Occasionally, a structure determination in the literature has been found without a corresponding entry in ICSD, *e.g.* YMnO_3 , see below. Cross references among multiple determinations would improve future ICSD releases.

The following number of entries were found for the space groups in class $6mm$: $P6mm - 0$, $P6cc - 1$, $P6_3cm - 33$ and $P6_3mc - 189$. In the present study, the atomic coordinates of each entry were examined in light of the structural criteria outlined above. The original literature was consulted for materials that appeared to satisfy these criteria.

The level of confidence that may be placed in a structurally based prediction of ferroelectricity depends both on the quality of the structural determination and on the magnitude of the predicted atomic displacements. The level is highest if no atomic displacement in the unit cell is greater than about 0.5 Å and if the atomic displacement used in (1) is less than about 0.3 Å. The level decreases both with increasing displacement magnitudes and the possibility of error in the determination.

The atomic coordinates and unit-cell dimensions in ten families and two different compounds crystallizing in point group $6mm$ that satisfy the structural criteria for ferroelectricity, together with the corresponding Δz displacements required for each structure either to become paraelectric or to reverse the sense of the polar

axis and the predicted Curie temperature of the associated phase transition, are presented below unordered together with a brief discussion of each. Ten additional predictions are reviewed but without atomic coordinates.

Each of the remaining 64 space groups with nonzero pyroelectric coefficients will be considered in subsequent papers, mostly taken in order of decreasing symmetry.

Ferroelectrics predicted in space group $P6_3cm$

$YInO_3$ family

The atomic coordinates of $YInO_3$, determined by Pistorius & Kruger (1976), are reproduced in Table 1. The unit-cell dimensions at room temperature are $a = 6.260$ (5), $c = 12.249$ (9) Å. A total of 167 observed reflections [$I > 1.65\sigma(I)$] in a model with anisotropic temperature factors for Y and In and isotropic temperature factors for O gave a final $R = 0.028$. The atomic coordinates of all atoms in the predicted paraelectric phase are given by xyz' , except for O(1) and O(2).^{*} The former atom moves to $\bar{x}Oz'$ as it exchanges identity with O(2) [*i.e.* these two O atoms undergo a Δx as well as a Δz displacement; values along the hexagonal (polar) axis only need be considered here]. With all atomic displacements $\Delta z < 0.4$ Å, the spontaneous polarization in $YInO_3$ is structurally reversible with corresponding predicted $T_c = 810$ K. Pistorius & Kruger (1976) report that the $LnInO_3$ series, with $Ln = Eu$ to Ho , is isostructural with $YInO_3$.

The atomic coordinates of $YGaO_3$ (ACBCA 31 2770)[†] are similar to those in Table 1, with $\Delta z[Y(1)] = 0.251$ and $\Delta z[Y(2)] = 0.178$ Å. This crystal is hence also structurally ferroelectric, with predicted $T_c = 1260$ K.

$YInO_3$ and $YGaO_3$ are each isostructural with $YMnO_3$ (COREA 256 1958, ACCRA 16 957), for which characteristic ferroelectric hysteresis loops have been reported; hence the above predictions are made with high confidence.

$Ba_5(ReO_5)_3Cl$ family

The atomic coordinates for a material hitherto unconnected with possible ferroelectric behavior, $Ba_5(ReO_5)_3Cl$, reported by Besse, Baud, Levasseur & Chevalier (1979), are presented in Table 2 but with a

^{*} The coordinate value of each atom along the polar direction, in polar space groups, is always given with respect to an arbitrary choice of origin, whereas in the paraelectric phase (which may not necessarily be stable) the origin is determined by symmetry.

[†] Coden-type references are given throughout this paper for most structure determinations that are cited without providing 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, and hence provides five letters only in each Coden.

Table 1. Atomic coordinates ($\times 10^4$) of $YInO_3$ at room temperature and in predicted paraelectric phase, with polar displacements

	x	y	z	z'	Δz (Å)
Y(1)	0	0	2664 (8)	2500	-0.201
Y(2)	3333	6667	2352 (5)	2500	0.181
In	3340 (12)	0	0	0	0
O(1)	3090 (44)	0	1698 (21)*	-1697.5	0.001
O(2)	6321 (56)	0	3303 (29)*	-3302.5	0.001
O(3)	0	0	4861 (33)	5000	0.170
O(4)	3333	6667	320 (24)	0	0.392

^{*} $x, 0, z$ is replaced by $\bar{x}, 0, \frac{1}{2} + z$ as O(1) and O(2) exchange identity.

Table 2. Atomic coordinates ($\times 10^4$) of $Ba_5(ReO_5)_3Cl$ at room temperature and in predicted paraelectric phase, with polar displacements

	x	y	z*	z'	Δz (Å)
Re	3919 (1)	0	2745 (5)	2500	-0.191
Ba(1)	6667	3333	4870	5000	0.101
Ba(2)	2618 (2)	0	7255 (6)	7500	0.191
O(1)	2980 (40)	0	960 (60)	0	-0.748
O(2)	5770 (20)	1290 (20)	2460 (30)	2500	0.031
O(3)	3900 (30)	1320 (40)	4470 (40)	5000	0.413
Cl(1)	0	0	630 (60) [†]	665	0.027
Cl(2)	0	0	9300 (60) [†]	9335	0.027

^{*} The origin has been translated by 0.013 along the polar axis from that given by Besse *et al.* (1979).

[†] Site disordered with 50% occupancy by Cl atom assumed.

shift in origin. The unit-cell dimensions of this member of the apatite family, in which the tetrahedral PO_4 or similar ion is replaced by the pyramidal ReO_5 ion, are $a = 10.935$ (7), $c = 7.795$ (5) Å. The structure was refined on 730 observed reflections ($F_{\min} \geq F_{\max}/20$) by least squares to give $R = 0.068$, using a model with anisotropic temperature factors for all atoms except Cl. It was necessary to assume the Cl atom was equally distributed over two sites, with an isotropic temperature factor taken as 1.5 \AA^2 , in order to achieve normal refinement. The atomic coordinates reported by Besse *et al.* imply atomic displacements of 0.292 Å by the Re atom but only 0 and 0.090 Å by the nearly equally massive Ba atoms. An origin shift of 0.013 along the polar axis gives equal but opposite displacements by Re and Ba(2). All atoms in this structure are then within 0.75 Å or less of the paraelectric (zero spontaneous polarization) state; by contrast, most apatites crystallize in centrosymmetric space groups, usually closely related to $6/m$ (Young, 1988). This apatite hence satisfies the structural criteria for ferroelectric behavior, with predicted $T_c = 730$ K.

A series of six other closely related apatites has also been reported, in which the Cl atom is substituted by F, Br, CO_3 , NO_3 , O_2 or (I, OH) (ANCPA 1980 575, MRBUA 14 675, ANCPA 1980 575, MCHPD 8 119, MRBUA 15 1255, MRBUA 14 675 respectively). Each of these structures has coordinates similar to those in Table 2 after a comparable shift in origin, with

maximum Δz for Re and corresponding T_c respectively of 0.224 Å and 1000 K for the F apatite, 0.190 Å and 725 K for the Br; 0.210 Å and 880 K for the carbonate (the O atoms in the carbonate group were not located); 0.181 Å and 655 K for the nitrate; 0.209 Å and 875 K for the superoxide (one O atom in the superoxide group was not located); and 0.212 Å and 900 K for the iodide, hydroxide apatite. The Curie temperatures predicted for this group of polar apatites are relatively high, and it is not presently known if these materials remain stable at elevated temperatures. However, it may be noted that other ferroelectric materials such as BaMnF_4 (Landolt-Börnstein, 1982) remain ferroelectric until melting or decomposing.

RbVBr₃ family

A neutron powder diffraction study by Hauser, Falk, Fischer & Güdel (1985) reported a phase transition in RbVBr₃ at 98 K from $P6_3/mmc$ either to $P6_3cm$ or $P\bar{3}c1$. Point groups $6mm$ and $\bar{3}m$ are each subgroups of $6/mmm$, and Hauser *et al.* (1985) refined the structure at 33 K in the former to $R_f^{nucl} = 0.073$ and in the latter to $R_f^{nucl} = 0.079$. The atomic coordinates reported in $P6_3cm$ are listed in Table 3. An overall isotropic temperature factor was varied, which refined to $B = 0.61$ (9) Å². The unit-cell dimensions at 33 K are $a = 12.746$ (2), $c = 6.248$ (2) Å. If the coordinates in Table 3 are close to correct, then the atomic displacements of V(1) and V(2) correspond to $T_c = 590$ K in the low-temperature ferroelectric phase. However, the phase formed above 98 K is expected to be the paraelectric prototype in which case it may be concluded either that the low-temperature space group is not $P6_3cm$ or that the displacements Δz for the V(1) and V(2) atoms should be closer to about 0.07 Å, *i.e.* if $z[V(1)] = 0$, then $z[V(2)] = 0.022$ rather than 0.055 (2) as reported.

A neutron powder diffraction study by Zandbergen (1981) on RbVI₃ and RbTiI₃ resulted in similar indeterminacy between space groups $P6_3cm$ and $P\bar{3}c1$ for both compounds, even at room temperature. The V atomic displacements at 293 K in the polar space group correspond to $T_c = 2130$ K in RbVI₃ and 1700 K in RbTiI₃. Further experiment is necessary to resolve the structural uncertainties associated with this family.

UF₃ and LaF₃

Results of determinations in space group $P6_3cm$ of these isostructural trifluorides are given in the ICSD database. Later work on LaF₃, not contained in the present release, shows that LaF₃ crystallizes in $P\bar{3}c1$ (ASBSDK B41 88, ASBSDK B41 91). The neutron powder study on UF₃ at room temperature (BUFCA 90 304) gave a slightly better fit in $P6_3cm$ than in $P\bar{3}c1$: the resulting atomic displacement by U to the mean fluorine plane, if the polar space group is accepted, of

Table 3. Atomic coordinates ($\times 10^3$) of RbVBr₃ at 33 K in $P6_3cm$ and in $P6_3/mmc$ (z') at 293 K, with polar displacements

	<i>x</i>	<i>y</i>	<i>z</i>	<i>z'</i>	Δz (Å)
V(1)	0	0	-29*	0	0.172
V(2)	333	667	27 (2)	0	-0.172
Rb	329 (4)	329	230 (3)	250	0.125
Br(1)	164 (4)	0	222	250	0.172
Br(2)	503 (3)	163 (2)	277 (2)	250	-0.172

* All *z* coordinates are shifted 0.0275 from those of Hauser *et al.* (1985) in order to place the origin midway between V(1) and V(2).

Table 4. Atomic coordinates ($\times 10^4$) of Fe₂Mo₃O₈ at 298 K for positive and negative spontaneous polarization, with polar displacements

	<i>x</i>	<i>y</i>	<i>z</i>	<i>z'</i>	2 Δz	Δz (Å)
Fe(1)	3333	6667	9504 (2)*	-9880	-376	-0.189
Fe(2)	3333	6667	5120 (2)	-5496	-376	-0.189
Mo	1460.3 (4)	2920.6	2500	7500	0	0
O(1)	0	0	3923 (9)	-3514	409	0.206
O(2)	3333	6667	1486 (9)	-1077	409	0.206
O(3)	4872 (5)	9744	3645 (5)	-3648	-3	-0.002
O(4)	1665 (5)	3330	6352 (5)	-6355	-3	-0.002

* xyz in $P6_3mc$ is equivalent to $\bar{x}, \bar{y}, \frac{1}{2} + z$.

about 0.15 Å gives $T_c = 450$ K, a result that should be regarded provisionally with caution.

Ferroelectrics predicted in space group $P6_3mc$

Fe₂Mo₃O₈ family

The atomic coordinates of Fe₂Mo₃O₈, also known as the mineral kamiokite, have been independently determined and refined by three different groups; the most recent values (Kanazawa & Sasaki, 1986) are given in Table 4. With lattice constants of $a = 5.781$ (1), $c = 10.060$ (1) Å at 298 K, refinement with 656 independent reflections [$F_o > 3\sigma(F_o)$] based upon a model with anisotropic thermal parameters for all atoms gave $R = 0.027$. It may be seen from Table 4 that replacement of the xyz coordinates for each atom by xyz' fully reverses the sense of the polar axis. For Fe(1) and Fe(2), a value of $|z| = 0.0308$ or 0.5308 is midway between the two polarities: similarly, midway values for the atom pairs O(1), O(2) and O(3), O(4) give zero spontaneous polarization. The effective Δz is hence the displacement from the midpoint value to the 298 K *z* coordinate. The relatively small Δz values in Table 4 clearly satisfy the structural criteria for ferroelectricity, hence the Fe-atom displacement allows the prediction that $T_c = 710$ K. The earlier references are ACBCA 38 1265 and JOPQA 36 379.

Zn₂Mo₃O₈ is isostructural {ACCRA 21 482, JACSA 79 5410; the entry for the latter in ICSD gives $z[\text{Zn}(1)] = 0.625$ instead of 0.0625} with Fe₂Mo₃O₈. The displacement Δz for the Zn atoms is 0.200 Å, hence T_c is predicted to be 800 K.

$\text{Co}_2\text{Mo}_3\text{O}_8$ is also isostructural (JOPQA 36 379), with Δz for Co = 0.302 Å and T_c hence predicted to be 1820 K. It may be noted that one atomic coordinate e.s.d. is equivalent to 345 K, a wide uncertainty in the predicted phase-transition temperature.

The fourth family member determined is $\text{Mn}_2\text{Mo}_3\text{O}_8$ (JOPQA 36 379), with $\text{Mn}[\Delta z] = 0.154$ (50) Å, hence $T_c \approx 470$ K. Three additional family members, $\text{Mg}_2\text{Mo}_3\text{O}_8$, $\text{Ni}_2\text{Mo}_3\text{O}_8$ and $\text{Cd}_2\text{Mo}_3\text{O}_8$ have been identified (JACSA 79 5410) but not structurally determined.

K_2MnF_6 family

The atomic coordinates of K_2MnF_6 , reported by Bukovec & Hoppe (1983), are given in Table 5. The unit-cell dimensions at room temperature are $a = 5.719$ (1), $c = 9.330$ (3) Å. Refinement of a model with anisotropic thermal parameters for all atoms, with 348 symmetry-independent reflections in which $F_o > 2\sigma(F_o)$, resulted in $R = 0.030$. It is apparent from Table 5 that a z -coordinate displacement of 0.351 Å by both F ions exchanges their identity and reverses the given value of each coordinate. Similarly for K(1) and K(2), as the Mn atom undergoes a displacement of 0.203 Å. Such an exchange results in reversing the spontaneous polarization direction; the possibility of minor Δx and Δy displacements to retain normal interatomic distances does not affect the prediction of ferroelectricity, although the polarization reversal may be less energetic in one direction than in the other. The corresponding $T_c = 820$ K. An earlier determination was reported in ZAACA 269 165.

Additional potential members of the K_2MnF_6 family, based on reports of unit-cell dimensions, include K_2CrF_6 , K_2TiF_6 , K_2RuF_6 , K_2RhF_6 and K_2PdF_6 . All five hexafluorides are candidates for ferroelectric behavior, but see K_2GeF_6 , Rb_2MnF_6 and Rb_2GeF_6 below.

$\text{Li}_2\text{Cr}_2\text{AlSbO}_8$ family

The atomic coordinates of $\text{Li}_2\text{Cr}_2\text{AlSbO}_8$ at room temperature are given in Table 6, as reported by Tarte, Cahay, Preudhomme, Hervieu, Choynet & Raveau (1982), on the basis of a powder diffraction study. The unit-cell dimensions are $a = 5.796$ (2), $c = 9.466$ (5) Å. Refinement based on 47 independent reflections, with isotropic thermal parameters, gave $R = 0.039$. The origin along the polar axis was shifted by 0.015 to give equal displacements by the two Li ions. The Cr, Al site is two-thirds occupied by Cr and one-third by Al. The value of z' for Li(1) is derived from the z coordinate of Li(2) at the equivalent position $0, 0, \frac{1}{2} + z$. Similar derivations are used for the O-atom z' coordinates. The atomic displacement from z to $-z'$ is $2\Delta z$, as pairs of Li and O atoms exchange identity to give a structure of opposite spontaneous polarization. Examination of

Table 5. Atomic coordinates ($\times 10^4$) of K_2MnF_6 at room temperature for positive and negative spontaneous polarization, with polar displacements

	x	y	z	z'	$2\Delta z$	Δz (Å)
K(1)	0	0	6383 (2)	-6384*	-1	-0.001
K(2)	3333	6667	8616 (2)	-8617*	-1	-0.001
Mn	3333	6667	4782	5000	218	0.203
F(1)	1825 (3)	8175	3721 (3)	-4097*	-376	-0.351
F(2)	5206 (2)	4794	903 (3)	-1279*	-376	-0.351

* $00z$ and $0, 0, \frac{1}{2} + z$; $\frac{1}{3}, \frac{2}{3}, z$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z$; and more generally $\bar{x}\bar{x}z$ and $\bar{x}, x, \frac{1}{2} + z$ are symmetry equivalent pairs of coordinates.

Table 6. Atomic coordinates ($\times 10^4$) for $\text{Li}_2\text{Cr}_2\text{AlSbO}_8$ at room temperature for positive and negative spontaneous polarization, with polar displacements

	x	y	z^*	z'	Δz (Å)†
Li(1)	3333	6667	-1010 (100)	270	-0.350
Li(2)	0	0	5270 (160)	-6010	-0.350
Cr } Al }	1724 (8)	\bar{x}	2301 (8)	-2699	-0.188
Sb	3333	6667	5060 (2)	-4940	0.057
O(1)	0	0	3170 (50)	-3950	-0.369
O(2)	3333	6667	1050 (40)	-1830	-0.369
O(3)	4820 (10)	\bar{x}	3610 (40)	-3890	-0.133
O(4)	1650 (30)	\bar{x}	6110 (40)	-6390	0.133

* All z coordinates were varied by Tarte *et al.* (1982) and have had 0.015 added here, in an origin shift.

† $\Delta z = (z + z')/2$, with exchange of Li(1), Li(2); O(1), O(2); and O(3), O(4) see text.

Table 6 shows that all Δz displacements required to reverse the polarity are less than 0.37 Å, hence the structure is potentially ferroelectric, with $T_c = 710$ K.

At least four isotypic family members have been identified, three by Tarte *et al.* (1982). $\text{Li}_2\text{CrAl}_2\text{SbO}_8$ has $\Delta z(\text{Sb}) = 0.188$ Å for the origin chosen by the authors, with corresponding $T_c = 710$ K. $\text{Li}_2\text{Cr}_2\text{FeSbO}_8$ has $\Delta z(\text{Sb}) = 0.271$ Å for an origin midway between the z coordinates of the two Li atoms, giving $T_c = 1470$ K. $\text{Li}_2\text{Fe}_3\text{SbO}_8$ has $\Delta z(\text{Sb}, \text{Fe}) = 0.145$ Å and $T_c = 420$ K for similar choice of origin. The fourth member is LiFeSnO_4 (JSSCB 50 196). For the same choice of origin, $\Delta z(\text{Sn}) = 0.325$ Å and hence $T_c = 2100$ K. Transformation to the hexagonal structure from the ramsdellite-type structure at about 1300 K has been reported (JSSCB 40 344). However, the possibility of a phase transition to the paraelectric structure at higher temperatures does not appear to have been studied.

Three additional materials with composition $\text{Li}_{1.6}\text{Sn}_{2.8}\text{Zn}_{1.6}\text{O}_8$, $\text{Li}_{1.6}\text{Sn}_{2.8}\text{Mg}_{1.6}\text{O}_8$, and $\text{Li}_{1.6}\text{Zn}_{1.6}\text{Ti}_{0.7}\text{Sn}_{2.1}\text{O}_8$ may also be members of the $\text{Li}_2\text{Cr}_2\text{AlSbO}_8$ family. These compounds were similarly studied (MRBUA 14 1381) by powder diffraction, using Cu $K\alpha$ radiation and fitting about 66 powder lines, some of which were overlapped. It is possible that some Zn or Mg was misidentified as Li, in which case the materials are isotypic with $\text{Li}_2\text{Cr}_2\text{AlSbO}_8$. In $\text{Li}_{1.6}\text{Sn}_{2.8}\text{Zn}_{1.6}\text{O}_8$,

$\Delta z(\text{Sn}) = 0.168 \text{ \AA}$ for $T_c = 560 \text{ K}$. In $\text{Li}_{1.6}\text{Sn}_{2.8}\text{Mg}_{1.6}\text{O}_8$, $\Delta z(\text{Sn}) = 0.236 \text{ \AA}$ for $T_c = 1110 \text{ K}$ and in $\text{Li}_{1.6}\text{Zn}_{1.6}\text{Ti}_{0.7}\text{Sn}_{2.1}\text{O}_8$, $\Delta z = 0.285 \text{ \AA}$ for $T_c = 1620 \text{ K}$. Single-crystal structural investigations of these three materials, also dielectric and other studies, may appropriately be made.

CsCuCl₃ family

The atomic coordinates of $\alpha\text{-CsCuCl}_3$ at 423 K, determined by Kroese, Maaskant & Verschoor (1974), are given in Table 7. A transition from the β - to α -phase at 293 K has been reported (SSCOA4 9 1707). The unit-cell parameters at 466 K are $a = 7.245 (7)$, $c = 6.150 (6) \text{ \AA}$. Refinement with 185 observed symmetry-independent reflections [$I > 2\sigma(I)$], based upon a model with anisotropic thermal parameters for all three atoms, gave $R = 0.041$ and $wR = 0.069$. Corresponding z coordinates in $P6_3/mmc$, the hypothetical paraelectric phase, are given as z' in Table 7. The atomic displacement Δz for Cl would become identical to that for Cs if the former were taken as the origin at $z = \frac{1}{4}$. This value of $\Delta z = 0.185 \text{ \AA}$ corresponds to $T_c = 680 \text{ K}$. It should be noted that the experimental coordinates in Table 7 are not significantly different from the paraelectric coordinates, although the corresponding indicators for the centrosymmetric space group rise to $R = 0.059$, $wR = 0.101$. Kroese *et al.* (1974) recognized that the α -phase should be ferroelectric, but found no conclusive evidence either for polarity or for nonpolarity in $\alpha\text{-CsCuCl}_3$.

The atomic coordinates in CsCrCl_3 are similar to those in Table 7 (JCPA 57 3771), with $\Delta z(\text{max.}) = 0.169 \text{ \AA}$ at room temperature and hence $T_c = 570 \text{ K}$. CsCrBr_3 (ACBCA 29 1529) and CsCrI_3 (ACBCA 35 1554) have also been reported isotypic with $\alpha\text{-CsCuCl}_3$, with $\Delta z(\text{max.}) = 0.140 \text{ \AA}$ and $T_c = 390 \text{ K}$ for the former and $\Delta z(\text{max.}) = 0.063 \text{ \AA}$ and resulting $T_c = 80 \text{ K}$ for the latter. The small atomic displacement and resulting T_c for CsCrI_3 are inconsistent with ferroelectricity at room temperature and further investigation of this material would be appropriate.

LiClO₄·3H₂O

The nuclear coordinates of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ at 294 K, determined by Lundgren, Liminga & Tellgren (1982) using neutron diffraction, are given in Table 8. Previous determinations by X-ray and neutron diffraction (ACBCA 33 3954, ACBCA 31 1735, KRISA 13 261, ZEKGA 88 198) are in good agreement. Refinement with 1284 unaveraged F^2 terms [$I > 3\sigma(I)$] gave $R(F^2) = 0.048$. The unit-cell parameters at 294 K are $a = 7.7192 (4)$, $c = 5.4531 (5) \text{ \AA}$. The origin for the z coordinates in Table 8 was shifted to place Li at $z = 0$; the z' coordinates correspond to the hypothetical paraelectric phase in which, for each atom at xyz' , there is an identical atom at $\bar{x}\bar{y}z'$. The maximum Δz of

Table 7. Atomic coordinates ($\times 10^3$) of $\alpha\text{-CsCuCl}_3$ at 423 K and of hypothetical paraelectric phase, with polar displacements

	x	y	z	z'^*	$\Delta z (\text{\AA})$
Cs	333	667	750	750	0
Cu	0	0	15 (6)	0	0.092
Cl	152 (3)	304 (6)	280 (15)	250	0.185

* Coordinates for space group $P6_3/mmc$.

Table 8. Atomic coordinates ($\times 10^5$) of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ at 294 K and of hypothetical paraelectric phase, with polar displacements

	x	y	z^*	z'	$\Delta z (\text{\AA})$
Li	0	0	0 (60)	0	0
Cl	66667	33333	22329	25000	0.146
O(1)	66667	33333	-3861 (19)	0	0.211
O(2)	56534 (4)	43466 (4)	31231 (16)	25000	-0.340
O(w)	-12232 (4)	12232 (4)	75116 (14)	75000	-0.006
H	-6662 (14)	26326 (12)	75711 (23)	75000	-0.039

* The origin along c in this neutron determination is shifted by $+0.22329$; see also footnote to Table 5.

0.340 \AA is comparable with the reported r.m.s. atomic amplitudes of thermal motion. Assuming the Cl-atom displacement is critical in evaluating (1), then $\Delta z = 0.146 \text{ \AA}$ and the corresponding $T_c = 430 \text{ K}$. The trihydrate is found to deliquesce at 368 K, with no evidence for a phase transition at lower temperatures (Abrahams, Gallagher & Liminga, 1988); hence the predicted transition temperature is unattainable. Dielectric studies at room temperature would be appropriate. It may be noted that the height of the potential barrier to be overcome on inversion of the ClO_4^- ion in course of polarization reversal has not been estimated; a sufficiently high barrier may cause the associated coercive field to approach or even exceed the dielectric breakdown strength of the crystal.

The structures of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ have been determined in $P6_3mc$ (MRBUA 14 1381), although the space group in untwinned crystals may be $Pmn2_1$. The supergroup atomic coordinates differ from those in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ by no more than about 0.15 \AA . Since $\Delta z \approx 0$ for Zn, Fe and Cl, T_c cannot be estimated for either structure.

K₆MgO₄ family

The atomic coordinates for K_6MgO_4 at room temperature, reported by Darriet, Devalette, Rouleau & Avallet (1974) are given in Table 9. The unit-cell dimensions are $a = 8.478 (5)$, $c = 6.585 (3) \text{ \AA}$. A total of 643 independent reflections, with $I_m > 1.5\sigma(I_m)$, was used to refine a model with isotropic thermal parameters and gave $R = 0.047$. The Mg atom occupies a nearly regular tetrahedron of O atoms, with $\text{Mg}-\text{O} = 2.02 \text{ \AA}$. Displacements along the polar axis of Δz for each atom as given in Table 9 create inversion centers

Table 9. Atomic coordinates ($\times 10^4$) of K_6MgO_4 at room temperature and of hypothetical paraelectric phase, with polar displacements

	x	y	z	z'	Δz (Å)
K(1)	1439 (1)	\bar{x}	0	0	0
K(2)	4648 (1)	\bar{x}	3216 (2)	2500	-0.471
Mg	6667	3333	2154 (4)	2500	0.228
O(1)	2022 (4)	\bar{x}	6158 (4)	5000	0.763
O(2)	6667	3333	5182 (9)	5000	0.120

corresponding to $P6_3/mmc$. The displacements by K(2) and O(1) are substantial but possible and would result in corresponding Δx displacements as the bonding is reorganized. In this event, $T_c = 1040$ K.

The atomic coordinates of Na_6ZnO_4 (ZAACA 409 69), on reversing the polar axis and rearrangement, are similar to those in Table 9 with $\Delta z(\text{Zn}) = 0.211$ Å and hence $T_c = 890$ K.

$Ti_{2.45}S_4$

The atomic coordinates for nonstoichiometric $Ti_{2.45}S_4$ at room temperature, as given in Table 10, were based upon 297 diffractometer data and refined by Norrby & Franzen (1970) with isotropic thermal parameters to give $R = 0.026$. Unit-cell dimensions are $a = 3.4198$ (4), $c = 11.444$ (2) Å. The occupancy of the Ti(2) site is reported to be 0.2273 (43). The only atom in this structure making an appreciable contribution to the polarization is Ti(2), and a displacement of 0.177 Å reduces this polarization to zero. The corresponding $T_c = 630$ K. $Zr_{2.46}Se_4$ is however isostructural but, as reported in RTCPA 87 1339, is close to a centrosymmetric atomic arrangement. Reinvestigation of both structures would be appropriate. A powerful test for the lack of inversion centers in this or other structures is the detection of second-harmonic generation by the material.

Al_5C_3N and $Al_7C_3N_3$

The atomic coordinates of Al_5C_3N at room temperature, determined by Jeffrey & Wu (1966), are given in Table 11. The unit-cell dimensions are $a = 3.281$, $c = 21.67$ Å (e.s.d.'s not stated). A total of 198 independent visually estimated structure factors led to $R = 0.13$ in refinement of a model with isotropic thermal parameters. Four of the five Al atoms and C(1) are centrosymmetrically arranged at room temperature. The displacements of the remaining atoms, see Table 11, fully satisfy the structural criteria for ferroelectricity, although it is noted that the structure with reversed spontaneous polarization has N and C(3) interchanged. The resulting configurational energy in this case will be slightly different from that with the original polarity, unless these two atom sites are randomly occupied. The atomic displacement $\Delta z[\text{Al}(3)] = 0.238$ Å and corresponds to $T_c = 1140$ K.

Table 10. Atomic coordinates ($\times 10^5$) for $Ti_{2.45}S_4$ at room temperature for positive and negative spontaneous polarization, with polar displacements

	x	y	z	z'	Δz (Å)
Ti(1)	33333	66667	75000	75000	0
Ti(2)	33333	66667	1551 (18)	-1551	0.177
S(1)	33333	66667	37711 (7)	37539*	0.010
S(2)	0	0	12461 (9)	12289*	0.010

*The z' coordinate of S(1) is given by $-(\frac{1}{2}+z)$ for S(2) and vice-versa.

Table 11. Atomic coordinates ($\times 10^3$) for Al_5C_3N at room temperature for positive and negative spontaneous polarization, with polar displacements

	x	y	z	z'	Δz (Å)*
Al(1)	333	667	45 (1)	-45	0
Al(2)	0	0	155 (1)	-155	0
Al(3)	333	667	261 (1)	-239	0.238
Al(4)	0	0	345 (1)	-345	0
Al(5)	333	667	455 (1)	-455	0
N	333	667	137 (2)	-133	0.087
C(1)	0	0	0	0	0
C(2)	0	0	248 (2)	-252	-0.043
C(3)	333	667	367 (2)	-363	0.087

* $\Delta z = (z + z')/2$, with exchange of Al(1), Al(5); Al(2), Al(4); and N, C(3), see text.

The homologous carbonitride $Al_7C_3N_3$ was similarly determined by Jeffrey & Wu (1966) with 318 photographically estimated F_m to give $R = 0.15$. Interchange of atoms Al(1) and Al(7), Al(2) and Al(6), Al(3) and Al(5), N(1) and N(3) also N(2) and C(3) results in a set of atomic displacements required to reverse the polarization sense that has no $\Delta z > 0.17$ Å except for Al(4), for which $\Delta z = 0.36$ (2) Å. The corresponding T_c is 2600(300) K.

β - KYb_3F_{10} family

The atomic coordinates of β - KYb_3F_{10} at room temperature, determined by Aléonard, Guitel, Le Fur & Roux (1976), are presented in Table 12. The unit-cell dimensions are $a = 8.067$ (2), $c = 13.203$ (4) Å. The structure was refined using 789 independent F_o , measured with $\lambda(\text{Ag } K\alpha)$, in a model with anisotropic thermal parameters and gave $R = 0.032$. It is seen from Table 12 that the largest atomic displacement by the metal atoms is $\Delta z[\text{Yb}(2)] = 0.132$ Å. However, several F atoms are required to undergo large displacements in order to form the hypothetical paraelectric phase. Such amplitudes, while possible, are not expected in a phase transition with $T_c = 350$ K as given by the Yb(2) displacement. It is noted that a test for piezoelectricity in β - KYb_3F_{10} was negative (MRBUA 10 1185), hence if the crystals are polar and also ferroelectric it is likely that they were electrically twinned, leading to parameter interactions in the structural solution.

RbEr_3F_{10} and $\text{NH}_4\text{Er}_3F_{10}$ are reported to be isotypic with β - KYb_3F_{10} (MRBUA 10 1185, JSTCA 17 147).

Table 12. Atomic coordinates ($\times 10^4$) for β -KYb₃F₁₀ at room temperature and of hypothetical paraelectric phase, with polar displacements

	<i>x</i>	<i>y</i>	<i>z</i>	<i>z'</i>	Δz (Å)
Yb(1)	5057.7 (3)	\bar{x}	0*	0	0
Yb(2)	1737.5 (3)	\bar{x}	2600.2 (5)	2500	-0.132
K(1)	0	0	-9 (15)	0	0.012
K(2)	3333	6667	7509 (7)	7500	-0.012
F(1)	3334.3 (6.7)	3362 (7)	1233 (5)	0	-1.628
F(2)	2220 (6)	\bar{x}	9647 (6)	0	0.466
F(3)	1840 (6)	\bar{x}	4359 (8)	5000	0.846
F(4)	1102 (7)	\bar{x}	7939 (6)	7500	-0.580
F(5)	3333	6667	2159 (10)	2500	0.450
F(6)	3333	6667	5461 (12)	5000	-0.609
F(7)	4833 (6)	\bar{x}	3253 (8)	2500	-0.994

* Origin taken at $z[\text{Yb}(1)] = 0$; the authors placed this coordinate at 0.01171.

Pr₈Ga₃Co family

The structure of this ternary alloy was determined on the basis of 211 independent reflections [$I \geq 1.96\sigma(I)$] and refined with anisotropic thermal parameters to give $R = 0.067$ (KRISA 29 708). The four independent Pr, the Ga and the Co atoms are each displaced less than about 0.30 Å from the corresponding paraelectric positions (the origin is shifted along the polar axis by 0.02 in this calculation). The resulting $T_c = 1800$ K. Many rare-earth metals may be substituted for Pr, forming isotopic structures.

Nd(BrO₃)₃·9H₂O family

This early structure determination (JACSA 61 1544) placed all seven independent atoms, excluding H, within one standard deviation of the corresponding position in space group $P6_3/mcm$. Since the crystal was shown to be pyroelectric, however, it is possible that the actual displacements are larger than reported and may satisfy the structural criteria for ferroelectricity. Further investigation is appropriate in order to clarify the structural details and predict the possible phase-transition temperature. Other rare earths are expected to substitute isostructurally for Nd.

BaNiO₃

X-ray powder data led to atomic coordinates and a value of $R = 0.084$, with $\Delta z(\text{Ni}) = 0.132$ Å, $\Delta z(\text{O}) = 0.120$ Å and zero displacement for Ba (JSSCB 3 349). The resulting prediction of $T_c = 350$ K should be regarded with caution. A single-crystal redetermination or other experimental investigation would be appropriate.

KAlSiO₄

Manually collected diffractometer data (228 independent reflections) show the crystal to be disordered [the O(1) atom is distributed over two mirror-related

equivalent sites]. Refinement gave $R = 0.098$ (AMMIA 62 336). Displacement of the Si and Al atoms along the polar axis by about 0.02 Å and displacement of the two independent O atoms by about 0.07 Å would give a paraelectric structure if the dipoles associated with the SiO₄ and AlO₄ tetrahedra were equivalent. Further investigation of this structure would be appropriate.

K₅Nb₃O₃F₁₄·H₂O

The atomic coordinates of K₅Nb₃O₃F₁₄·H₂O (KOKHD 2 554) at room temperature satisfy the structural criteria for ferroelectricity. An origin shift of 0.0065 along the *c* axis gives $\Delta z[\text{Nb}(1)] = \Delta z[\text{Nb}(2)] = 0.224$ Å. All other atomic displacements are less than 0.19 Å, except for O, F(8) at 0.665 Å, O(11) at 0.539 Å and O, F(6) at 0.310 Å. The corresponding value of $T_c = 1000$ K. It is unlikely that this hydrate remains stable much above 375 K, hence the prediction may best be tested dielectrically.

4H-GaSe polytype

All atomic coordinates in this polytype are either of the form 0,0,*z* and 0,0,2*Δz*-*z* for half the Ga and Se atoms or $\frac{1}{3},\frac{2}{3},z$ and $\frac{1}{3},\frac{2}{3},2\Delta z-z$ for the remaining half (ACBCA 31 2841). A displacement of Δz by each atom would result in a centrosymmetric structure, space group $P6/mmm$. The largest individual Δz is 0.088 Å for Se(3) and Se(4). With r.m.s. thermal displacements of $\bar{u}[\text{Se}(3)] = 0.10$ and $\bar{u}[\text{Se}(4)] = 0.15$ Å, reinvestigation of this structure in the higher symmetry space group would be appropriate.

(Al₂O₃)₅·H₂O

One Al and all O atoms in this structure (BCSJA 42 2247) are close either to 000; $\frac{1}{3},\frac{2}{3},0$; $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $x,\bar{x},0$; or $x,\bar{x},\frac{1}{4}$; the remaining two independent Al atoms have *z* coordinates related by $z_1 \approx \frac{1}{2} - z_2$, following an origin shift of 0.012 along the polar axis. The largest atomic displacement by an Al atom required in order to transform the structure to the hypothetical paraelectric phase is about 0.43 Å. Although this displacement is feasible, the resulting T_c is unusually high at 3700 K. The hydrate is expected to lose water above 375 K, but a dielectric investigation would be appropriate.

TaSe₂

Structure determination based on 14 powder lines recorded with Cu *Kα* radiation led to a final value of $R(I) = 0.157$, with atomic positions no further than 0.19 Å from the paraelectric structure (JCOMA 17 111) in which, for each atom at $x_1y_1z_1$ another is present at $x_1y_1z_2$ with $z_1 + \frac{1}{2} = z_2 + \Delta z$. The largest Δz displacements, for Se(2) and Se(3), correspond to $T_c = 730$ K. However, the accuracy of the determination is low and it would be appropriate to reinvestigate this structure.

$Ba_3CuSb_2O_9$

A total of 390 independent reflections measured on $Ba_3CuSb_2O_9$ at room temperature led to a structure which refined, with anisotropic thermal parameters, to give $R = 0.03$ (ZAACA 442 280). All metal atoms are within 0.09 \AA of the paraelectric structure if the Cu atom and Sb(2) randomly occupy their assigned O-atom octahedra as Ba(2) and Ba(3) exchange identity on reversing the spontaneous polarization. The Cu—O and Sb(2)—O distances are not significantly different at about 2.06 \AA . The largest atomic displacement required for the structure to become paraelectric is 0.13 \AA by O(1) and O(3) as these atoms exchange identity. However, the corresponding T_c is only 160 K, hence reinvestigation of the structure in space group $P6_3/mmc$ would be appropriate.

Nonpolar atomic arrangements assigned to space group $P6_3cm$

A number of structural investigations carried out in space group $P6_3cm$ result in atomic arrangements that are nonpolar and that should hence be reexamined in a centrosymmetric space group, investigated for possible second-harmonic generation, or both. A typical determination is $BaTiS_3$ (ACCRA 16 135) at 973 K with atomic coordinates: Ba in $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$; Ti in $0, 0, \frac{1}{2}$; and S in $\frac{1}{6}, \frac{5}{6}, \frac{1}{4}$ based on 31 powder lines which gave $R = 0.11$. The symmetry-equivalent coordinates in $P6_3cm$ are Ba in $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$; Ti in 000; and S in $\frac{5}{6}, \frac{1}{6}, \frac{3}{4}$, resulting in a centrosymmetric arrangement. Additional examples are NH_4FeCl_3 (ISJCA 8 737), $Nb_{0.92}S$ (JCOMA 19 421), $BaMnO_3$ (ACCRA 15 179), PbI_2 (ZEKGA 111 372), $CrSe$ (JPCSA 3 238), PtO_2 (ADCSA 98 39), $LiGaGe$ (ZENBA 25 1305), K_2GeF_6 (ZAACA 269 173), Rb_2MnF_6 and Rb_2GeF_6 (ZAACA 269 165), $LiI(H_2O)_3$ (ZEKGA 88 198), and $CuBr$ (ELCAA 22 701).

Inorganic materials in space groups $P6mm$ and $P6cc$

The latest release of ICSD at the present time contains no entries under space group $P6mm$ and only one entry under space group $P6cc$. The latter is $KMn_2Zn_3Si_{12}O_{30}$ (KRISA 16 721) and it does not satisfy the structural criteria for ferroelectricity.

New ferroelectric crystals predicted in point group $6mm$

The approach adopted in the present study has identified eight new families of compounds and enlarged a ninth. These families together contain over 30 different new candidate structures that, with seven further new materials not associated with family groups, are

predicted to be ferroelectric. In addition, three other families containing over 10 different members together with four more individual materials may also be ferroelectric. The only materials crystallizing in point group $6mm$ listed as ferroelectric by Landolt-Börnstein (1981) belong to the $YMnO_3$ family, which is isomorphous with the $YInO_3$ family. It is anticipated that the total number of known pure ferroelectrics will be considerably increased once the predictions made in this study and in those to follow have been experimentally confirmed.

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A Model for Vitamin B₆–Amino-Acid-Related Metal Complexes. Neutron Diffraction Study of Aqua(*N*-salicylidene-glycinato)copper(II) Hemihydrate at 130 K*

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Abstract

A neutron diffraction study of aqua(*N*-salicylidene-glycinato)copper(II) hemihydrate, [Cu(C₉H₇NO₃)(H₂O)]·0.5H₂O, *M_r* = 267.7, a model for vitamin B₆–amino-acid-related metal complexes, has been carried out at 130 K. Least-squares refinement based on 3800 reflections [(sinθ/λ)_{max} = 0.786 Å⁻¹] converged at *R*(*F*²) = 4.5%. The crystal is monoclinic, space group *C2/c*, *Z* = 8 with cell parameters at 130 K: *a* = 17.030 (3), *b* = 6.665 (1), *c* = 17.469 (5) Å, β = 111.13 (1)°, *V* = 1849.50 Å³. The bond distances between non-H atoms have been determined with estimated standard deviations in the range 0.0008–0.0012 Å; the corresponding values for distances involving H atoms are 0.0017–0.0020 Å. The presence of a Cu^{II} ion does not significantly change the bond distances around the α-C atom from those observed in glycine or glycyglycine. There are, however, indications of differences in distance and direction relative to the π system for the two α-C–H bonds. These bond vectors are inclined at angles of 30 and 71° to the plane of the conjugated π system. A planar conjugated π-system is stabilized by chelation to the Cu ion.

Introduction

Pyridoxal [vitamin B₆, formula (1)] amino-acid Schiff bases are key intermediates in the metabolic reactions

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of amino acids catalyzed by enzymes, which require pyridoxal phosphate as a cofactor. These reactions are transamination, decarboxylation, α-, β-elimination, racemization, etc. (Guirard & Snell, 1964). Many of these reactions are related to non-enzymatic model reactions in which pyridoxal is the catalyst and a metal ion replaces the apoenzymatic protein (Braunstein & Shemyakin, 1953; Metzler, Ikawa & Snell, 1954; Longenecker & Snell, 1957; Dunathan, 1971; Holm, 1973). Formula (2) gives one of the important forms of these Schiff bases. When a metal ion is present, it replaces the hydroxyl proton (4), and the structure is stabilized by bonding to the N atom and to the carboxylate and phenolate O atoms. The three donor atoms are locked in, resulting in a planar conformation of the tridentate ligand. A strong electron-withdrawal effect on the C atoms adjacent to the azomethine N is proposed. The planar conformation facilitates the electron transfer through the conjugation of the pyridine ring and the azomethine group with the amino-acid side chain (Martell, 1982). The result is a labilization of one of the three bonds *a*, *b*, *c* on the α-C atom of the amino-acid moiety, preparing it for the catalytic reaction. Catalytic activities are also observed with derivatives of salicylaldehyde, (3) (Ikawa & Snell, 1954; Eichhorn & Marchand, 1956; Ando & Emoto, 1969, 1975), although they are not effective transamination substrates (Wroblewski & Long, 1977). The key question is: What is the mechanism of activation of the amino-acid pyridoxal metal intermediate complexes? Inductive effects leading to bond weakening at the α-C atom of the amino-acid moiety as the main driving force for reactions have been discussed by Perault, Pullman & Valdemoro (1961), who calculated the energy changes associated with the different transition states of the Schiff bases. They considered the variations of resonance energy associated with the formation of the transitional Schiff bases and the