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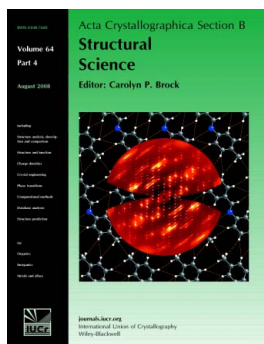
Inorganic structures in space group $P3m1$; coordinate analysis and systematic prediction of new ferroelectrics

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Inorganic structures in space group $P3m1$; coordinate analysis and systematic prediction of new ferroelectrics

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ICSD Release 2007/1 contains 47 families of inorganic crystal structures, some single-member only, within the 311 entries listed under the polar space group $P3m1$. Coordinate analysis reveals 12 such families to be candidate ferroelectrics, over a range of confidence levels. Selection is based on the detection of an approach to nonpolar supergroup symmetry, within specified limits, by the atomic arrangement as reported in a confirmed polar space group. The primary source of uncertainty in such predictions is the reliability of the underlying structural determination. The candidates include In_2ZnS_4 , TlSn_2F_5 , Cu_7Te_4 , NaMnSe_2 , $\text{Na}_2\text{In}_2(\text{Mo}_3\text{O}_8)(\text{MoO}_4)_2$, $\text{Nb}_3\text{Br}_7\text{S}$, Nb_3TeI_7 , fencooperite, $\text{Bi}(\text{HCOO})_3$, $\text{Li}(\text{NpO}_2)(\text{CO}_3)(\text{H}_2\text{O})_2$, $\text{LiPtD}_{0.66}$ and $\text{Ag}_3(\text{MoO}_3\text{F}_3)(\text{Ag}_3(\text{MoO}_4)\text{Cl})$. A total of 20 structures examined are likely to be nonpolar, a further 20 have reduced predictive properties and three others are more likely to retain $P3m1$ symmetry over a wide thermal range. Substantial uncertainties associated with many of the listed 163 CdI_2 , 69 ZnS and 10 SiC polytype structures, together with their low potential for use as possible ferroelectrics, led to their exclusion from fuller analysis.

1. Introduction

1.1. Framework

Eliminating the polar axis from a pyroelectric crystal structure, by temperature or pressure change, necessarily results in a phase transition. The number of inorganic materials structurally determined and reported in the literature as polar differs strikingly from that reported as nonpolar. The Inorganic Crystal Structure Database Release 2007/1 (ICSD, FIZ Karlsruhe/ILL, 2007) lists a total of 87 393 nonpolar inorganic materials compared with only 12 850 polar entries, mostly determined under ambient conditions. A material listed in both classes is likely to undergo a known phase transition; other listed structures may undergo a phase transition which is as yet unreported. A total of 2242 phase transitions in inorganic materials of well defined stoichiometry are listed by Tomaszewski (1992). Atomic displacements within a unit cell between polar and nonpolar phases are generally less than ~ 1 Å along the polar and ~ 1.5 Å in a general direction. Differences between a structure above and below the phase transition temperature T_{trans} do not generally exceed such limits.

The systematic examination of inorganic crystal structures in all polar space groups, beginning with those listed (Abrahams, 1988) in the highest ($P6_3cm$) and followed by the listings in lower symmetry space groups, has led most recently to the analysis of all structures determined in the space group $R3$

(Abrahams, 2006, 2007). ICSD release 2007/1 contains 311 entries in the space group $P3m1$, one of six within the trigonal system, see *International Tables for Crystallography* (Vol. A, 1987; *ITA*). The 163 CdI_2 , 69 ZnS_2 and 10 SiC polytypes, most of which were determined before 1980, form the majority of such entries, see also §1.3.

1.2. Summary of prior and present results for point group 3

A total of 21 inorganic structures or families in the space group $P3$ satisfy the structural criteria for ferroelectricity (Abrahams, 2000), with 16 additional structures in the space groups $P3_1$ or $P3_2$ (Abrahams, 2003). A further 37 such candidates were identified in the space group $R3$ (Abrahams, 2006, 2007). A crystal that exhibits ferroelectricity is characteristically capable of being polarized under an electric field to form one of two or more different orientational states, with each such state changeable to the other by an appropriate field application.

Coordinate analysis of 68 individual structures reported in the space group $P3m1$, excluding most of the polytypes noted above, results in 12 families that satisfy the criteria for ferroelectricity, four of which have known family members. Each remaining structure is taken as representing a family for which its other members are not yet known. The space group $P3m1$ has four supergroups, namely $P\bar{3}m1$, $P\bar{6}m2$, $P6_3mc$ and $P6mm$; the symmetry of all but the last is approached by at least one of the structures examined hereafter. See Tables 1–12.

1.3. Polytypes in space group $P3m1$

A compound is defined as polytypic by Guinier *et al.* (1984) ‘if it occurs in several different structural modifications, each of which may be regarded as built up by stacking layers of (nearly) identical structure and composition, and if the modifications differ only in their stacking sequence’. The space group $P3m1$ contains a high percentage of polytypes, in many of which only the onefold Wyckoff positions are populated; the positive and negative ions present in such materials alternate along the c axes of unit cells having the typical dimensions $a \simeq 4$ and $c \simeq (3\text{--}3.5)n \text{ \AA}$ for $2 \leq n \lesssim 120$.

The majority of earlier polytype studies in $P3m1$ were based on model fitting to visually estimated reflection intensities from oscillation or other diffraction photographs; refinement methods were seldom used, hence the derived structures are generally without uncertainty estimates. The onefold Wyckoff positions as given are not always unique, the structure often remaining conserved under different choices of position, *cf.* §1.6. A sample may also contain related polytypes.

The determinations in §§§3.1, 3.3 and 3.4 (see Table 10), and elsewhere are representative of the CdI_2 polytype structures reported, in which Cd and I atoms with $c/2H$ separation¹ regularly alternate along the polar direction (*cf.* Palosz, 1980, 1982). Such $ABABAB\dots$ polytypes in which A represents one layer of Cd^{2+} ions and B two layers of I^- ions, are not

¹ H is the Ramsdell (1947) symbol, see Guinier *et al.* (1984).

necessarily polar and hence not candidates for ferroelectric behavior unless the structure departs from such regularity. The ZnS polytypes are only similarly sampled, see Tables 10 and 11. In view of the difficulties in detecting small atomic departures from regularity by the methods used, and findings such as Varn & Canright’s (2001) that, with the exception of the SiC polytype family (see *e.g.* Table 12), other common polytypes exhibit a ‘finite probability for the ground state to be degenerate and disordered’, polytype studies are no more than sampled in the present study.

1.4. $P3m1$ space group–supergroup relationships

The development of polarity, on heating a structure with the space group $P3m1$ through a phase transition at the ferroelectric Curie temperature T_C , is expected to result in a transformation either to the minimal non-isomorphic nonpolar supergroup $P\bar{3}m1$ or to $P\bar{6}m2$, see also §1.2. Each individual, pair or other group of related atoms in such a structure below T_C is necessarily closely related to a Wyckoff position in the resulting supergroup for all such transitions from ferroelectric to paraelectric phases. In the tables that follow, the Wyckoff position for each independent atom is given both in $P3m1$ and that expected in the appropriate supergroup. A listing of all such relevant relationships from *ITA* has been deposited in the supplementary material² to facilitate their use. Unit-cell axes are assumed to be without an integral change in length, *e.g.* from a to $n(a + \delta a)$ for n an integer at a predicted phase transition.

1.5. Structural criteria for predicting ferroelectricity

The structural criteria used in this paper for the prediction of ferroelectricity, discussed more fully elsewhere (Abrahams, 2006), are:

(i) that the total displacement $\Delta\xi_i$ of the i th atom between its location in the ferroelectric phase reported at $x_i y_i z_i$ and that in the paraelectric phase is $1.5 \gtrsim \Delta\xi_i \gtrsim 0.1 \text{ \AA}$,³ or the r.m.s. thermal or static displacement u_i of the i th atom;

(ii) that the i th atom forming the shortest least-ionic bonds in the unit cell undergoes no *polar* displacement $\Delta z_i \gtrsim 1 \text{ \AA}$ between the location $x_i y_i z_i$ and that at which the resulting spontaneous polarization $P_s \rightarrow 0$ (*i.e.* for $z_i \rightarrow z'_i$). The Curie transition temperature T_C from the ferroelectric to the paraelectric phase is related to the maximum displacement by a ‘homopolar’ metal atom forming such a bond, as given by Abrahams *et al.* (1968) and also by Kroumova *et al.* (2002).

² Supplementary data, including atomic coordinates of structures predicted to be likely new ferroelectrics in which there are more than ten independent atoms, or which exhibit other relationships, together with the atomic coordinates of all other inorganic structures reported in the space group $P3m1$ together with a brief description of each experiment and its subsequent analysis, for this paper are available from the IUCr electronic archives (Reference: BK5074). Services for accessing these data are described at the back of the journal.

³ Where each atom at x, y, z in the space group $P3m1$ is considered as displaced from its location x'_i, y'_i, z'_i in a hypothetical supergroup, with total displacement $\Delta\xi_i = [(x_i - x'_i)^2 + (y_i - y'_i)^2 + (x_i - x'_i)(y_i - y'_i) + (z_i - z'_i)^2]^{1/2}$ in a trigonal setting.

Table 1

Modified atomic positions for In_2ZnS_4 (Donika, Radautsan, Kiosse *et al.*, 1971) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å [44637] (see footnote 3).

$$a = 3.85 \text{ (2)}, c = 12.34 \text{ (6)} \text{ \AA}, z^* = z - 0.238; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{6}m2$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
In1	1(c)†	2(i)	0.6667	0.3333	-0.169	0.6667	0.3333	-0.157	0	0	-0.15	0.15	0.09
In2	1(c)		0.6667	0.3333	0.144	0.6667	0.3333	0.157	0	0	-0.16	0.16	0.09
Zn	1(a)	1(b)	0	0	0.454	0	0	0.5	0	0	-0.57	0.57	0.09
S1	1(a)	2(g)	0	0	-0.231	0	0	-0.244	0	0	0.16	0.16	0.09
S2	1(b)		0	0	0.257	0	0	0.244	0	0	0.16	0.16	0.09
S3	1(b)	1(c)	0.3333	0.6667	0.031	0.3333	0.6667	0	0	0	0.38	0.38	0.09
S4	1(b)	1(d)	0.3333	0.6667	0.516	0.3333	0.6667	0.5	0	0	0.20	0.20	0.09

† Reported $\frac{1}{3}, \frac{2}{3}, z$ coordinates for In1 in Wyckoff location 1(b) replaced by the alternate 1(c) Wyckoff location, see §2.1.3.

Table 2

Modified atomic coordinates in KSn_2F_5 (Vilminot *et al.*, 1980) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å, for $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$ [38028, 200969] (see footnote 3).

$$a = 4.06, c = 9.45 \text{ \AA}; z^* = z - 0.0311; \text{KSn}_2\text{F}_5: \text{comparable coordinates expected for the isostructural ferroelectric candidate TlSnF}_5.$$

	Wyckoff $P3m1$	Position $P\bar{3}m1$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	Occ.	u_{iso}
Sn1	1(b)	2(d)	0.3333	0.6667	0.3243 (2)	0.3333	0.6667	0.3256	0	0	-0.01	0.01	1	0.14
Sn2	1(c)		0.6667	0.3333	0.6731 (2)	0.6667	0.3333	0.6744	0	0	-0.01	0.01	1	0.14
K	1(a)	1(a)	0	0	0.019	0	0	0	0	0	0.18	0.18	1	0.13
F1	1(b)	2(d)	0.3333	0.6667	0.131 (2)	0.3333	0.6667	0.125	0	0	0.06	0.06	1	0.17
F2	1(c)		0.6667	0.3333	0.882 (2)	0.6667	0.3333	0.875	0	0	0.07	0.07	1	0.18
F3	1(a)	2(c)	0	0	0.304 (5)	0	0	0.295	0	0	0.09	0.09	0.5	0.21
F4	1(a)		0	0	0.715 (6)	0	0	0.705	0	0	0.09	0.09	0.5	0.22
F5	3(d)	6(i)	0.767 (3)	0.233 (3)	0.246 (5)	0.774	0.226	0.270	-0.03	0.03	-0.23	0.23	0.333	0.21
F6	3(d)		0.218 (3)	-0.218 (3)	0.706 (4)	0.226	0.774	0.730	-0.03	0.03	-0.23	0.23	0.333	0.21

1.6. Choice of origin in space group $P3m1$

The c axis is identifiable with any of the threefold axes in the space group $P3m1$ having x, y coordinates $0, 0; \frac{1}{3}, \frac{2}{3}$; or $\frac{2}{3}, \frac{1}{3}$. The final selection, and also the choice of z coordinate for the origin, is arbitrary but may result in pairs of atoms that approach supergroup equivalence without ready recognition. An illustrative example is provided by six members of the AMB_2 family, in which A is Li, Na, Cu or Ag, B is S, Se or Te and M is Mn, Sc or Al. The original choice of origin and sense of polar direction obscured their near-isostructural relationship, now shown very clearly in §2.5 and §S2 of the supplementary material. Origin translation has proven advisable for a number of structures considered below.

1.7. Algorithmic coordinate analysis

The methods outlined in Abrahams (2007) for detecting pseudosymmetry by structural coordinate analysis have been augmented algorithmically using locally developed software (Harvey & Abrahams, 2008). The algorithm exhaustively

analyzes each set of atomic coordinates, for structures solved and refined in a polar space group, on presentation in CIF format. The resulting critical comparison of pseudosymmetrically-associated pairs of atoms yields an output comparable to those in Tables 1–9.

1.8. Confidence in and validation of the predicted ferroelectric state

The confidence level in each of the following property predictions is necessarily a function of the structure determination reliability. Many polytypes, for example, were not well determined, see §1.3. Qualitative surrogates for the confidence level in such cases, such as structural aspects of the study that may be open to question, hence become necessary. These may include, *inter alia*, the identification of possible but previously undetected atomic locations that allow completion of a full structural approach to supergroup symmetry, see *e.g.* §4.19. Since boundaries between property classes depend on the underlying structural reliability, the possibility exists that some

Table 3

Modified atomic positions for Cu_7Te_4 (Baranova, 1967) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å [43048] (see footnote 3).

$$a = 8.28, c = 7.22 \text{ \AA}; z^* = z - 0.126; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{3}m1$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Te1	1(a)	2(c)	0	0	-0.184	0	0	-0.202	0	0	0.13	0.13	0.16
Te3	1(a)		0	0	0.220	0	0	0.202	0	0	0.13	0.13	0.16
Cu1	1(b)	2(d)	0.6667	0.3333	-0.108	0.6667	0.3333	-0.075	0	0	-0.24	0.24	0.16
Cu2	1(c)		0.3333	0.6667	0.042	0.3333	0.6667	0.075	0	0	-0.24	0.24	0.16
Te2	3(d)	6(i)	0.506	0.494	0.193	0.506	0.494	0.302	0	0	-0.79	0.79	0.16
Te4	3(d)		0.506	0.494	0.589	0.506	0.494	0.698	0	0	-0.79	0.79	0.16
Cu3	3(d)	6(i)†	0.812	0.188	0.321	0.812	0.188	0.262	0	0	0.43	0.43	0.16
Cu6	3(d)		0.188	0.812	0.797	0.188	0.812	0.738	0	0	0.43	0.43	0.16
Cu4	3(d)	6(i)†	0.188	0.812	0.394	0.188	0.812	0.329	0	0	0.47	0.47	0.16
Cu5	3(d)		0.812	0.188	0.736	0.812	0.188	0.671	0	0	0.47	0.47	0.16

† The alternative pairing of Cu3 with Cu5, also Cu4 with Cu6, resulting in $\Delta z = \Delta\xi$ magnitudes of 0.20, 0.21 and 0.69, 0.69 Å, respectively, may be noted.

Table 4

Modified atomic positions for NaMnSe_2 (Kim & Hughbanks, 1999) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å [50818] (see footnote 3).

$$a = 4.2330 (7), c = 6.9420 (6) \text{ \AA}; z^* = z - 0.0998; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{6}m2$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{33}
Mn	1(a)	1(b)	0	0	0.5260 (8)	0	0.0	0.5	0	0	0.18	0.18	0.17
Se1	1(a)	1(a)	0	0	-0.0998	0	0	0	0	0	-0.69	0.69	0.15
Se2	1(b)	1(d)	0.3333	0.6667	0.4135 (7)	0.3333	0.6667	0.5	0	0	-0.60	0.60	0.15
Na	1(c)	1(e)	0.6667	0.3333	0.160 (2)	0.6667	0.3333	0	0	0	1.11	1.11	0.13

may be open to redrawing. Validation of predicted properties similarly rests, as always, upon the provision of independent experimental evidence, see *e.g.* Abrahams (2006).

1.9. Presentation of structural analysis

The discussion of each family reported in the space group $P3m1$ by ICSD release 2007/1 and identified in §2 as a new ferroelectric candidate by atomic coordinate analysis is presented below in full, unless the structure contains more than 10 independent atoms or more than one table is provided for a family. All such larger and additional tables are presented in §4 of the supplementary material. The order of presentation throughout follows the ICSD accession number of each determination and is given in bold type. Results for the remaining structures, including those more likely to be nonpolar, have reduced predictive properties or remain stable in the space group $P3m1$ over the full thermal range, are presented with minimal explanatory material in Tables 10–12, respectively. Each such structure is discussed more fully, with

corresponding coordinate analysis, in §§5–10 of the supplementary material.

2. Predicted new inorganic ferroelectrics in space group $P3m1$

2.1. In_2ZnS_4 family⁴

2.1.1. $\text{In}_{1.53}\text{Zn}_{4.1}\text{S}_8$ [16312]. Nb-filtered Mo $K\alpha$; 666 diffractometric I_{obs} ; uncorrected for absorption and extinction; $R = 0.189$; modified 8H8-ZnS polytype (Gnehm & Niggli, 1972). All 16 independent atoms are in onefold Wyckoff locations and are nonstoichiometric. The distorted tetrahedra of S atoms form about the Zn sites, three of which are shared with In, with $2.31 \lesssim d_{\text{Zn-S}} \lesssim 2.49$ Å. The In3 site is reported to be ~10% occupied, contain no Zn and form a strongly distorted octahedron with 3 $d_{\text{In-S}} = 2.55$ and 3 at 2.77 Å, $\sigma(d_{\text{In-S}}) \simeq 0.2$ Å; Shannon's (1976) radii give $d_{\text{Zn(IV)-S}} \simeq$

⁴ Including isopointal (defined by Lima-de-Faria *et al.*, 1990) and comparable structures reported by ICSD in the same space group. Flexibility in the latter class precludes use of the precise isoconfigurational structure-type category introduced by Allmann & Hinek (2007).

Table 5

Modified atomic positions for Nb₃Br₇S (Khvorykh *et al.*, 1995) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å [81078] (see footnote 3).

$$a = 7.1012 (6), c = 6.3040 (9) \text{ \AA}; z^* = z - 0.0254; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{6}m2$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Nb	3(<i>d</i>)	3(<i>j</i>)	0.19738 (8)	0.80262	0.1972 (4)	0.19738	0.80262	0	0	0	1.24	1.24	0.08
Br1	1(<i>a</i>)	1(<i>a</i>)	0	0	-0.0254	0	0	0	0	0	-0.16	0.16	0.10
Br2	3(<i>d</i>)	3(<i>k</i>)	0.3361 (3)	0.16805	0.4256 (4)	0.3361	0.16805	0.5000	0	0	-0.47	0.47	0.11
Br3	3(<i>d</i>)	3(<i>j</i>)	0.5021 (1)	0.4979	0.9300 (5)	0.5021	0.4979	1.0000	0	0	-0.44	0.44	0.11
S	1(<i>b</i>)	1(<i>d</i>)	0.3333	0.6667	0.4725 (10)	0.3333	0.6667	0.5000	0	0	-0.17	0.17	0.08

Table 6

Modified atomic positions for Nb₃TeI₇ (Smith & Miller, 1998) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz , $\Delta\xi$ and u_{iso} displacements in Å³ [86724] (see footnote 3).

$$\text{Origin translated } +\frac{2}{3}, \frac{1}{3}, 0; a = 7.642 (1), c = 6.897 (1) \text{ \AA}; z^* = z + 0.0094; \Delta x = (x - x')a, \Delta y = (y - y')a \text{ and } \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P3m1$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Nb	3(<i>d</i>)	3(<i>f</i>)	0.53325 (9)	0.46675 (9)	0.5094	0.5	0.5	0.5	0.25	-0.25	0.06	0.26	0.10
Te	1(<i>c</i>)	2(<i>d</i>)	0.6667	0.3333	0.2109 (4)	0.6667	0.3333	0.2443	0	0	-0.30	0.30	0.10
I1	1(<i>b</i>)		0.3333	0.6667	0.7223 (3)	0.3333	0.6667	0.7557	0	0	-0.30	0.30	0.11
I2	3(<i>d</i>)		0.83605 (8)	0.16395 (8)	0.7731 (3)	0.83542	0.16458	0.7445	0.01	-0.01	0.13	0.13	0.11
I3	3(<i>d</i>)	6(<i>i</i>)	0.16522 (7)	0.83478 (7)	0.2841 (3)	0.16458	0.83542	0.2555	0.01	-0.01	0.13	0.13	0.12

2.44, $d_{\text{In(VI)-S}} \simeq 2.64 \text{ \AA}$, see also §§2.1.2 and 2.1.3. Table S1(*a*) shows that all atomic coordinates in this polytype with $c(\text{In}_{1.53}\text{Zn}_{4.1}\text{S}_8) \simeq 2c(\text{In}_2\text{ZnS}_4)$, see §2.1.3, satisfy the supergroup $P\bar{3}m1$ with $\Delta\xi \lesssim 0.57 \text{ \AA}$ and hence the criteria for ferroelectricity, *cf.* §1.5. The largest $\Delta\xi$ is related to Zn4/In2 and Zn5 with site occupancies, as also are Zn3 and In3, reported nonidentical; confirmation of the predicted property by physical measurement or structural reinvestigation is strongly advisable.

2.1.2. In_{2.02}Zn_{6.58}S₁₀ [16313]. Nb-filtered Mo $K\alpha$; 184 photometric precession film I_{obs} ; no absorption corrections; final $R = 0.265$; modified 10H10-ZnS polytype (Gnehm & Niggli, 1972). All 19 atoms present occupy onefold Wyckoff locations, with four Zn atoms reportedly sharing sites with In and forming distorted tetrahedra; In2 occupies an unshared distorted octahedron with 3 $d_{\text{In-S}}$ at 2.52, 3 at 2.77 Å and $\sigma(d_{\text{In-S}}) \simeq 0.2 \text{ \AA}$, see also §§2.1.1 and 2.1.3. Table S1(*b*) in this polytype with $c(\text{In}_{2.02}\text{Zn}_{6.58}\text{S}_8) \simeq 2.5c(\text{In}_2\text{ZnS}_4)$, see §2.1.3, shows that all atomic coordinates satisfy the supergroup $P\bar{3}m1$ within $\Delta\xi \lesssim 0.83 \text{ \AA}$, hence also the criteria for ferroelectricity with a high T_c , *cf.* §1.5. Identical site occupancy by the atomic pair with the largest $\Delta\xi$, *viz.* Zn1/In1 and Zn8, is expected but reported otherwise. As in §2.1.1, physical measurement or structural reinvestigation is strongly advisable.

2.1.3. In₂ZnS₄ [44637]. Visually estimated Mo $K\alpha$ Weissenberg films, 142 $F(0kl) > 0$, no absorption correction, B_{iso} (Donika *et al.*, 1972). Refinement of the z coordinates gave

$R = 0.167$ for a model with one In octahedrally coordinated at $d_{\text{In-S}} = 2.62 \text{ \AA}$, the other In and the Zn atom tetrahedrally coordinated with 3 $d_{\text{In-S}} = 2.25 \text{ \AA}$ and 1 $d_{\text{In-S}} = 2.47 \text{ \AA}$, *cf.* Shannon's (1976) radii in §2.1.1. If, however, In1 is located at Wyckoff location 1(*c*) in $\frac{2}{3}, \frac{1}{3}, z$ rather than at 1(*b*) in $\frac{1}{3}, \frac{2}{3}, z$ as reported, then Table 1 shows no atom to be further than 0.57 Å from fully satisfying the $P\bar{6}m2$ supergroup symmetry. Such a change, resulting in distorted octahedral coordination about both In atoms, with Zn remaining tetrahedral, has no effect on about half the $|F(hkl)|$. Coordinate uncertainties were not presented but are probably comparable to the given $u_{\text{iso}} \simeq 0.1 \text{ \AA}$. If the proposed change and the remaining coordinates can be confirmed, then the crystal would satisfy the criteria for ferroelectricity with a high likely value for T_c .⁵ If not, the structure would more likely belong to the category of Table 12.

2.2. TlSn₂F₅ and KSn₂F₅ [38028]

Prepared at 500 K, $T_{\text{trans}}(\text{TlSn}_2\text{F}_5) \simeq 358 \text{ K}$, melts at 474 K; Mo $K\alpha$ Weissenberg films, visual intensity estimates, exhibits diffuse X-ray scattering not observed in KSn₂F₅, structure closely comparable to that in Table 2 (Vilminot *et al.*, 1980). Thermally dependent nonlinear optical activity in TlSn₂F₅,

⁵ Two polytypes of In₂ZnS₄ have been reported with unit cells in which a is essentially unchanged and $c \simeq 2c'$, two others with $c \simeq 3c'$, and another with $c \simeq 6c'$, in space groups $P6_3mc$, $P\bar{3}m1$, $R3m$, $R\bar{3}m$ and $R3m$, respectively (Donika, Radautsan, Semiletov *et al.*, 1971; Donika *et al.*, 1972; Lopez-Rivera *et al.*, 2001; Lappe *et al.*, 1962; Biyushkina *et al.*, 1989).

Table 7

Modified atomic positions in $\text{Li}(\text{NpO}_2)(\text{CO}_3)(\text{H}_2\text{O})_2$ (Charushnikova *et al.*, 2004) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz and u_{eq} displacements in Å [151878] (see footnote 3).

$$a = 5.061(1), c = 6.643(1) \text{ \AA}; z^* = z + 0.0143; \Delta x = (x - x')a, \Delta y = (y - y')a \text{ and } \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{6}m2$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Np	1(c)	1(e)	0.6667	0.3333	0.0052 (8)	0.6667	0.3333	0	0	0	0.03	0.03	0.14
Li	1(a)	1(a)	0	0	-0.165 (19)	0	0	0	0	0	-1.10	1.10	0.22
O1	1(c)		0.6667	0.3333	0.283 (3)	0.6667	0.3333	0.278	0	0	0.03	0.03	0.28
		2(i)											
O2	1(c)		0.6667	0.3333	-0.272 (2)	0.6667	0.3333	-0.278	0	0	0.04	0.04	0.13
O3	3(d)	3(j)	0.628 (6)	0.814 (3)	0.012 (7)	0.628	0.814	0	0	0	0.08	0.08	0.18
O4	1(a)	1(b)	0	0	0.564 (8)	0	0	0.5	0	0	0.42	0.42	0.21
O5	1(b)	1(d)	0.3333	0.6667	0.567 (6)	0.3333	0.6667	0.5	0	0	0.43	0.43	0.20
C	1(b)	1(c)	0.3333	0.6667	0.004 (7)	0.3333	0.6667	0	0	0	0.03	0.03	0.18

Table 8

Modified atomic positions in $\text{LiPtD}_{0.66}$ (Nacken & Bronger, 1978) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz and u_{eq} displacements in Å [200045] (see footnote 3).

$$a = 2.728, c = 4.226 \text{ \AA}; z^* = z + 0.056; \Delta x = (x - x')a, \Delta y = (y - y')a \text{ and } \Delta z = (z^* - z')c.$$

	Wyckoff $P3m1$	Position $P\bar{6}m2$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	Occ.	u_{iso}
Pt	1(a)	1(a)	0	0	0.056	0	0	0	0	0	0.24	0.24	1	0.10
Li	1(b)	1(d)	0.3333	0.6667	0.556	0.3333	0.6667	0.5	0	0	0.24	0.24	1	0.05
D1	1(a)	1(b)	0	0	0.426	0	0	0.5	0	0	-0.31	0.31	0.33	0.21
D2	1(b)	1(c)	0.3333	0.6667	0.961	0.3333	0.6667	1.0	0	0	-0.16	0.16	0.33	0.23

Table 9

Modified atomic positions in $\text{Ag}_3(\text{MoO}_3\text{F}_3)(\text{Ag}_3(\text{MoO}_4)\text{Cl})$ (Maggard *et al.*, 2003) with hypothetical x', y', z' coordinates and the Δx , Δy , Δz and u_{eq} displacements in Å [413082] (see footnote 3).

$$a = 7.4488(6), c = 5.9190(7) \text{ \AA}; z^* = z + 0.02694; \Delta x = (x - x')a, \Delta y = (y - y')a \text{ and } \Delta z = (z^* - z')c. \text{ Origin translated } \frac{1}{3}\frac{1}{3}\frac{1}{3}0.$$

	Wyckoff $P3m1$	Position $P\bar{3}m1$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{eq}
Ag1†	3(d)		0.15913 (6)	0.84087	0.21994 (8)	0.1659	0.8341	0.2329	-0.05	0.05	-0.08	0.11	0.11
		6(i)											
Ag2†	3(d)		0.82731 (5)	0.17269	0.75409 (10)	0.83409	0.1659	0.7671	-0.05	0.05	-0.08	0.11	0.12
Mo1	1(b)		0.6667	0.3333	0.2638 (3)	0.6667	0.3333	0.2752	0	0	-0.07	0.07	0.09
		2(d)											
Mo2	1(a)		0.3333	0.6667	0.7135 (2)	0.3333	0.6667	0.7248	0	0	-0.07	0.07	0.10
Cl	1(c)	1(b)	0	0	0.5204 (7)	0	0	0.5	0	0	0.12	0.12	0.12
F†	3(d)	3(f)	0.4497 (3)	0.5503 (7)	0.4698 (9)	0.5	0.5	0.5	-0.37	0.37	-0.18	0.55	0.12
O1†	3(d)		0.7938 (5)	0.2062 (1)	0.1521 (12)	0.7918	0.2083	0.1560	0.01	-0.02	-0.02	0.03	0.13
		6(i)											
O2†	3(d)		0.21042 (10)	0.7897 (5)	0.8402 (12)	0.2083	0.7918	0.8440	0.02	-0.02	-0.02	0.03	0.11
O3	1(b)		0.6667	0.3333	0.5658 (18)	0.6667	0.3333	0.5523	0	0	0.08	0.08	0.12
		2(d)											
O3‡	1(a)		0.3333	0.6667	0.4611	0.3333	0.6667	0.4476	0	0	0.08	0.08	0.12

† Coordinates of the form $x, 2x, z$ replaced by the form $x, \bar{x}, 0$. ‡ O3' assumed present, see §2.12.

typical of a phase transition from $P3m1$ to $P\bar{3}m1$. With $0.01 \lesssim \Delta\xi \lesssim 0.23 \text{ \AA}$ and $0.13 \lesssim u_{\text{iso}} \lesssim 0.22 \text{ \AA}$ TiSn_2F_5 , and possibly also KSn_2F_5 , appears to be a ferroelectric candidate. Vilminot & Schulz (1988) reported $T_{\text{trans}}(\text{KSn}_2\text{F}_5) \simeq 378 \text{ K}$ with $P\bar{3}$ symmetry noted above T_{trans} . Yamada *et al.* (2004), on the basis of Mo $K\alpha$ diffractometry, absorption corrections, $T = 200 \text{ K}$, $677 I_{\text{meas}} > 2\sigma(I_{\text{meas}})$, $R = 0.040$, $wR^2 = 0.091$; also, at $T = 350 \text{ K}$, $667 I_{\text{meas}}$, $R = 0.043$, $wR^2 = 0.089$, report both KSn_2F_5 phases in space group $P\bar{3}$ with $T_{\text{trans}}(\text{KSn}_2\text{F}_5) \simeq 428 \text{ K}$ in fresh preparations; Yamada *et al.* (2004) reported T_{trans} to be time dependent and did not confirm a transition from $P3$ to $P\bar{3}$ in

KSn_2F_5 . Observation of second harmonic generation (SHG) at ambient temperature, but not above T_{trans} , despite conflicting evidence, suggests the retention of TiSn_2F_5 and, possibly, KSn_2F_5 as ferroelectric candidates until further relevant evidence is reported.

2.3. Cu_7Te_4 [43048]

Electron diffraction; 50 total $|\Phi(h0l)^2|$ estimates, eight resolved; Patterson potential projections along a and c axes; overall B ; $R = 0.26$ (Baranova, 1967). The Cu_7Te_4 structure is

Table 10

Structures reported in space group $P3m1$ that are as likely nonpolar (related synopses and tables deposited in supplementary materials, see footnote 2).

§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Phase transition restrictions and footnotes
3.1	32H-CdI ₂	Prasad & Srivastava (1970), Pałosz (1980)	6279	S8	All $\Delta\xi(I) = 0$; all $\Delta\xi(Cd) = 1.68$	Undetermined	$\bar{P}6m2$	All 32 I, also all 16 Cd, atom coordinates satisfy $\bar{P}6m2$ exactly with all Cd displaced $c/64^{(1)}$
3.2	NaLiZnO ₂	Hoppe (1983)	40458	S9	$0.0 \lesssim \Delta\xi \lesssim 0.01$	$0.06 \lesssim u_{33} \lesssim 0.11$	$\bar{P}3m1$	All coordinates satisfy $\bar{P}3m1^{(2)}$
3.3	16H ₁₂ -CdI ₂	Sarna <i>et al.</i> (1984)	49572	S10	All $\Delta\xi(I) = 0$; all $\Delta\xi(Cd) = 1.68$	Undetermined	$\bar{P}6m2$	With a changed onefold Wyckoff position for two of a total 16 I and one of a total 8 Cd atoms ⁽³⁾
3.4	22H ₁₁ -CdI ₂	Sarna <i>et al.</i> (1984)	49574	S11	All $\Delta\xi(I) = 0$; all $\Delta\xi(Cd) = 1.71$	Undetermined	$\bar{P}6m2$	Coordinates of all 22 I atoms satisfy $\bar{P}6m2$ exactly, as also all 11 Cd atoms with $z' = z + 1/44^{(4)}$
3.5	12L-ZnS	Kiflawi & Mardix (1970)	107137	S12	All $\Delta\xi(S) = 0$; all $\Delta\xi(Zn) = 0.78$	Undetermined	$\bar{P}3m1$	With $z[Zn12]$ assumed 0.1 larger than reported, also $z' = z - 1/48$ for all 12 S atoms ⁽⁵⁾
3.6	Pb ₁₇ Nb ₁₇ O _{59.5}	Bernotat-Wulf & Hoffmann (1981)	17039	S13	$0.06 \lesssim \Delta\xi(Nb,Pb) \lesssim 0.29$; $0.03 \lesssim \Delta\xi(O) \lesssim 0.94$	$0.07 \lesssim u_{iso} \lesssim 0.29$	$\bar{P}3m1$	Coordinates of all 18 Nb and Pb, also 20 of the 28 O, atoms satisfy $\bar{P}3m1$ symmetry within $\Delta\xi \lesssim u_{iso}^{(6)}$
3.7	6H-PbI ₂	Mitchell (1959)	24264	S14	All $\Delta\xi(Pb)$, $\Delta\xi(I) = 0$	Undetermined	$\bar{P}3m1$	Coordinates of all 3 Pb and 6 I atoms satisfy $\bar{P}3m1$ exactly ⁽⁷⁾
3.8	(Cd _{0.5} Pb _{0.5}) ₃ -OSiO ₄	Eysel & Breuer (1983)	36480	S15	$0.08 \lesssim \Delta\xi \lesssim 0.46$	Undetermined	$\bar{P}6m2$	Assuming both O4 and O6 are in Wyckoff positions 1(b) or 1(c) instead of 1(a) as reported ⁽⁸⁾
3.9	Cu _{0.8} Ag _{0.96} Te	Avilov <i>et al.</i> (1974)	41905	S16	$0.0 \lesssim \Delta\xi \lesssim 1.06$	$0.13 \lesssim u_{eq} \lesssim 0.22$	$\bar{P}3m1$	Electron diffraction study; 32 of 36 independent atoms satisfy criteria; 4 have $2.16 \lesssim \Delta\xi \lesssim 2.65$ Å ⁽⁹⁾
3.10	Cu _{1.81} Te	Baranova <i>et al.</i> (1973)	42156	S17	$0.02 \lesssim \Delta\xi \lesssim 1.39$	0.16 for all atoms	$\bar{P}3m1$	Electron diffraction study. Three additional Cu of a total 26 Cu, 2 Te of a total 12 Te, are assumed ⁽¹⁰⁾
3.11	Cu _{0.45} In _{3.17} Se ₅	Gulay <i>et al.</i> (2004)	54750	S18	$0.0 \lesssim \Delta\xi \lesssim 0.17$	$0.09 \lesssim u_{eq} \lesssim 0.17$	$\bar{P}6m2$	Assuming the reported $z(\text{Se}2)$ to be in error ⁽¹¹⁾
3.12	BaTiO _{2.67}	Woodward <i>et al.</i> (2004)	54785	S19	All $\Delta\xi \lesssim 1.30$ except N3	Undetermined	$\bar{P}3m1$	All coordinates and occupancies were assumed, not refined ⁽¹²⁾
3.13	BN	Kupčik <i>et al.</i> (1994)	56315	S20	All except N3	$0.04 \lesssim u_{eq} \lesssim 0.05$	$F\bar{4}3m$	Pseudo-hexagonal symmetry, nonpolar twin-model refined ⁽¹³⁾
3.14	Si ₆ H ₃ (OH) ₃	Dettlaff-Weglikowska <i>et al.</i> (1997)	56605	S21	$0.30 \lesssim \Delta\xi \lesssim 1.17$	Undetermined	$\bar{P}6m2$	$z(\text{Si},\text{O})$ refined with 18 $F(hk0)$, H (x,y,z) assumed, not refined ⁽¹⁴⁾
3.15	Al ₅₁ Ca ₄ Cr ₇ †	Czech <i>et al.</i> (1984)	57537	S22	$0.0 \lesssim \Delta\xi \lesssim 0.98$	$0.01 \lesssim u_{eq} \lesssim 0.15$	$\bar{P}6m2$	Assuming one or more undetermined Cr atoms and exchange of x and y for one Al atom ⁽¹⁵⁾
3.16	Ca _{0.95} Li _{1.05} S	Müller & Voltz (1974)	58911/ 107334	S23	All $\Delta\xi \lesssim 0.07$ except $\Delta\xi(\text{Li}6) \simeq 0.45$	Single unstated overall u_{iso}	$\bar{P}6m2$	Assuming $z(\text{Li}6) = 0.5$, then all $\Delta\xi \lesssim 0.01$ Å ⁽¹⁶⁾
3.17	YBa ₂ Cu ₃ O _{6.5}	Li <i>et al.</i> (1989)	68420	S24	$0.02 \lesssim \Delta\xi \lesssim 0.26$	$0.06 \lesssim u_{eq} \lesssim 0.15$	$\bar{P}3m1$	HREM suggests Cu and Y ordering leads to $\bar{P}3m1$, unequal occupation to $\bar{P}3m1^{(17)}$
3.18	BiTeI	Shevelkov <i>et al.</i> (1995)	79364	S25	$0.06 \lesssim \Delta\xi \lesssim 0.13$	$0.12 \lesssim u_{eq} \lesssim 0.16$	$\bar{P}3m1$	$R = 0.054$ in $\bar{P}3m1$ versus a 1993 value of $R = 0.075$ in $\bar{P}3^{(18)}$
3.19	YH _{0.667}	Garces <i>et al.</i> (2005)	152861	S26	$0.22 \lesssim \Delta\xi \lesssim 0.51$	Undetermined	$\bar{P}6m2$	Sense of all $\Delta z(\text{Y})$ opposite that of all $\Delta z(\text{H})$. Model may be in error ⁽¹⁹⁾
3.20	Eu ₈ I ₉ (CN)(NCN) ₃	Liao & Dronskowski (2006)	172030	S27	$0.07 \lesssim \Delta\xi \lesssim 1.58$	$0.13 \lesssim u_{eq} \lesssim 0.19$	$\bar{P}6m2$	Criteria for ferroelectricity not met by N1, Eu4 or I2 ⁽²⁰⁾

(1) Although a full $c/64$ Å displacement by all Cd atoms would result in an unlikely planar trigonal coordination, the resulting $\bar{P}6m2$ symmetry together with extensive but unassigned diffuse scattering places the analysis in doubt. Notably, onefold Wyckoff position reassignment for four I and three Cd atoms does not change the resulting interatomic distances. (2) Translation of the origin by $\frac{1}{2}c, 0$ reveals a centrosymmetric atomic arrangement. (3) The three onefold Wyckoff position changes are without effect on the interatomic distances. (4) Supergroup $\bar{P}6m2$ symmetry is fully satisfied by the I atoms, also by the Cd atoms under a $c/44$ Å displacement. Reassignment of onefold Wyckoff positions for the Cd₂Cd10 and Cd₃Cd9 pairs has no effect on the interatomic distances, see also footnote (1). (5) In addition, a different onefold Wyckoff position is assigned to three Zn and four S atoms; following redetermination by current methods, both $\bar{P}3m1$ and the alternative possibility of $\bar{P}6m2$ as the supergroup should be investigated. (6) Except for the O9/O18, O14/O15 pairs with $\Delta\xi \simeq 0.9, 0.4$ Å in addition to the O25/O28 pair for which $\Delta\xi \simeq 0.6$ Å, with $u_{iso} \simeq 0.3$ Å, also atoms O24 and O27. The latter two may be related to unreported atoms O24' and O27'; further, the atoms designated as 'Nb6' and 'Pb6' may have been misidentified as Pb6 and Nb6. (7) The change in Wyckoff positions reported for Pb2 and I3 has no effect on the interatomic distances. (8) (Cd_{0.5}Pb_{0.5})OSiO₄ is reported as undergoing a phase transition from low ($P1$) to high ($\bar{P}3m1$) symmetry at 1013 K, also as not being a true compound but a solid solution of the formula (Cd_{1-x}Pb_x)₃O[SiO₄]. (9) Assuming two atoms in error with corrected coordinates and a third, assumed overlooked, atom. (10) Closely related to Cu_{0.8}Ag_{0.96}Te, see §3.9, atoms in both electron diffraction studies may have been overlooked and the space group misassigned. (11) The space group was probably misassigned. (12) Full structure determination required for definitive results. (13) R could not be reduced below ~ 0.2 for a model in the space group $\bar{P}3m1$, but gave $R = 0.053$ on refinement as for cubic borazone. (14) The given coordinates proposed clearly approach $\bar{P}6m2$ symmetry; a full structure determination with improved H atom location is required for definitive results, see Tables S21(a,b). (15) All atoms except Al4, Al6, Cr11 and Cr2 deviate less than 0.98 Å from nonpolar symmetry. (16) As reported, Li6 is too close to Ca1; if $z(\text{Li}6)$ is located as proposed, the space group becomes indistinguishable from $\bar{P}6m2$. (17) Occupancies of 0.7 were assumed for each O site with an exchange of Cu and Y in the $\bar{P}3m1$ cell, but the HREM investigation was only qualitative;

Table 10 (continued)

$P\bar{3}m1$ requires identical occupation at Cu3 and Y sites. (18) The centrosymmetric structure in Table S25 shows the earlier choice of $P3m1$ is dubious. Powder patterns for the two space groups are very similar, hence further investigation of BiTeI is required. (19) Model assumed in a study of the Fermi surface and H ordering. If the structure is experimentally justifiable, it would meet the criteria for ferroelectricity. (20) Lighter atoms present may be misassigned due to the influence of the four independent Eu and three I atoms, but with I2 and Eu4 displacements of ~ 1.4 Å, further structural study is advisable. † Formula stated as $Al_{48}Ca_4Cr_7$ corresponds to that offered by ICSD.

related both to that of $Cu_{0.8}Ag_{0.96}Te$, cf. §3.9, and $Cu_{1.81}Te$, cf. §3.10, with similar a axes and x, y coordinates, but $c(Cu_7Te_4) \simeq c(Cu_{0.8}Ag_{0.96}Te, Cu_{1.81}Te)/3$. Table 3 shows an approach by the structure of Cu_7Te_4 to $P\bar{3}m1$ supergroup symmetry, with $\Delta\xi_{\max} \lesssim 0.80$ Å for the ten independent atoms, cf. Tables S17 and S18. Although the criteria for ferroelectricity are met, the confidence level of this prediction is diminished by the low ratio of data-to-parameters varied.

2.4. LiMnSe₂ family

2.4.1. LiMnSe₂ [50817]. Mo $K\alpha$, single-crystal diffractometry, ψ -scan absorption corrections, 113 independent $I(hkl) > 2\sigma I(hkl)$ at 293 K, U^{ij} , $R = 0.051$, $wR^2 = 0.1044$, Flack parameter $x = 0$ (Kim & Hughbanks, 1999), unlocated Li atom. Mn, Se1 and Se2 satisfy the symmetry of the supergroup $P\bar{6}m2$ with $\Delta\xi_{\max} \lesssim 0.52$ Å and $u_{33} \simeq 0.15$ Å, see Table S2(a). The apparent lack of opposed-polarity domains in the crystal studied suggests nonpolar rather than polar symmetry; if confirmed, the material could not be ferroelectric. However, both a formation temperature above 1275 K and the possibility of a moderately high T_C are consistent with the $\Delta\xi_{\max}$ magnitude. Calorimetric and/or dielectric investigation is necessary for confirmation.

2.4.2. LiMnTe₂ [unlisted, ICSD release 2007-1]. Mo $K\alpha$, single-crystal diffractometry, ψ -scan absorption corrections, 164 independent $I(hkl) > 4\sigma I(hkl)$, $R = 0.0501$, $wR^2 = 0.0918$ at 293 K, U^{ij} , Flack parameter not reported (Kim *et al.*, 1998). The atomic coordinates are closely comparable to those in §2.4.1 with $\Delta\xi_{\max} \simeq 0.57$ Å and $u_{33} \simeq 0.15$ Å, see Table S2(b). If the structure determination proves to be confirmable, then LiMnTe₂ satisfies the criteria for ferroelectricity.

2.4.3. NaMnSe₂ [50818]. Mo $K\alpha$, ψ -scan absorption correction, 143 independent $I(hkl) > 2\sigma I(hkl)$, $R = 0.0474$, $wR^2 = 0.0937$, Flack parameter $x = 0$ (Kim & Hughbanks, 1999). Values of $d_{Mn-Se} \simeq 2.58$ Å in LiMnSe₂ are similar to those in §2.4.1. All four independent atoms satisfy the symmetry of the supergroup $P\bar{6}m2$, with $\Delta\xi_{\max} \lesssim 1.11$ Å, see Table 4; since $u_{33} \simeq 0.15$ Å, the criteria for ferroelectricity are satisfied, noting however that ξ_{\max} appears to exceed the maximum expected polar displacement, cf. §1.5. The large $\Delta\xi_{\max}$ associated with such a transition to a nonpolar space group would require an elevated, but possible, T_C in view of $T > 1125$ K at preparation. The reported lack of opposite-polarity domains, as in §2.4.1, is again suggestive of nonpolarity.

2.4.4. NaMnTe₂ [Unlisted, ICSD release 2007-1]. Mo $K\alpha$, single-crystal diffractometry, ψ -scan absorption correction, 232 independent $I(hkl) > 4\sigma I(hkl)$, $R = 0.0341$, $wR^2 = 0.0795$ at 293 K, U^{ij} , Flack parameter not reported (Kim & Hughbanks,

1999). Translation of the origin by $\frac{2}{3}\frac{1}{3}1 - z$ as in Table S2(c) reveals a structure very similar to that in Tables 4 and S2(a, b), with $\Delta\xi_{\max} \simeq 1.25$ Å and $u_{33} \simeq 0.15$ Å; the criteria for ferroelectricity are again satisfied, with high expected T_C . Dielectric and/or calorimetric investigation of the §2.4 family is again appropriate.

2.4.5. CuScS₂ [15298]. Zr-filtered Mo $K\alpha$; absorption correction; overall u_{iso} , 91 $F_{obs}(hkl)$ with $l = 0, 1$ and 2 , $R = 0.087$ (Dismukes *et al.*, 1971). Semiconductor, band gaps at 2.30 and 1.8 eV. Application of a $\frac{2}{3}\frac{1}{3}0.1103$ origin translation reveals that the atomic coordinates in Table S2(d) bear a strong family resemblance to those in Table 4, with no atom further than ~ 0.85 Å from satisfying a onefold Wyckoff location in the space group $P\bar{6}m2$, see Table S2(d), hence also the conditions for ferroelectricity. The corresponding T_C is expected to be high but possible, given the 1325 K preparation temperature. Dielectric investigation remains appropriate.

2.4.6. II-AgAlS₂ [25356]. Prepared from chalcopyrite (I-AgAlS₂) at 25 kbar and 575 K, absorption-corrected Cu K X-ray powder $I(00l)$, trial-and-error determination, u_{iso} not varied, $R(I) = 0.083$ (Range *et al.*, 1974). The Al atom occupies a distorted octahedron with all $d_{Al-S} = 2.388$ Å, Ag a highly distorted tetrahedron with $1 \times d_{Ag-S} = 2.46$ Å, $3 \times d_{Ag-S} = 2.73$ Å; Shannon's (1976) radii give $d_{Al-S} = 2.38$ Å, $d_{Ag-S} = 2.84$ Å. As with Table S2(d), an origin translation by $\frac{2}{3}\frac{1}{3}1 - z$ reveals a strong family resemblance between the coordinates in Table S2(e) and those in Table 4. Each atom is close to a onefold Wyckoff location in the space group $P\bar{6}m2$, but with departures of the independent S atoms as large as 1.34 Å along the polar axis. Such departures exceed the limit in §1.5 and may also exceed the thermal stability range, but the material remains worthy of further investigation.

2.5. Na₂In₂(Mo₃O₈)(MoO₄)₂ [65821]

Mo $K\alpha$ diffractometry, 1111 independent $F_{obs}^2 \geq 3\sigma(F_{obs}^2)$, decay, absorption and extinction corrections, U^{ij} , site occupancies, $R = 0.035$ in $P3m1$, 0.106 in $P\bar{3}m1$ (Collins *et al.*, 1989). All atoms satisfy the supergroup $P\bar{3}m1$ symmetry with $\Delta\xi \lesssim 0.05$ Å, except for the O4, O8 pair for which $\Delta\xi \simeq 0.26$ Å, see Table S3. Both In atoms occupy slightly distorted octahedra, two Mo form tetrahedra and Mo3 a strongly distorted octahedron. Na1 is also octahedral with $d_{Na-O} = 3 \times 2.48$, 3×2.51 Å, while Na2 and Na3 occupy strongly distorted tetrahedra with $d_{Na-O} \lesssim 2.6$ Å. The criteria for ferroelectricity are hence fulfilled by this structure with the largest $\Delta\xi \simeq 0.26$ Å by the O4, O8 pair, suggestive of a moderate T_C value.

Table 11
Structures reported in space group $P3m1$ with reduced predictive properties.

§§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Phase transition restrictions and footnotes
4.1	CdGaInS ₄	Mekhtiev <i>et al.</i> (1977), Kyazimov & Amiraslanov (1983)	2465 20785	S28	$0.03 \lesssim \Delta\xi \lesssim 0.50$	Undetermined	$P\bar{6}m2$ $P\bar{3}m1$	Choice of $P3m1$ space group is likely inappropriate; the polytype determination of 1983 with $2 \times c$ -axis reported space group $P\bar{3}m1^{(1)}$
4.2	12H ₆ -CdI ₂	Chadha (1974)	6066	S29	All $\Delta\xi = 0$	Undetermined	$P\bar{3}1c$	Assuming incorrect onefold Wyckoff positions for 3 Cd and 2 I atoms, space group misassignment is likely ⁽²⁾
4.3	(a) 24L-ZnS (b) 12L-ZnS	Brafman <i>et al.</i> (1967), Mardix <i>et al.</i> (1967) Kiflawi & Mardix (1970)	15738 107137	S30(a) S30(b)	All $\Delta\xi = 0$	Undetermined	$P\bar{6}m2$ $P\bar{3}m1$	(a) assuming $z(S_i) = z(\text{Zn}_i) + 1/32$, the likely space-group symmetry is fully satisfied; (b) reducing all $z(S_i)$ by 1/48 fully satisfies $P\bar{3}m1$ symmetry ⁽³⁾
4.4	8H8-In _{1.53} Zn _{4.1} S ₈	Gnehm & Niggli (1972)	16312	S31	$0.01 \lesssim \Delta\xi \lesssim 0.16$ for all atoms except Zn1, In and Zn8 with $\Delta\xi = 0.83$	All $u_{\text{iso}} = 0.08$	$P\bar{3}m1$	Space group is likely to be misassigned, with further study advisable ⁽⁴⁾
4.5	K ₂ NaUCl ₆	Aurov <i>et al.</i> (1983)	20914	S32	All $\Delta\xi = 0$	Undetermined	$P\bar{3}m1$	Alternative onefold Wyckoff locations for K4, K6 lead to space group $P\bar{3}m1^{(5)}$
4.6	KNaSO ₄	Okada & Ossaka (1980)	26014	S33	$0.01 \lesssim \Delta\xi \lesssim 0.09$ for all atoms	$0.10 \lesssim u_{\text{iso}} \lesssim 0.28$	$P\bar{3}m1$	Space group most likely misassigned ⁽⁶⁾
4.7	I-K ₂ LiAlF ₆	Winkler (1954), Graulich <i>et al.</i> (1998)	27672	S34	All $\Delta\xi = 0$ except 4 K and 4 F atoms with $ \Delta\xi_{\text{exp}} \simeq 1.10$ Å	Undetermined	$P\bar{3}m1$ $R\bar{3}m$	Early structure approaches $P\bar{3}m1$; later study reports a doubled c axis ⁽⁷⁾
4.8	LiYMo ₃ O ₈ LiScMo ₃ O ₈ LiInMo ₃ O ₈	de Benedittis & Katz (1965), McCarroll (1977)	28525 28526 30579	S35	$0.03 \lesssim \Delta\xi \lesssim 0.30$	Undetermined	$P\bar{6}m2$	Assuming O1 is in Wyckoff position 1(c) instead of 1(a), space group likely to be misassigned ⁽⁸⁾
4.9	β -CuI	Kurdyumova & Baranova (1961) Sakuma (1988) Keen & Hull (1994, 1995)	30363 84217 78429 80230	S36(a) S36(b) S36(c) S36(d)	$0.061 \lesssim \Delta\xi \lesssim 0.92$	$0.23 \lesssim u_{\text{iso}} \lesssim 0.44$	$P\bar{6}m2$	ED study gave incorrect unit cell; XRD study approaches $P\bar{6}m2$; ND study places β -phase in $P\bar{3}m1$, with Cu disordered ⁽⁹⁾
4.10	BaVO _{2.5}	de Beaulieu & Müller-Buschbaum (1982)	32657	S37	$0.02 \lesssim \Delta\xi \lesssim 0.16$	$0.01 \lesssim u_{\text{iso}} \lesssim 0.26$	$P\bar{6}m2$	Space group most likely misassigned; further study advisable ⁽¹⁰⁾
4.11	Na(Cu _{0.67} Fe _{0.22} -Zn _{0.11}) ₂ S ₂	Kaplunnik <i>et al.</i> (1990)	39255	S38	$\Delta\xi \lesssim 0.01$	$0.06 \lesssim u_{\text{eq}} \lesssim 0.14$	$P\bar{3}m1$	Space group most likely to be misassigned ⁽¹¹⁾
4.12	T'-Cr _{0.68} Se	Wehmeier <i>et al.</i> (1970)	42703	S39	All $\Delta\xi = 0$	Undetermined	$P\bar{3}m1$	Space group is most likely to be misassigned ⁽¹²⁾
4.13	Fe ₁₀ O ₁₄ (OH) ₂	Eggleton & Fitzpatrick (1988) Michel <i>et al.</i> (2007)	56287 unlisted	S40	$0.12 \lesssim \Delta\xi \leq 0.31$ centrosymmetric	Undetermined $0.08 \lesssim u_{\text{iso}} \lesssim 10$	$P\bar{3}m1$ $P6_3mc$	Initial space group most likely misassigned; pair distribution function of total X-ray scattering gives improved fit in $P\bar{6}_3mc^{(13)}$
4.14	CoGaInS ₄	Depero <i>et al.</i> (1991) Haeuseler <i>et al.</i> (1990)	86413 86414 69015	S41(a) S41(b) S41(c)	$0.01 \lesssim \Delta\xi \lesssim 0.02$	$0.13 \lesssim u_{\text{iso}} \lesssim 0.14$	$P\bar{3}m1$ $P\bar{3}m1$	The highly likely space-group misassignment is confirmed on origin translation ⁽¹⁴⁾ Centrosymmetry determined
4.15	LaNdO _{1.75} S	Kuz'micheva <i>et al.</i> (1980)	86550	S42	$0.07 \lesssim \Delta\xi \lesssim 0.12$	$0.02 \lesssim u_{\text{iso}} \lesssim 0.09$	$P\bar{3}m1$	Space group most likely misassigned ⁽¹⁵⁾
4.16	Cs ₃ Sb ₂ I ₉	Arakcheeva <i>et al.</i> (1999)	89694 89695	S43	$0.03 \lesssim \Delta\xi \lesssim 0.18$	$0.18 \lesssim u_{\text{iso}} \lesssim 0.28$	$P\bar{3}m1$	Space group most likely misassigned ⁽¹⁶⁾
4.17	Ba(Fe _{0.5} Ta _{0.5})O ₃	Li <i>et al.</i> (2004)	99484	S44	$0.04 \lesssim \Delta\xi \lesssim 0.10$	Undetermined	$P\bar{3}c1$	Space group most likely misassigned ⁽¹⁷⁾
4.18	AlCuMg	Komura (1962)	109103	S45	All $\Delta\xi = 0$	Undetermined	$P\bar{6}m2$	Space group most likely misassigned ⁽¹⁸⁾
4.19	CuCeSnD _{0.33} CuLaSnD _{0.47}	Maehlen <i>et al.</i> (2005)	152855 152857	S46(a) S46(b)	$0.03 \lesssim \Delta\xi \lesssim 0.26$	$0.04 \lesssim u_{\text{iso}} \lesssim 0.10$	$P\bar{3}m1$	Space group of both materials most likely misassigned ⁽¹⁹⁾
4.20	Ni ₂ H	Khodyrev <i>et al.</i> (1978)	201088	S47	$0.00 \lesssim \Delta\xi \lesssim 0.01$	$u_{\text{iso}} = 0.28$	$P\bar{3}m1$	Space group most likely misassigned ⁽²⁰⁾

(1) 1977 results are consistent with a space group that more likely corresponds to that reported by Kyazimov & Amiraslanov (1983) for the polytype with $c' \simeq 2c$. (2) With Cd1, Cd5, Cd6 also I6, I8 in alternative onefold Wyckoff positions, all atoms exhibit $P\bar{3}1c$ symmetry. (3) Both ZnS₄ and SZn₄ tetrahedra in the 24-L polytype have $d_{\text{Zn-S}} \simeq 2.346$ Å. The 24-L and the 12-L polytypes become fully centrosymmetric on modifying the reported z coordinates as noted. (4) If structural reinvestigation supports the pseudosymmetry noted, then the material would become a candidate for ferroelectricity. (5) Assuming K₂NaUCl₆ is isostructural with K₂NaAlF₆, an alternate Wyckoff onefold location choice for two K atoms leads to fully satisfying $P\bar{3}m1$ symmetry. Graulich *et al.* (1998) later reported K₂LiAlF₆ in a unit cell with doubled c axis and the space group $R\bar{3}m$. (6) Structural redetermination may be expected to confirm $P\bar{3}m1$ symmetry. (7) The 1998 study reports rhombohedral centrosymmetry, with a doubled c -axis unit cell. (8) Further structural study is advisable to locate the Li atom unambiguously, a result that might place this structure in Table 12. Sm and In isomorphously replace Y. (9) Cu disorder over two sites. Second neutron diffraction study confirms the

Table 11 (continued)

formation of β -CuI at 647 K in the space group $P\bar{3}m1$. (10) $P\bar{6}m2$ is the more likely space group at the (unstated, probably ambient) determination temperature. (11) Origin displacement of $\frac{2}{3}, -0.2332$ shows that the space group is most likely $P\bar{3}m1$. (12) The T' -phase, reported as 'conveniently but not exclusively described in the space group $P\bar{3}m1$ ' should clearly be reassigned to $P\bar{3}m1$. (13) Direct Fourier transformation of total X-ray scattering reveals a unit cell with doubled a axis and hexagonal symmetry. (14) The X-ray and neutron studies in Tables 42(b, c) are shown to confirm, under origin translation, the earlier choice of space group $P\bar{3}m1$. (15) Assuming equal occupation of the La and Nd sites by both atoms, with all $\Delta\xi \lesssim 0.12$ Å and comparable u_{iso} , the space group is most likely $P\bar{3}m1$. (16) The authors note the lack of second-harmonic generation favors the space group $P\bar{3}m1$; together with the present analysis, the noncentrosymmetric option may be eliminated. (17) Since u_{iso} is likely comparable to $\Delta\xi_{\text{max}}$, the higher symmetry of the space group $P\bar{3}c1$ is more probable. (18) Assigning alternative Wyckoff positions to four atoms results in a perfect fit to $P\bar{6}m2$ symmetry. (19) Assuming an overlooked D atom in Wyckoff position 1(b), $P\bar{3}m1$ symmetry is more likely; other aspects of this and the CeCuSnD_{0.33} determinations remain questionable. (20) With $u_{\text{iso}} \gg \Delta\xi$ for all atoms, structural redetermination is expected to confirm $P\bar{3}m1$ symmetry.

2.6. Nb₃Br₇S [81078]

Prepared at ~ 1075 K, Mo $K\alpha$ diffractometry, ψ -scan absorption correction, 481 independent $F_{\text{obs}} \geq 6\sigma(F_{\text{obs}})$, U^{ij} , $R = 0.0395$ (Khvorykh *et al.*, 1995). The S and five Br atoms form distorted octahedra around Nb with $d_{\text{Nb-Br}} = 2.54\text{--}2.80$ Å. All atoms satisfy the symmetry of supergroup $P\bar{6}m2$ with the largest displacement $\Delta\xi(\text{Nb}) = 1.24$ Å for $0.08 \lesssim u_{\text{iso}} \lesssim 0.11$ Å. The criteria for ferroelectricity are hence satisfied, see Table 5. If this structure with its large polar displacement is verifiable, see §1.5, it is expected to be ferroelectric with high T_C .

2.7. Nb₃TeI₇ family

2.7.1. Nb₃TeI₇ [86724]. Prepared at 925 K, Mo $K\alpha$ diffractometry, 283 independent $F_{\text{obs}} \geq 4\sigma(F_{\text{obs}})$, absorption corrections, U^{ij} , $R = 0.0264$, $wR = 0.0588$ (Smith & Miller, 1998). An origin translation of $\frac{2}{3}, \frac{1}{3}, 0$ as in Table 6 reveals an approach by all atoms to the symmetry of the supergroup $P\bar{3}m1$, with $\Delta\xi_{\text{max}} \simeq 0.30$ Å assuming both Te and I sites (atomic numbers 52 and 53) to be equally occupied. Since $u_{\text{iso}} \lesssim 0.12$ Å, Nb₃TeI₇ then satisfies the criteria for ferroelectricity. The central Nb notably occupies a distorted edge-sharing octahedron of five apical I and one Te atom, with $d_{\text{Nb-Te}} = 2.71$, $d_{\text{Nb-I}} = 2.74$ Å. Smith & Miller (1998) also reported a polytype of Nb₃TeI₇, with doubled c axis and space group $P6_3mc$, a supergroup of $P\bar{3}m1$.

2.7.2. Ta_{1.34}Nb_{1.66}TeI₇ [92517]. Prepared at 725 K, annealed at 820 K, Mo $K\alpha$ diffractometry, 320 independent $F_{\text{obs}} \geq 2\sigma(F_{\text{obs}})$, absorption corrections, U^{ij} , $R = 0.0228$, $wR = 0.0603$ (Smith & Miller, 2000). All comparable coordinates in Nb₃TeI₇ and Ta_{1.34}Nb_{1.66}TeI₇ are very similar, assuming an origin difference of $c/4$ and noting the replacement of I3(x) in Table 6 by the corresponding 6(i) location for I2 at $\sim 2x$ in Table S4(a). The effect of partially replacing Nb by Ta is hence minor, on the approach to supergroup $P\bar{3}m1$ symmetry, for which $\Delta\xi_{\text{max}} \lesssim 0.30$ Å in the former and $\lesssim 0.27$ Å in the latter, or on the comparable values of T_C in each material, assuming both can be confirmed as polar.

2.7.3. Ta_{0.86}Nb_{2.14}TeI₇ [92518]. Prepared at ~ 725 K, Mo $K\alpha$ diffractometry, 317 independent $F_{\text{obs}} \geq 2\sigma(F_{\text{obs}})$, absorption corrections, U^{ij} , $R = 0.0232$, $wR = 0.0552$ (Smith & Miller, 2000). The cell dimensions and atomic coordinates of this alloy of Nb and Te, as in §2.7.2(b), become comparable to those in Table 6 following an origin translation of $c/4$ and interchange of I2 and I3. The resulting coordinates in Table S4(b), as in Table S4(a), approach the symmetry of supergroup

$P\bar{3}m1$ with $\Delta\xi_{\text{max}} \lesssim 0.27$ Å and $u_{\text{iso}} \lesssim 0.12$ Å. Hence, if Ta_{0.86}Nb_{2.14}TeI₇ is confirmed as polar, it is most likely ferroelectric, see also §§2.7.1 and 2.7.2. Four additional closely related variants of Ta_xNb_{3-x}TeI₇ have been reported by the authors.

2.8. C₂H_{3.38}Ba₆Cl_{1.62}Fe₃O_{31.38}Si₈, fencooperite [92798]

Mo $K\alpha$ diffractometry, 1335 independent $F_{\text{obs}} \geq 4\sigma(F_{\text{obs}})$, absorption corrections, U^{ij} , $R = 0.038$, $wR^2 = 0.091$ (Grice, 2001). All fencooperite atoms listed in Table S5 satisfy the symmetry of supergroup $P\bar{6}m2$ within $\Delta\xi \lesssim 0.11$ Å, except those in the independent CO₃²⁻ ions, *viz.* the C1,C2 pair with $\Delta\xi \simeq 0.35$ Å and the O8,O9 pair with $\Delta\xi \simeq 0.85$ Å and $u_{\text{iso}} \lesssim 0.22$ Å. The structure would hence satisfy the criteria for ferroelectricity if all ionic dimensions in such a phase transition were to remain normal. Refinement in $P\bar{6}m2$, based on the ambient temperature data, results in $R = 0.051$ with $d_{\text{C-O}} = 1.451$ Å, O—C—O = 96.1° (Grice, 2007), whereas refinement in $P\bar{3}m1$ confirms the indicators above with $d_{\text{C1-O8, C2-O9}} = 1.293, 1.302$ Å and both O—C—O = 119.9°, *i.e.* very comparable to $d_{\text{C-O}} = 1.293$ Å, O—C—O = 120° in *e.g.* calcite. If a phase transition in fencooperite were detectable at $T_C > T_{\text{ambient}}$, the resulting O8,O9 coordinates would be expected to differ significantly from those in Table S5, with such a T_C marking the onset of the ferroelectric state.

2.9. Bi(HCOO)₃ [151262]

Mo $K\alpha$ visually estimated Weissenberg I_{obs} , Patterson sections, 513 independent $F(hkl)$, β_{ij} , $R = 0.053$ (Stålhandske, 1969). The resulting structure, see Table S6, approaches the symmetry of supergroup $P\bar{3}1m$ with $\Delta\xi_{\text{max}} \simeq 0.8$ Å for 4 O atoms, all $u_{\text{iso}} \lesssim 0.26$ Å and a resulting T_C that may exceed the thermal phase stability. The Bi atoms form highly distorted octahedra with $\langle d_{\text{Bi-O}} \rangle = 2.45$ Å and average independent angle O—C—O = 120.8 (3.8)°; the latter is close to normal, indicative of an appropriate solution. Dielectric and/or calorimetric investigation would be appropriate.

2.10. Li(NpO₂)(CO₃)(H₂O)₂ [151878]

Prepared at 415 K, Mo $K\alpha$ diffractometry, 581 independent $F_{\text{obs}} > 2\sigma(F_{\text{obs}})$, absorption corrections, U_{eq} , $R = 0.0532$, $wR^2 = 0.1128$ (Charushnikova *et al.*, 2004). The reported structure approaches supergroup $P\bar{6}m2$ symmetry, with the largest polar displacement being -1.10 Å, by Li; all other atoms have opposite polar sense with $\Delta\xi \lesssim 0.4$ Å and $u_{\text{iso(max)}} \lesssim 0.28$ Å, see Table 7. Assuming that the irregularly eight-coordinated

Table 12

Structures reported in space group $P3m1$ that are likely without a change in phase.

§§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Possible space group	Structural problems and footnotes
5.1	$5H\text{-Si}_5\text{C}_5$	Gevorkyan <i>et al.</i> (1976)	107204	S48	$ \Delta\xi \lesssim 0.31$	Undetermined	$P\bar{3}m1$	Equal but opposite displacement by Si from that of C atoms ⁽¹⁾
5.2	$[\text{CoI}[\text{NP}(\text{CH}_3)_3]_4\cdot 3\text{CH}_2\text{Cl}_2$	Abram <i>et al.</i> (1996)	404305	S49(a)	Inapplicable	$0.16 \lesssim u_{\text{iso}} \lesssim 0.52$	$P6_3mc$	Coordinates not reported for 7 C and 2 Cl atoms ⁽²⁾
5.3	$[\text{ZnI}[\text{NP}(\text{CH}_3)_3]_4\cdot 3\text{CH}_2\text{Cl}_2$	Abram <i>et al.</i> (1996)	404306	S49(b)	Inapplicable	$0.16 \lesssim u_{\text{iso}} \lesssim 0.52$	$P6_3mc$	Coordinates not reported for 7 C and 2 Cl atoms ⁽³⁾

(1) Author's model results in perfect tetrahedra. An approach to $P\bar{3}m1$ via a change in Wyckoff location is not possible in view of the resulting but unlikely coordination changes. Noting the $6H$ polytype forms in space group $P6_3mc$, further investigation of Si_5C_5 would be appropriate. (2) Atomic coordinates reported only for 4 Co, 4 I, 4 N, 4 P, 8 C and 4 Cl atoms, those for the remaining 7 C and 2 Cl atoms were omitted. Evidence for a possible c -glide plane, also possible $2x, x$ and $x, 2x$ relationships are suggestive of an approach to higher symmetry, but the effect of the missing atoms, given a final $R = 0.033$, is unknown. (3) As in footnote (2) but with Zn substituted therein for Co.

Np^{5+} ion with atomic number 93 is not a source of uncorrected systematic error in $z(\text{Li})$, the criteria for ferroelectricity at ambient temperatures are met. Further structural study, in view of the large apparent displacement by the Li atom, see §1.5, is advisable.

2.11. $\text{LiPtD}_{0.66}$ [200045]

Prepared at 725 K, X-ray and neutron powder data, individual B_j , no additional experimental information noted nor provided subsequently, $R_{\text{int}} = 0.061$ (Nacken & Bronger, 1978). The largest departure from the symmetry of supergroup $P\bar{6}m2$ by any independent atom in the unit cell is 0.31 Å by D1, with $u_{\text{iso}} \simeq 0.21$ Å. Both $\Delta\xi(\text{Pt})$ and $\Delta\xi(\text{Li}) = 0.24$ Å with $u_{\text{iso}} = 0.10, 0.05$ Å, respectively, see Table 8. Alternatively, an origin translation of $\frac{1}{3}, \frac{2}{3}, 0$ results in an approach to the supergroup $P\bar{3}m1$, assuming the Pt and Li sites are equally occupied, with all atoms no further than 0.24 Å from such symmetry, see Table S7. If the structure determination is reliable, then the criteria for ferroelectricity are satisfied but confirmation by a full redetermination or dielectric investigation is strongly advisable.

2.12. $\text{Ag}_3(\text{MoO}_3\text{F}_3)(\text{Ag}_3(\text{MoO}_4)\text{Cl})$ [413082]

Prepared at 455 K, Mo $K\alpha$ diffractometry at 153 K, 563 independent $I_{\text{obs}} \geq 2\sigma(I_{\text{obs}})$, absorption corrections, U^{ij} , Flack parameter 0.47 (7), $R = 0.024$, $wR^2 = 0.074$ (Maggard *et al.*, 2003). Eight of the nine independent atoms present in Table 9 clearly approach the symmetry of the supergroup $P\bar{3}m1$, with $0.07 \lesssim \Delta\xi \lesssim 0.55$ Å and $u_{\text{eq}} \lesssim 0.13$ Å, and hence satisfy the criteria for ferroelectricity since the material is reported to generate second harmonics with an intensity approximately $10\times$ that of quartz. Atom O3 fails these criteria, however. If the approach to higher symmetry by all other atoms in the structure is not by chance, and if an overlooked atom such as $O3'$ for example (Table 9, in *italic*) were present, approximately related to O3 by a $2(d)$ Wyckoff location in space group $P\bar{3}m1$ with both O3 and $O3'$ sites half-occupied, then the criteria for ferroelectricity would be fulfilled. The corresponding changes in I_{calc} for such disorder are small with resulting interatomic contacts either close to or within the normal range. Hence, if $O3'$ were present and all other coor-

dinates confirmed, then the crystal would satisfy the criteria for ferroelectricity with a moderate value expected for T_C . If not, then the structure would more likely belong in the category of Table 12.

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