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Inorganic structures in space group *P*31*m*; coordinate analysis and systematic prediction of new ferroelectrics

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The 62 entries listed in ICSD release 2009/1 under polar space group *P*31*m* correspond to 31 families of inorganic crystal structures, some with only one member. Coordinate analysis reveals, over a wide confidence range, 11 of these families as ferroelectric candidates. One includes the well known improper ferroelectric GASH (guanidinium aluminum sulfate hexahydrate), $[(C(NH_2)_3)Al(SO_4)_2(H_2O)_6]$, another the previously predicted ferroelectric $CsNO_3$ phase II. Those remaining include $K_3Nb_3B_2O_{12}$, the minerals schairerite, galeite and lizardite 1*T*, $LaNi_5D_6$ and γ-$CaNi_5D_{6.1}$, $Ca(OCl)_2$-$Ca(OH)_2$, $[N(CH_3)_4]_2Mo_3S_{13}$, $Li_{17}Ag_3Sn_6$ and $Cs_3As_5O_9$. Candidate selection is based upon detecting an approach by the reported atomic arrangement to the symmetry of a corresponding nonpolar supergroup. A further 13 families are typified by their reduced predictive properties, with four others likely to remain polar at higher temperatures and the remaining three noted as having a unit cell larger than reported or a misassigned space group. The primary sources of uncertainty in structurally based predictions of ferroelectricity are the reliability of the underlying structural determination and the upper limit assigned to the cationic displacement magnitudes required to achieve supergroup symmetry.

1. Introduction

1.1. Ferroelectric phase transitions

A thermal or pressure change that eliminates the polar axis of a pyroelectric crystal necessarily results in a ferroelectric phase transition. The 2009/1 release of the Inorganic Crystal Structure Database (ICSD, FIZ Karlsruhe/ILL, 2009) contains 105 322 nonpolar *versus* 15 472 polar entries, many determined under ambient conditions; a material listed in both classes is potentially indicative of a ferroelectric phase transition. Such a crystal, below the transition temperature, is capable in principle of forming two stable orientational states switchable from one to the other by the application of an appropriate electric field. The total number of such materials listed by ICSD now likely exceeds the 2242 phase transitions presented by Tomaszewski (1992). It is notable that relatively few phase transitions have been studied through the structural change from polar to centrosymmetric; all relevent studies of such transitions report major cationic displacements less than ~ 0.25 Å along the polar, ~ 0.5 Å along a general direction. Further structural studies of such high-temperature phase transitions would allow a closer definition of these upper displacement limits.[1]

[1] The highest phase-transition temperatures from ferroelectric to nonpolar presently reported are ~ 1773 K for $La_2Ti_2O_7$ (Nanamatsu *et al.*, 1974) and ~ 1615 K for $Sr_2Nb_2O_7$ (Nanamatsu *et al.*, 1972), *cf.* equation (1).

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The present series of systematic studies, seeking to examine all known polar inorganic crystal structures for indications of possible ferroelectricity, began with those listed in the highest symmetry polar space group, *viz.* $P6_3cm$ (Abrahams, 1988), followed by those studied in space groups of successively lower symmetry. Examination of the structures reported in the space group $P31m$, directly after that for structures with space group $P3m1$ (Abrahams, 2008), departs from the standard *International Tables for Crystallography* sequence to allow a ready contrast between the structural characteristics of materials in space groups exhibiting an apparently minor symmetry change. In the present case, the fivefold decrease in number of ICSD entries from 328 in space group $P3m1$, to 62 in the space group $P31m$, is notable.

1.2. Prior and present results for point group 3

A total of 21 single-member inorganic structural families with the space group $P3$ have been shown to satisfy the structural criteria for ferroelectricity, with 16 families identified in space groups $P3_1$ or $P3_2$, of which five contain two members, 29 families in the space group $R3$, of which two include two members, and 12 in space group $P3m1$, of which four families contain a total of 13 members (Abrahams, 2000, 2003, 2006, 2007, 2008); the structures in space groups $P31c$, $P3c1$, $R3m$ and $R3c$ within the trigonal system remain unexamined. The coordinate analysis reported below for the entries in space group $P31m$ reveals 32 families of which 11 are ferroelectric candidates; one is GASH (guanidinium aluminum sulfate hexahydrate), $[(C(NH_2)_3)Al(SO_4)_2(H_2O)_6]$, a known ferroelectric since 1956, another is $CsNO_3$ phase II predicted in 2003 to be ferroelectric. Only one family contains two members *viz.* $LaNi_5D_6$ and γ-$CaNi_5D_{6.1}$, with none presently containing more.

1.3. Contrasting structural characteristics in space groups $P3m1$ and $P31m$

A total of 163 CdI_2, 69 ZnS and 10 SiC structures, among the 311 entries reported under space group $P3m1$ in ICSD Release 2007/1, are polytypes.[2] By contrast, not a single polytype appears among the 62 entries listed under symmorphic space group $P31m$ in the 2009/1 release of ICSD, in accordance with Iglesias' (2006) sapient observation that polytype formation is restricted to the space group $P3m1$ and its supergroups by the required presence of mirror planes normal to the central bond. The paucity of minerals reported with $P3m1$ symmetry provides further contrast with the eight mineral families exhibiting $P31m$ symmetry,[3] as does the number of repeated structural investigations which also differ strongly. A total of 13 separate determinations of lizardite $1T$, seven of $LaNi_5D_6$ and seven of cronstedtite, all with $P31m$ symmetry at ambient conditions, together account for $\sim 43\%$ of all inorganic structural studies reported for this space group. By contrast, no structure with $P3m1$ symmetry has been reported more than twice.

1.4. $P31m$ space group–supergroup relationships

A structure with the space group $P31m$, on heating, may undergo a transition to a phase with minimal nonisomorphic supergroup symmetry $P\bar{3}1m$, $P\bar{6}2m$, $P6_3cm$ or $P6mm$. In the present investigation, the experimental atomic coordinates of members in 11 different families are found to approach either $P\bar{3}1m$ or $P\bar{2}m$ symmetry closely enough to be indicative of such a phase transition; no such approach was detected either to $P6_3cm$ or $P6mm$. Although the supergroup coordinates thus derived are not necessarily identical to those that subsequently may be determined experimentally, they are expected to be close. In the tables that follow, the Wyckoff position of each independent atom is given both in the space group $P31m$ and in the expected supergroup.[4] Unit-cell axes without integral change of length are assumed at the predicted phase transitions.

1.5. Structural criteria for predicting ferroelectricity

Three structural criteria form the basis for predicting that a material may be likely to exhibit ferroelectricity, see Abrahams (2006) for a fuller discussion. These are:

(i) that the structure determination is fundamentally correct,

(ii) that the total ith cation displacement ($\Delta\xi_i$),[5] between a reported $x_iy_iz_i$ location and that in the assumed paraelectric phase, is $1.5 \gtrsim \Delta\xi_i \gtrsim 0.05$ Å with $\Delta\xi_i$ not less than the r.m.s. thermal or static displacement of the ith cation u_i, and

(iii) that the bonds formed by the ith cation are among the shortest and strongest in the unit cell and require no polar displacement $\Delta z_i \gtrsim 0.5$ Å for the spontaneous polarization P_s to be reduced to zero (*i.e.* for $z_i \rightarrow z_i'$).

The Curie transition temperature T_C, *i.e.* from the ferroelectric to the paraelectric phase, is related to such a maximum displacement Δz_i between the two phases by

$$T_C = (\kappa/2k)(\Delta z_i)^2 \text{ K}, \qquad (1)$$

in which the force constant κ is $5.52\,(25) \times 10^4$ kPa and Boltzmann's constant k is $1.380658\,(12) \times 10^{-23}$ J K^{-1}, resulting in $\kappa/2k = 2.00\,(9) \times 10^4$ K Å^{-2} (Abrahams *et al.*, 1968).[6]

Application of (1) to the ferroelectric crystal with the highest T_C presently reported, *i.e.* $La_2Ti_2O_7$ with $T_C \simeq 1773$ K (see footnote 1), gives $\Delta z_{Ti} \simeq 0.30$ Å; higher displacements are possible in principle, as suggested in (iii) above, but as yet have not been reported. The well known ferroelectric $BaTiO_3$,

[2] ICSD Release 2009/1 lists a total of 328 entries in the space group $P3m1$.

[3] Fencooperite is the only mineral reported in $P3m1$, whereas schairerite, galeite, lizardite $1T$ and $9T$, cronstedtite, holtedahlite, satterlyite and långbanite form in $P31m$.

[4] Multiplicity, Wyckoff letters and the corresponding coordinates for all positions in the space group $P31m$ and in supergroups $P\bar{3}1m$ and $P\bar{6}2m$ may be found conveniently listed in *International Tables for Crystallography*, Vol. A (2002).

[5] With $\Delta\xi_i$ defined as $[(\Delta x)^2 + (\Delta y)^2 + (\Delta x{\cdot}\Delta y) + (\Delta z)^2]^{1/2}$ in space group $P31m$, where the ith atom located at x_i, y_i, z_i is considered displaced from its x_i', y_i', z_i' location in the hypothetical (nonpolar) supergroup, and $\Delta x = (x_i - x_i')a$, $\Delta y = (y_i - y_i')a$, $\Delta z = (z_i - z_i')c$.

[6] The applicability of (1) is now widely demonstrable. A modified approach was offered by Kroumova *et al.* (2002).

with experimental T_C = 393 K, corresponds to Δz_{Ti} = 0.14 Å by (1) and has reported Δz_{Ti} values ranging from 0.10 to 0.12 Å, see the summary in Abrahams (2009). With coordinate uncertainties $\sim$ 0.02 Å, the determined and predicted Δz_{Ti} values for $BaTiO_3$ are without significant disagreement.

1.6. Origin choice in space group *P*31*m* and algorithmic analysis

The *c* axis may be identified with any threefold axis in the space group *P*31*m* and may be assigned *x*, *y* coordinates 0,0; 1/3,2/3; or 2/3,1/3. The choice of *z* coordinate origin is arbitrary but, although discretionary, care is required in making it to avoid the generation of related but unrecognized pairs of atoms approaching supergroup equivalence.

The algorithmic coordinate software of Harvey & Abrahams (2010), used in deriving several of the present results, remains under development.

1.7. Confidence in and validation of predicted ferroelectric structures

The confidence level in all property predictions presented below is a function both of structure-determination reliability and the magnitudes of all the resulting atomic departures from supergroup symmetry. Author-provided 'estimated standard deviations' are often underestimates, lighter atoms in larger structures determined earlier may have been omitted, see *e.g.* §§2.2 and 2.3, and structural models may not have been fully refined, see *e.g.* §2.6; these and other problems prevent the assignment of standard confidence measures to the following predictions, hence each subsection in §2 is provided with a qualitative indication of confidence. In all cases, validation of a property prediction necessarily rests upon the results of subsequent experiment, see *e.g.* Abrahams (2006).

1.8. Presentation of structural analysis

All families reported in the ICSD release 2009/1 as forming in the space group *P*31*m* and identified by atomic coordinate analysis in §2 as new potential ferroelectric candidates are presented below in full, unless the structure contains more than ten independent atoms or requires more than a single table. In each such case, the accompanying larger and/or additional tables, together with those for structures not meeting the criteria in §1.5, are provided as supplementary material.[7] The presentation order follows that of the ICSD accession number, given in bold type within square parentheses for each determination. Structures with reduced predictive properties are presented in §3; structures more likely to remain polar at higher temperatures in §4, and those considered misassigned to space group *P*31*m* in §5.

[7] Supplementary data, including tables containing the atomic coordinates of structures with more than ten independent atoms in the space group *P*31*m*, together with any extra tables, and all tables with structures not meeting the criteria in §1.5, designated by the letter 'S' for this paper, are available from the IUCr electronic archives (Reference: BK5094). Services for accessing these data are described at the back of the journal.

2. Predicted/possible new inorganic ferroelectrics in the space group *P*31*m*

2.1. $K_3Nb_3B_2O_{12}$, sub- and full-cell [968, 969][8]

Choisnet *et al.* (1977) measured a total of 410 anomalous dispersion-corrected subcell I_{obs} using graphite-monochromated Mo $K\alpha$, refining them to R = 0.12 in the space group *P*31*m*. Coordinate analysis shows $\Delta\xi < u_{iso}$ for all resulting atomic locations, see Table S1(*a*), hence the structure is indistinguishable in principle from that expected in the centrosymmetric supergroup $P\bar{6}2m$. A total of 1500 superstructure $F_{obs} \geq 0.05F_{max}$, mostly described as very weak and with measurement precision reduced by the strong substructure reflections present, were refined in the space group *P*31*m* to R = 0.08 for the 62 independent atoms in a unit cell with $a_{full\ cell} \simeq 4a_{subcell}$ and Laue symmetry no higher than 6/*mmm*. Coordinate analysis, see Table S1(*b*), shows that no cation location in the full cell differs more than $\sim$ 0.19 Å, nor any O location more than $\sim$ 0.26 Å, from satisfying $P\bar{6}2m$ symmetry. Hence, although the subcell structure appears not to differ significantly from centrosymmetry, acceptance of the present full cell structure would satisfy the criteria for ferroelectricity. The confidence level for physical property prediction on the basis of the present structural determination is not high; it is, however, capable of being raised sharply by redetermination with greater accuracy. Second harmonic detection, dielectric or calorimetric investigation would also enhance the confidence level.

2.2. $Na_{21}(SO_4)_7F_6Cl$, Schairerite [4289]

Fanfani *et al.* (1975) used 2536 $I_{obs} > 3\sigma(I_{obs})$ of a total 2921 independent graphite-monochromated I_{obs}, for the structural refinement of schairerite in the space group *P*31*m*, reaching a final R = 0.070. Coordinate analysis, see Table S2, shows that all 14 Na, 10 S, both independent Cl and the six F anions present satisfy the conditions in §1.5 for ferroelectricity, with no cation displaced more than 0.21 Å and no Cl, S or F anion further than $\sim$ 0.42 Å from satisfying $P\bar{3}1m$ supergroup symmetry. Three single and one pair of O atoms, however, appear unacceptably far from such symmetry. If three matching O atoms had inadvertently been overlooked and a fourth either mislocated or overlooked, then the conditions of §1.5 would be met and schairerite could be predicted as a new ferroelectric.[9] Higher accuracy remeasurement is clearly advisable. It may be noted that all O-atom positions are not necessarily fully occupied.

2.3. $Na_{15}(SO_4)_5F_4Cl$, Galeite [4290]

Structural refinement of 2078 independent $I_{obs} > 3\sigma(I_{obs})$ for the mineral galeite, measured with graphite-monochromated Mo $K\alpha$ in the space group *P*31*m*, led Fanfani *et al.* (1975) to their lowest R = 0.070. The formula

[8] Family includes $K_3Ta_3B_2O_{12}$.

[9] See footnote to Table S2; with $\sim$ 95% of all other atoms present in acceptable conformity with centrosymmetry, such locational errors for some of the lightest atoms are not implausible.

Table 1
Averaged, modified lizardite 1*T*-atomic positions (see Table S4 for all experimental coordinates) with hypothetical $x'y'z'$ coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å [17046, 67332, 67333, 75933, 75934, 81102, 82411, 87436, 87437, 87438, 87506, 202358, 245887] (see footnote 4).

a = 5.332 (3), c = 7.233 (4) Å; $z^* = z - 0.0090$, including both H atoms.

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	$\langle x\rangle$	$\langle y\rangle$	$\langle z\rangle$	$\langle z\rangle^*$	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Mg	3*c*	3*g*	0.3325	0.0	0.4520	0.4430	0.3325	0.0	0.5	0.0	0.0	−0.41	0.41	0.11
Si	2*b*	2*c*	1/3	2/3	0.0704	0.0614	1/3	2/3	0.0	0.0	0.0	0.44	0.44	0.08
O1	2*b*	2*d*	1/3	2/3	0.2901	0.2811	1/3	2/3	0.5	0.0	0.0	−1.58	1.58	0.10
O2	3*c*	3*f*	0.5054	0.0	−0.0114	−0.0204	0.5054	0.0	0.0	0.0	0.0	−0.15	0.15	0.10
O3	3*c*	3*g*	0.6655	0.0	0.5850	0.5760	0.6655	0.0	0.5	0.0	0.0	0.55	0.55	0.12
O4	1*a*	1*b*	0.0	0.0	0.2951	0.2861	0.0	0.0	0.5	0.0	0.0	−1.55	1.55	0.09
H1	3*c*	3*g*	0.6278	0.0	0.716	0.7070	0.6278	0.0	0.5	0.0	0.0	1.50	1.50	0.16
H2	1*a*	1*a*	−0.0042	0.0	0.175	0.166	0.0	0.0	0.0	−0.02	0.0	1.20	1.20	0.16

Table 2
Modified atomic positions for $LaNi_5D_{5.5}$ based on Noréus *et al.* (1983) neutron scattering data [38402] with hypothetical $x'y'z'$ coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å (see Table S4 for all five independently measured sets of coordinates [20188, 38402, 200242, 638253, 638254] (see also footnote 4).

a = 5.336 (1), c = 4.259 (1); $z^* = z - 0.0122$, for all atoms.

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	x	y	z	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
La	1*a*	1*a*	0.0	0.0	0.0	−0.0122	0.0	0.0	0.0	0.0	0.0	−0.052	0.05	0.24
Ni1	2*b*	2*c*	0.3333	0.6667	0.980 (5)	0.9678	0.3333	0.6667	1.0	0.0	0.0	−0.137	0.14	0.16
Ni2	3*c*	3*g*	0.499 (1)	0.0	0.496 (5)	0.4838	0.499	0.0	0.5	0.0	0.0	−0.069	0.07	0.16
D1	3*c*	3*f*	0.470 (1)	0.0	0.092 (5)	0.0798	0.47	0.0	0.0	0.0	0.0	0.340	0.34	0.15
D2	6*d*	6*k*	0.189 (2)	0.864 (3)	0.493 (4)	0.4808	0.189	0.864	0.5	0.0	0.0	−0.082	0.08	0.17

$n(Na_2SO_4)\cdot(nNaF_{n-1}Cl)$ is shared by schairerite, see §2.2 with $n = 7$, and galeite with $n = 5$. Coordinate analysis shows that all Na, S and Cl ions in galeite, and also 12 of the 17 independent O ions, satisfy the conditions for ferroelectricity with acceptable displacements from $P\bar{6}2m$ symmetry, see Table S3. At least three O atoms, however, appear misplaced, *cf.* schairerite, resulting in apparent $\Delta\xi$(O) magnitudes ranging from $\sim$ 1.6 to 1.7 Å. Should structural redetermination find either that the reported positions for these three O atoms are in error, or locate the related but overlooked atoms, then galeite and also schairerite would be predicted as most likely ferroelectric.

2.4. $Mg_3Si_2O_5(OH)_4$, lizardite 1*T* [17046, 67332, 67333, 75933, 75934, 81102, 82411, 87436, 87437, 87438, 87506, 202358, 245887]

Thirteen separate crystal structure studies of the mineral lizardite 1*T*, with the basic composition $Mg_3Si_2O_5(OH)_4$, have been reported. Following ICSD order, the first is by Mellini (1982), the next two by Mellini & Zanazzi (1989), two by Mellini & Viti (1994), one by Krstanović & Karanović (1995), one by Gregorkiewitz *et al.* (1996), three by Guggenheim & Zhan (1998), one by Zhukhlistov & Zvyagin (1998), one by Mellini & Zanazzi (1987), with the last Mercier & Le Page's (2008) 'ideal' structure. Analysis of the coordinates in Table 1, using the fully averaged set in Table S4, reveals the Mg cation departs $\sim$ 0.41 Å, the Si ion $\sim$ 0.44 Å from supergroup $P\bar{6}2m$ symmetry with O and H ionic departures ranging from $\sim$ 0.15 to $\sim$ 1.55 Å. The Mg^{2+} and two O^{2-} ionic displacements approach the upper bound in §1.5(iii), the former corresponding to $T_C \simeq 3400$ K by (1), a temperature that is likely well above decomposition. The possibility that Lizardite 1*T* might prove capable of dielectric poling at temperatures between ambience and decomposition is worthy of investigation: if so, it would be a new ferroelectric; if not, it would more appropriately fall within the category of §3.

2.5. $LaNi_5D_6$ [20188, 38402, 87127, 200242, 638240, 638253, 638254]; γ-$CaNi_5D_{6.1}$ [54478]

Bowman *et al.* (1973) used X-ray powder diffraction to derive a set of coordinates for $LaNi_5D_6$ with $R \simeq 0.26$. Both Fischer *et al.* (1977) and Andresen (1977) refined the structure of $LaNi_5D_6$ by neutron powder diffraction, reporting final R values of 0.054 and 0.04, respectively, while Burnasheva *et al.* (1978), also using neutron powder diffraction, reported R = 0.124. Noréus *et al.* (1983) refined the $LaNi_5D_6$ structure to R = 0.083 using the intensities of 92 neutron diffraction powder lines, while Furrer *et al.* (1977) used similar techniques to obtain R = 0.064. The results of all six analyses, see Table S5, show several coordinates that depart from average, but nevertheless exhibit pseudosymmetric near-identities with $D2y_{[20188]} \simeq D2y_{\text{all other reports}} - \frac{1}{2}$, and $Ni1z_{[200242,\ 638254]} \simeq Ni1z_{\text{all other reports}} + \frac{1}{2}$. No analysis, however, results in atomic positions that depart more than $\sim$ 0.3 Å from $P\bar{3}1m$ symmetry; additionally, the coordinates of all atoms including D2 are closer to $P\bar{6}2m$ than $P\bar{3}1m$ symmetry. Taking Noréus *et*

Table 3
Modified atomic positions for γ-$CaNi_5D_{6.1}$ based on Yoshikawa *et al.* (1998) [54478] with hypothetical x' y' z' coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å (isomorphous with $LaNi_5H_{5.6}$ structure); see footnote 4.

a = 5.333 (1), c = 4.262 (1) Å; $z^* = z + 0.033$ based on Ca(z) and Ni(z) only.

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	x	y	z	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Ca	1a	1a	0.0	0.0	0.0	0.033	0.0	0.0	0.0	0.0	0.0	0.141	0.14	0.19
Ni1	3c	3g	0.508 (4)	0.0	0.45 (1)	0.483	0.508	0.0	0.5	0.0	0.0	−0.072	0.09	0.08
Ni2	2b	2c	0.3333	0.6667	−0.05 (1)	−0.017	0.3333	0.6667	0.0	−0.0	0.0	−0.072	0.07	0.08
D1	3c	3f	0.52 (1)	0.0	0.06 (1)	0.093	0.52	0.0	0.0	0.0	0.0	0.396	0.40	0.20
D2	6d	6k	0.18 (1)	0.82 (1)	0.6 (1)	0.633	0.18	0.82	0.5	0.0	−0.0	0.567	0.57	0.20

Table 4
Modified atomic positions for $Ca(OCl)_2(Ca(OH)_2)_2$ based on Aleksandrova *et al.* (1968) [20283] with hypothetical x' y' z' coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å (see footnote 4).

a = 6.31 (20), c = 6.49 (2) Å; $z^* = z - 0.018$ based on Ca(z) and Cl(z) only.

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	x	y	z	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Ca	3c	3f	0.6667	0.0	0.0	−0.018	0.6667	0.0	0.0	0.0	0.0	−0.12	0.12	n/d†
Cl	2b	2d	0.3333	0.6667	0.536	0.518	0.3333	0.6667	0.5	0.0	0.0	0.12	0.12	n/d
O1	1a	1a	0.0	0.0	0.213	0.195	0.0	0.0	0.0	0.0	0.0	1.27	1.27	n/d
O2	2b	2c	0.3333	0.6667	0.213	0.195	0.3333	0.6667	0.0	0.0	0.0	1.27	1.27	n/d
O3	3c	3g	0.3333	0.0	0.787	0.769	0.3333	0.0	0.5	0.0	0.0	1.75	1.75	n/d

† Not determined or reported.

al.'s (1983) elastic and inelastic neutron scattering measurements as both typical and among the most reliable in Table S5, the maximum departure by La or Ni from $P\bar{6}2m$ symmetry, *viz.* ~0.14 Å, corresponds to $T_C \simeq 390$ K, see Table 2. $LaNi_5D_6$, as also isomorphous $LaNi_5H_6$, hence meets the criteria for ferroelectricity.

Comparable results for the isostructural γ-phase of $CaNi_5D_{6.1}$ have been reported by Yoshikawa *et al.* (1998), who refined their neutron diffraction powder data to R = 0.0226, see Table 3. The largest departure by a metal ion in γ-$CaNi_5D_{6.1}$ from $P\bar{3}1m$ or $P\bar{6}2m$ symmetry is Δz(Ca) $\simeq$ 0.14 Å, identical to Δz(Ni1) in $LaNi_5D_6$ if the $D(z)$ values in the former are neglected in scaling; the criteria in §1.5 are hence met by both deuterides.

2.6. $Ca(OCl)_2(Ca(OH)_2)_2$ [20283]

The 'probable' structure for $Ca(OCl)_2(Ca(OH)_2)_2$ as determined by Aleksandrova *et al.* (1968), on the basis of 23 X-ray powder diffraction intensities, was neither refined nor were the H atoms located; no subsequent study has been reported. The model, however, shows both Ca and Cl ions apparently displaced ~ 0.12 Å, with O1 and O2 each displaced ~ 1.27 Å, from supergroup $P\bar{6}2m$ symmetry assuming O3 occupies Wyckoff position 3g above such a hypothetical transition. The resulting ambient displacement of O3 is then ~ 1.75 Å as in Table 4, with all O(z) positions neglected in origin scaling. The resulting Ca and Cl ion-displacement magnitudes correspond to $T_C \simeq 288$ K, and hence are suggestive of ferroelectricity; all three independent O displacements, however, are questionably large. Structural redetermination, calorimetry and/or dielectric measurements are thus necessary in order to clarify the properties of $Ca(OCl)_2(Ca(OH)_2)_2$.

2.7. $CsNO_3$ phase II [29392]

Ferroni *et al.* (1957) characterized ambient $CsNO_3$ as exhibiting trigonal symmetry, with Z = 1 and space group $P31m$, undergoing a transition at ~ 434 K to cubic symmetry. DeLacy & Kennard (1971), however, determined the ambient space group to be $P3_1$ with Z = 9, a result independently confirmed by others including Pohl & Gross (1993), Liu *et al.* (2001), and Zhou *et al.* (2005). Based on the 1993 determination, $CsNO_3$ phase II had previously been shown (Abrahams, 2003) to satisfy the structural criteria required for ferroelectricity. Although ambient $CsNO_3$ may also be assigned to §5, the positive property prediction suggests the present assignment as more appropriate.

2.8. $(C(NH_2)_3)Al(SO_4)_2(H_2O)_6$ [30566, 34261]

GASH was experimentally discovered to be ferroelectric by Holden *et al.* (1956).[10] Based on 882 diffractometrically measured F_{obs} and previously published coordinates, Schein *et al.* (1967) reduced R to 0.035 by least-squares refinement. Very similar results, presented in the same paper, were also obtained for the isomorphic Cr compound GCrSH. Previous refinements by Geller & Katz (1962),[11] and also Lingafelter *et*

[10] Guanidinium aluminum sulfate hexahydrate is commonly referred to as GASH.
[11] Reference to Geller & Katz (1962) is missing from ICSD release 2009/1.

Table 5
Modified atomic positions for $[N(CH_3)_4]_2(Mo_3S_{13})$ based on Bensch & Schur (1998) with hypothetical x' y' z' coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å [56429] (see footnote 4).

a = 11.223 (5), c = 5.887 (3) Å; $z^* = z + 0.0334$ (Mo and five S atoms); $z^* = z - 0.1927$ (all atoms).

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	x	y	z	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Mo1	3c	3f	0.19280 (6)	0.66668 (6)	0.0126 (1)	0.0460	0.1406	0.0	0.0	0.0	0.0	0.271	0.27	0.14
S1	3c		−0.2562 (2)	0.0	0.0351 (5)	0.0685	−0.2138	0.0	0.1480	0.47	0.0	−0.468	0.66	0.19
		6i												
S3	3c		−0.1714 (2)	0.0	−0.2608 (4)	−0.2274	−0.2138	0.0	−0.1480	−0.47	0.0	−0.467	0.66	0.17
S2	1a	1a	0.0	0.0	0.3126 (7)	0.3460	0.0	0.0	0.5	−0.27	0.0	−0.901	0.94	0.16
S4	3c		0.3081 (2)	0.0	0.2706 (5)	0.3040	0.3324	0.0	0.1706	−0.27	0.0	0.785	1.10	0.19
		6i												
S5	3c		0.3567 (2)	0.0	−0.0706 (6)	−0.0372	0.3324	0.0	−0.1706	0.27	0.0	0.785	1.10	0.20
N1	2b	2d	0.6667	0.3333	0.477 (2)	0.5104	0.6667	0.3333	0.5	0.0	0.0	0.06	0.06	0.19
C1	2b	2c	0.6667	0.3333	0.211 (3)	0.244	0.6667	0.3333	0.0	0.0	0.0	1.44	1.44	0.20
C2	6d	6k	0.7957 (8)	0.4562 (8)	0.55 (2)	0.583	0.7957	0.4562	0.5	0.0	0.0	0.49	0.49	0.20
H1	6d		0.6707	0.4159	0.1567	0.1901	0.6068	0.4365	0.2221	0.72	−0.23	−0.19	0.66	0.28
		12l												
H6	6d		0.802	0.4571	−0.2875	−0.2541	0.8297	0.3932	−0.2221	−0.31	0.72	−0.19	0.65	0.27
H2	6d		0.5841	0.2548	0.1567	0.1901	0.5841	0.2548	0.1901	0.0	0.0	0.00	0	0.28
		12l												
H3	6d		0.7452	0.3293	0.1567	0.1901	0.7452	0.3293	0.1901	0.0	0.0	0.00	0	0.28
H4	6d		0.7961	0.5377	0.4993	0.5327	0.6713	0.5410	0.5256	1.40	−0.04	0.04	1.38	0.27
		12l												
H5	6d		0.8729	0.4535	0.4852	0.5186	0.8697	0.3287	0.5256	0.04	1.40	−0.04	1.42	0.27

al. (1966), reported that their least-squares refinement produced large parameter interactions, possible origins for which gave rise to vigorous discussion in the literature. Anomalously, all atomic locations determined by Schein *et al.* (1967) approach $P\bar{6}2m$ supergroup symmetry within the criteria of §1.5, as may be seen in Table S6, except for S and O in both sulfate groups which instead approach $P\bar{3}1m$ supergroup symmetry.

GASH decomposes at ∼475 K, *i.e.* below a Curie temperature that is hence undeterminable at ambient pressure. The hypothetical phase transition to higher symmetry may thus be regarded as improper, see *e.g.* Ishibashi & Takagi (1976) and Kobayashi *et al.* (1972). In addition to the anomalous symmetry relationships noted above, with its possible connection to the relative rigidity of the $C(NH_2)^{3+}$ and SO_4^{2-} ions, the structurally related, ambient, spontaneous polarization magnitude $P_s = 3.5 \times 10^{-3}$ C m^{-2} is unusually low; further study of the structure and properties of both GASH and GCrSH is clearly appropriate.

2.9. $[N(CH_3)_4]_2Mo_3S_{13}$ [56429, 110357]

A total of 1268 $[N(CH_3)_4]_2Mo_3S_{13}$ $I_{obs} > 2\sigma I_{obs}$, measured diffractometrically by Bensch & Schur (1998) using graphite-monochromated Mo $K\alpha$ were fully corrected and refined to include all H atom locations for a final $R(F) = 0.036$. A polar axis origin based only on the z coordinates of Mo and the five S atoms, see Table 5, shows Mo to be within 0.27 Å of Wyckoff position 3f in the supergroup $P\bar{6}2m$, all S atoms within 0.66–1.10 Å, and the N and C atoms within 1.44 Å of comparable positions. $(N(CH_3)_4)_2Mo_3S_{13}$ hence approaches and possibly exceeds the presently undetermined upper displacement limits for ferroelectricity, see §1.5(iii). A material with identical formula and comparable lattice constants was reported by Lu *et al.* (2002) in the space group $P3$ and refined to $R(F)$ = 0.0667; the resulting atomic coordinates are unrelated to those above, to which reference was not made. Examination of Lu *et al.*'s experimental intensity data by means of *PLATON* (Bensch, 2009) revealed the presence of the mirror-symmetry plane expected in space group $P31m$, hence the 2002 structure appears inappropriate. The possibility of ferroelectricity in $(N(CH_3)_4)_2Mo_3S_{13}$ is sufficient to warrant dielectric investigation.

2.10. $Li_{17}Ag_3Sn_6$ [170571]

A total of 2972 reflections attributed to the Zintl phase $Li_{17}Ag_3Sn_6$, of which 801 are independent, were measured diffractometrically by Lupu *et al.* (2004) using Mo $K\alpha$; initial refinement led to the formula $Li_{18}Ag_3Sn_6$, but one Li with a large U_{eq} value was rejected in the final refinement, giving R = 0.0446 for $I > 2\sigma(I)$ and the atomic coordinates in Table S7.[12] The remaining Li7 located at 0, 0, −0.132 is the only atom that fails to fulfill the criteria for ferroelectricity, with all other atoms less than 0.2 Å from satisfying the symmetry of the supergroup $P\bar{6}2m$. If an Li8 atom, with coordinates as in footnote 12, were overlooked then both the supergroup symmetry and the initial chemical formula would be satisfied; the resulting 11 nearest neighbors around Li8 would be closely comparable to those about all other Li sites except Li7, which is too close at $d_{Li7-Li8}$ = 2.25 Å. Alternative equal-occupancy locations for atoms Li7 and Li8 at 0, 0, ±0.174 would eliminate this problem, with all other interatomic distances remaining

[12] The initial coordinates used for Li8 were not given, but are predicted to be 0, 0, ∼0.132.

Table 6
Modified atomic positions for $Cs_3(As_5O_9)$ based on Emmerling & Röhr (2003) with hypothetical x' y' z' coordinates and the Δx, Δy, Δz, $\Delta\xi$ and u_{iso} displacements in Å [413151] (see footnote 4).

a = 8.455 (3), c = 6.0262 (19) Å; $z^* = z + 0.0085$ based on metal atoms only.

	Wyckoff position													
	$P31m$	$P\bar{6}2m$	x	y	z	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Cs1	3c	3f	0.3663 (9)	0.0	0.0	0.0085	0.3663	0.0	0.0	0.0	0.0	0.05	0.05	0.03
As1	3c	3g	0.7392 (16)	0.0	0.5033 (3)	0.5118	0.7392	0.0	0.5	0.0	0.0	0.07	0.07	0.03
As2	2b	2d	0.3333	0.6667	0.4711 (3)	0.4796	0.3333	0.6667	0.5	0.0	0.0	−0.12	0.12	0.03
O1	3c	3f	0.6872 (11)	0.0	0.2358 (17)	0.2443	0.6872	0.0	0.0	0.0	0.0	1.47	1.47	0.05
O2	6d	6k	0.2863 (12)	0.4722 (11)	0.6221 (11)	0.6306	0.2863	0.4722	0.5	0.0	0.0	0.79	0.79	0.06

acceptable; it is noted that the occupancy sum of both Li sites may be less than 2.

The resistivity ρ of intermetallic $Li_{17/18}Ag_3Sn_6$ is presently unknown. Han *et al.* (2005) report the 'polar intermetallic' $Tb_3Zn_{3.6}Al_{7.4}$ has $\rho \simeq 26$ μΩ cm at 2 K, increasing linearly to ~ 50 μΩ cm at ambience. The resistivity of doped ferroelectrics is not incomparable, with $\rho_{BaTiO3} \gtrsim 10^{10}$ Ω cm for pure $BaTiO_3$ reportedly reduced to $\sim 4 \times 10^4$ Ω cm for samples doped with 0.05 atom % La^{3+} (Brutchey *et al.*, 2008); $Li_{17/18}Ag_3Sn_6$ may hence be an attractive candidate for current device applications.

2.11. $Cs_3As_5O_9$ [413151]

Emmerling & Röhr (2003) measured a total of 2668 $F_{obs}(Cs_3As_5O_9) > 2\sigma(I_{obs})$ diffractometrically, refining them to a final R = 0.0316 for the atomic coordinates in Table 6. Materials of such compositions were not previously known. A scale factor based only on the metal atom z coordinates results in no cationic displacement larger than 0.12 Å from supergroup $P\bar{6}2m$ symmetry, with O displacements of ~ 0.8 and 1.5 Å; a z-coordinate correction based on all atoms increases the cation displacements to ~ 0.4 Å, but reduces that of O to less than ~ 1 Å. Either model, or an intermediate, clearly approaches the criteria for ferroelectricity. Calorimetric, second harmonic and/or dielectric study would hence be particularly appropriate in view of the possibility that, should the expected T_C be observed not far above ambience, $Cs_3As_5O_9$ might have dielectric properties comparable with $BaTiO_3$.

3. Structures with reduced ferroelectric predictive properties

3.1. $\{Fe_3[(Si_{0.685}Fe_{0.315})_2O_5](OH)_4\}$, cronstedtite 1*T* [18193, 89909, 89910, 158233, 158234, 158235, 158236]

Seven structural determinations of the mineral cronstedtite 1*T* have been reported. Steadman & Nuttall (1963), noting the mineral crystallizes in eight different polymorphic forms, investigated the 1-layer type in the space group $P31m$ by two-dimensional projection along the a and c axes. Their 87 independent F_{obs}, measured with Co $K\alpha$ data, refined to $R \simeq 0.15$ for the atomic cordinates in Table S8(a). Two additional determinations have been reported by Hybler *et al.* (2000) and four by Hybler (2006). The former, noting both 3*T* and $2H_2$ polytypes are less common, used two 1*T* samples to determine 1652 and 1602 F_{obs}, respectively, reporting final R values of 0.0307 and 0.0224; Hybler (2006) measured 1553–2104 F_{obs} on 1*T* samples from four other locations, reaching final R values ranging from 0.0148 to 0.0301 for the coordinates in Table S8(a). The Fe2 cation at $z = \frac{1}{2}$ (see Table S8b for coordinates averaged over the results of all seven studies) requires no displacement along the polar axis, but the tetrahedrally bonded shared-site Fe1,Si cation would require a displacement of ~ 0.72 Å to satisfy supergroup symmetry. The criteria for ferroelectricity, see §1.5, are hence unlikely to be met by cronstedtite 1*T*.

3.2. Yb_2SO_2 [23583, 109335]

Ballestracci & Rossat-Mignod's (1969) refinement of the Yb_2SO_2 neutron diffraction powder pattern measured at room temperature assumed the space group '$P3m$' and led to $R \simeq 0.03$ for the atomic coordinates in Table S9; cooling to 1.5 K revealed unit-cell doubling owing to antiferromagnetic array formation. The structure of Yb_2SO_2 at ambience, as also that of Tb_2O_2S, Dy_2O_2S and Ho_2O_2S, had been reported previously in the space group '$P\bar{3}m$' by Eick (1958) following Zachariasen's (1949) assignment of the centrosymmetric space group to isomorphous Ce_2O_2S, La_2SO_2 and Pu_2SO_2. Table S9 shows that, with z^* values based on the predominant Yb neutron scattering, all three independent atoms approach either supergroup $P\bar{3}1m$ or $P\bar{6}2m$ symmetry, both of which have identical one- and twofold Wyckoff positions, within 1.4 Å; the lack of coordinate uncertainties may be noted. If Yb_2SO_2 were confirmed to be acentric at ambience, it would then be a candidate for exhibiting ferroelectricity, but space-group assignment uncertainty, together with the low structural precision (~ 0.07 Å), indicates the need for further study before property prediction is appropriate.

3.3. $K_3V_5O_{14}$ [24068, 75219]

Byström & Evans (1959) refined 63 visually estimated $I(hk0)$, 51 $I(hk1)$ and 93 $I(h0l)$ to obtain an overall $R \simeq 0.14$ for the atomic coordinates in Table S10(a); Z was not listed. Analysis shows no cation to be further than ~ 0.17 Å, nor any O ion than ~ 0.84 Å, from satisfying $P\bar{6}2m$ symmetry, *i.e.* this structure appears to offer a strong case for exhibiting ferroelectricity, with an estimated T_C not far above ambience. However, Evans & Brusewitz (1994) subsequently measured

3590 reflections diffractometrically on a newly prepared crystal. The resulting 359 independent averaged F_{obs}, on redetermination, gave the coordinates in Table S10(*b*) with $R = 0.057$ for double the number of independent atoms listed in Table S10(*a*) except for K, with $Z = 1$. Table S10(*b*) shows all like atoms form pairs located at *xyz* and $xy\bar{z}$, in full accordance with $P\bar{6}2m$ symmetry, except for the single K1 atom in Wyckoff position 3(*c*). A missing K2 atom, possibly overlooked inadvertently, may be located at $\sim$ K1($xy\bar{z}$) in satisfaction of supergroup symmetry. A new refinement of $K_3V_5O_{14}$ was reported by Ozeki *et al.* (1987) in an abstract identifying the space group as $P31m$, but without coordinates or other detail. Li *et al.* (2004) subsequently reported the generation of second harmonics by $K_3V_5O_{14}$, supportive of inversion center absence. Further investigation of the composition, symmetry and properties of $K_3V_5O_{14}$ is hence appropriate.

3.4. $Na_2ZnCl_4(H_2O)_3$ [24269]

Brehler (1960) measured 35 I_{obs} by Cu $K\alpha_1$ powder diffractometry in order to determine the five coordinate-variables in $Na_2ZnCl_4(H_2O)_3$, reporting $R = 0.16$. No atom in the resulting structure approaches the symmetry of any relevant supergroup closely, as may be seen in Table S11. Remeasurement and redetermination with higher structural accuracy would be appropriate.

3.5. $H_{4.4}Al_{1.27}Fe_{0.1}Mg_2O_9Si_{1.4}$, lizardite 9*T* [24427]

A total of 149 1*T* $F(hkl)$, measured diffractometrically by Jahanbagloo & Zoltai (1968) using Cu $K\alpha_1$, refined to $R = 0.102$ for the $\bar{3}m$ diffraction symmetry observed in a unit cell with $a = 5.295$ (4), $c = 63.99$ (6) Å and $I(00l)$ with $l = 3n$ (*cf.* lizardite 1*T* with $a \simeq 5.332$, $c \simeq 7.233$ Å in §2.4). The resulting 1*T* subcell coordinates, see Table S12, approach supergroup $P\bar{6}2m$ symmetry with no $|\Delta\xi| > 0.24$ Å, suggestive of ferroelectricity in this Al-serpentine if the nine-layer unit-cell structure retains the one-layer symmetry. The authors, however, suggested the symmetry of the full 18-layer structure is more closely approximated by $P31c$. A definitive study of this mineral is hence still awaited.

3.6. AuCd [58408]

Alasafi & Schubert's (1977) refinement of their 287 diffractometrically measured $F(hkl)$ using Mo $K\alpha$ led to $R = 0.08$ for the coordinates in Table S13. Although all atoms as reported are within ~ 0.5 Å of $P\bar{3}1m$ symmetry, Au and Cd displacements of such magnitude are unlikely; the 301 K martensitic transformation reported by Noda *et al.* (1988) increases such improbability further. The ~ 8 μΩ cm electrical resistivity observed at 300 K, with a maximum at ~ 595 K (Mukherjee *et al.*, 1984), eliminates AuCd from consideration as a practical ferroelectric candidate. AuCd alloy martensitic transformations have been studied extensively with alloys having atomic ratios ~ 1.1 reported to undergo such transitions as β_1 ($Pm\bar{3}m$) to β_1' ($Pmma$) phase at ~ 353 K and, with slightly smaller Cd content, to the β_1'' ($P31m$) phase at ~ 575 K, see Wallace *et al.* (1968). Structural redetermination would be appropriate.

3.7. $Mg_{12}(PO_3OH)(PO_4)_6(OH,O)_6$, holtedahlite [64769, 67048] and $(Fe,Mg)_{12}(PO_3OH)(PO_4)_5(OH,O)_6$, satterlyite [94842]

The structures of both synthetic and natural holtedahlite were determined by Rømming & Raade (1989) on the basis of 718 diffractometrically measured $I_{obs} > 3\sigma(I_{obs})$ for the former, 1202 for the latter, with $R = 0.033$ and 0.031. Partial substitution of the P1 site in natural holtedahlite by the C atom of a CO_3^{2-} group led to the present selection of results only for synthetic holtedahlite. Coordinate analysis, see Table S14, shows many atomic positions in synthetic holtedahlite far from meeting the structural requirements for ferroelectricity, with displacement magnitudes of ~ 0.4 Å for Mg and ~ 0.7 Å for P; the displacements in natural holtedahlite are closely comparable. The mineral holtedahlite is hence not a ferroelectric candidate.

The structure of satterlyite, isostructural with synthetic holtedahlite, was determined and refined by Kolitsch *et al.* (2002) to $R = 0.0215$ using 2320 unique $F_{obs} > 4\sigma(F_{obs})$, see Table S15.[13] Neither holtedahlite nor satterlyite is likely to be ferroelectric in view of the required cationic and P displacement magnitudes. Other properties of both minerals, however, are worthy of further investigation.

3.8. $[(CH_3)_4N]_2Mo_3Se_{13}$ [66870]

Liao *et al.* (1995) refined 438 diffractometrically measured $I_{obs} > 3\sigma(I_{obs})$ by the use of graphite-monochromated Mo $K\alpha$. The resulting atomic coordinates, see Table S16, have $R = 0.060$ in a space group noted both as No. 157 and as '$P3_1m$'. Coordinate analysis shows that all five independent Se ions require displacements ranging from 0.6 to 1.2 Å in order to satisfy the symmetry of supergroup $P\bar{6}2m$, although $\Delta\xi$(Mo) is only 0.05 Å. Such required displacement magnitudes by Se effectively eliminate the possibility that $[(CH_3)_4N]_2Mo_3Se_{13}$ might be ferroelectric.

3.9. $TiO_{0.3}D_{0.1}$ [71816]

Kajitani *et al.* (1991) measured 612 F_{obs} with Mo $K\alpha$ radiation, discarding all F_{obs} with $2\theta < 66°$ because of 'possible overlap of reflections', in addition to 120 $F_{obs} > 0$ determined by the use of neutron radiation with $\lambda = 1.019$ Å. Refinement gave $R = 0.102$ and 0.150, with atomic coordinates for the former listed in Table S17.[14] Displacement magnitudes of ~ 0.31 Å by both independent Ti ions, required for a ferroelectric phase transition with a transition temperature of ~ 1800 K, are unlikely in a unit cell with volume as small as ~ 111 Å^3; $TiO_{0.3}D_{0.1}$ is hence not predicted to be ferroelectric.

[13] The satterlyite x, y, z coordinates reported are replaced in Table S15 by $1-x, 1-y, 1-z$ to simplify comparison with those of holtedahlite in Table S14.

[14] The refined neutron study coordinates were not presented. The O4 atom in the X-ray study is listed as sharing Wyckoff position 1(*a*) with D2.

3.10. $Cs_4Au_6S_5$ [82557]

A total of 453 fully corrected $F_{obs} > 3\sigma(F^2_{obs})$, measured diffractometrically with graphite-monochromated Mo $K\alpha$ by Klepp & Weithaler (1996), led on refinement to $R = 0.048$ for the coordinates in Table S18. The possibility of an Au cation undergoing an ~ 0.8 Å displacement in a phase transition approaches zero, hence $Cs_4Au_6S_5$ is not expected to be ferroelectric.

3.11. $Ba_{10}Cl_{3.7}F_{31.3}Fe_3Mn_3$ [82861]

Darriet *et al.*'s (1996) refinement of 1384 independent F_{obs}, with $I_{obs} > 3\sigma(I_{obs})$, resulted in $R = 0.0275$ for the coordinates in Table S19. The strongly disordered structure was solved and refined assuming a $Ba_{10}(MnFeF_{10}Cl)_3FCl$:$Ba_{10}(MnFeF_{11})_3Cl_2$ ratio of 17:3. As a consequence, eight pairs of atoms exhibit averaged separations as small as ~ 0.55 Å between Ba4 and Ba5, ~ 0.72 Å between Mn1 and Mn2, ~ 0.67 Å between two F7 atoms, and ~ 1.09 Å between F9 and Cl3, with other pairs of atoms also apparently very close. Uncertainties associated with the nature of this disorder, including its possible heat treatment dependence, effectively eliminates confidence in any present structurally based prediction of $Ba_{10}Cl_{3.7}F_{31.3}$-Fe_3Mn_3 properties.

3.12. NiTi [156442]

The structure of NiTi, a shape memory alloy, has been widely investigated. Gong *et al.*'s (2006) *ab initio* study of the premartensitic rhombohedral NiTi phase proposed $P31m$ as the lowest energy space group at 0 K. Krishnan *et al.* (2008), Strutt *et al.* (2008), Goryczka & Morawiec (2004) and Sitepu (2003) among others have proposed space groups $P3$ or $P\bar{3}$, $P3$, $P\bar{3}$, and $P3$, respectively, with many closely comparable atomic coordinates among models. Lekston *et al.* (1999) theoretically derived and experimentally confirmed the space group of isostructural $Ni_{48.7}Ti_{50}Co_{1.3}$ at ambience to be $P31m$, but did not determine the atomic coordinates. Examination of Gong *et al.*'s (2006) coordinates shows two Ni atoms ~ 0.44 Å and two Ti atoms ~ 0.25 Å from $P\bar{3}1m$ symmetry, see Table S20; both required displacements are large enough that the likelihood of a ferroelectric phase transition in NiTi approaches zero. The resistivity of NiTi has been reported by Kovalev *et al.* (1975) as 0.715 μΩ m.

3.13. $V[C(NH_2)_3](SO_4)_2(H_2O)_6$ [170206]

Refinement of 2444 vanadium guanidinium hexaquadisulfate $I_{obs} > 2\sigma(I_{obs})$, measured diffractometrically by Tragenna-Piggott *et al.* (2004) using Mo K, resulted in $R = 0.0215$. Coordinate analysis shows no atom to be further than ~ 0.4 Å, with most within ~ 0.2 Å, of corresponding locations that satisfy supergroup $P\bar{3}1m$ symmetry, see Table S21. Although the atomic displacement criteria for ferroelectricity are almost satisfied, the large $\Delta z(V1) \simeq 0.36$ Å displacement, together with the major reorientations required by the guanidinium, hydroxyl and sulfate ions, preclude any prediction of ferroelectricity with moderate confidence; dielectric study at ambience, however, would be appropriate for this possibly improper ferroelectric, *cf.* §2.8.

4. Structures likely to remain polar at higher temperatures

4.1. $Mn_{13}SbSi_{12}O_{24}$, långbanite [69610]

The structure of the mineral långbanite was determined by Moore *et al.* (1991) using 3654 $F_{obs} > 2\sigma(F_{obs})$ and refined to $R = 0.065$. The atomic arrangement, noted as 'remarkable', contains unusual double-hexagonally close-packed cations that do not share polyhedral faces but do share more than 45% of all edges. The atomic displacements required to achieve supergroup symmetry, see Table S22, range from ~ 0.16 to 2.70 Å for all atoms, with $\Delta\xi$(Mn) as large as 1.8 Å and $\Delta\xi$(Si) as large as 2.7 Å. Polar långbanite is hence not a viable candidate for the exhibition of ferroelectricity.

4.2. $Ba_{21}Al_{40}$ [170238]

$Ba_{21}Al_{40}$, one of eight binary and ternary intermetallics studied by Amerioun *et al.* (2004), was refined with 1184 $I_{obs} > 2\sigma(I_{obs})$ measured diffractometrically with Mo $K\alpha$ to yield $R = 0.024$. The resulting atomic positions do not approach the symmetry of any relevant supergroup closely; six of the nine independent Ba atoms present have $2.0 \gtrsim \Delta\xi \gtrsim 2.5$ Å with six of the 13 independent Al atoms having $1.6 \gtrsim \Delta\xi \gtrsim 3.3$ Å with respect to $P\bar{3}1m$ symmetry, see Table S23. Inversion centers are hence unlikely to develop in $Ba_{21}Al_{40}$ at elevated temperatures.

4.3. $Pb(C(CN)_3)_2$ [171702]

A total of 4946 $Pb(C(CN)_3)_2$ reflections measured diffractometrically by Deflon *et al.* (2006) using Mo $K\alpha$ resulted in 1445 independent $I_{obs} > 2\sigma(I_{obs})$, leading on refinement to $R = 0.0324$ for the atomic coordinates in Table S24. The independent Pb atoms are displaced 0.27 and 0.39 Å, the C and N atoms between 0.24 and 1.28 Å, from supergroup symmetry. The displacement required by Pb2 in order to achieve nonpolarity significantly exceeds the largest known Δz values, and hence is most unlikely. $Pb(C(CN)_3)_2$ is thus expected to remain polar until decomposition at elevated temperatures.

4.4. $Pb(ReO_4)_2$ [201430]

The 3402 $Pb(ReO_4)_2$ reflections measured diffractometrically by Picard *et al.* (1984) using Mo $K\alpha$ yielded a total of 567 independent $I_{obs} > 0$. Structure solution and refinement gave the atomic coordinates in Table S25, with $R = 0.066$. The largest departure from supergroup $P\bar{6}2m$ symmetry by Re or Pb is 0.34 Å for the former, 0.42 Å for the latter; none of the six O atoms depart more than ~1.2 Å. The displacement sense for all four metal atoms is opposite that of all six O atoms, hence is unlikely; an independent structural determination, preferably by neutron diffraction,[15] is advisable before any property prediction for $Pb(ReO_4)_2$ is made.

[15] Indebtedness to an anonymous referee for this suggestion is gratefully acknowledged.

5. Structures misassigned to space group $P31m$

5.1. $2PbCO_3 \cdot Pb(OH)_2$, hydrocerussite [16630]

The unit cell of basic lead carbonate, reported by Cowley (1956) in an electron diffraction study as exhibiting $P31m$ symmetry, was subsequently shown by Martinetto *et al.* (2002) to be related to another cell larger by the factor $\sim 3^{1/2}$, with rhombohedral symmetry and space group $R\bar{3}m$. The centrosymmetric structure of hydrocerussite thus eliminates its further consideration within the present context.

5.2. $Ag_5Pb_2O_6$ [24038, 172975]

An approximate structure for $Ag_5Pb_2O_6$ with $R \simeq 0.48$ was presented by Byström & Evers (1950) on the basis of 52 visually estimated $F_{obs} > F_{max}$, see Table S26(*a*). Coordinate analysis shows that none of the six independent atoms departs more than ~ 0.09 Å from $P\bar{3}1m$ symmetry, hence is indicative of a misassigned space group. Independent confirmation of centrosymmetry has been provided by several authors, with Yoshii *et al.* (2007) most recently reporting a neutron diffraction determination in space group $P\bar{3}1m$ with final R = 0.0248, see Table S26(*b*), *i.e.* $Ag_5Pb_2O_6$ is indeed nonpolar.

5.3. $Cd_{0.61}Pt_{3.05}Zn_{4.27}$ [654683]

Khan & Schubert (1970) reported the structure of three CdPtZn compositions of different symmetry, one of which assumed the space group to be $P31m$ on the basis of 28 I_{obs} derived from a Cu $K\alpha$ Guinier X-ray diffraction powder pattern. The analysis in Table S27 shows that the structural coordinates exhibit supergroup $P\bar{6}2m$ symmetry, hence the space-group designation currently listed by ICSD requires correction.

Access to ICSD has been through the Windows® version issued jointly by Fachinformationszentrum and the National Institute of Standards and Technology in cooperation with the International Union of Crystallography. It is a pleasure to thank Professor J. Kobayashi for his much appreciated comments, Professors W. Bensch and P. Photinos for their most valued personal communications, two anonymous referees for very helpful suggestions and Anna Beauchamp, Coordinator of Interlibrary Loans at Southern Oregon University, for providing full copies of the many references used in this study. Support by the National Science Foundation (grant No. DMR-0137323) is gratefully acknowledged.

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