

Systematic prediction of new ferroelectrics in space group *R3*. I

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Release 2005/1 of the Inorganic Crystal Structure Database contains 158 entries under the space group *R3*. The first 81 together with 15 related entries include 52 different structure types, 10 of which represent families that have two or more isostructural members. There are 18 types that satisfy the structural criteria for ferroelectricity with a confidence level that necessarily depends upon the reliability of each structural determination. Among them, $(\text{LiTaO}_3)_9 \cdot \text{Ta}_2\text{O}_5$ and the $\text{CsCd}(\text{NO}_2)$ family are known ferroelectrics. The remaining 16 include the high-intensity higher-order harmonic generator $\text{II-BaB}_2\text{O}_4$, not previously recognized as ferroelectric. The other predicted ferroelectrics are $\text{Te}(\text{OH})_6 \cdot \text{NaF}$, the $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ family, $\text{Li}_3\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$, SeNbF_9 , $\text{Al}_2(\text{H}_2\text{PO}_4)_3 \cdot \text{PO}_4 \cdot 6\text{H}_2\text{O}$, $[\text{Cr}(\text{OCN}_2\text{H}_4)_6] \cdot [(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)_3 \cdot (\text{H}_2\text{O})_{1.5}]$, $\text{NaZnBr}_3 \cdot 5\text{H}_2\text{O}$, III- Ag_3SI , Tl_2S , the $\text{Ba}_3\text{Yb}_4\text{O}_9$ family, the $\text{Fe}_{10.7}\text{Ru}_{1.3}\text{As}_5$ family, $\text{Sr}_{17}\text{Ta}_{10}\text{S}_{42}$, Pb_8Sb_3 and the $\text{Sc}_7\text{I}_{12}\text{C}$ family. Six structures reported in the space group *R3* most likely exhibit mirror symmetry, with three experimental confirmations. The other 19 structures are most likely nonpolar, with six experimental confirmations. The capacity for physical property prediction by the remaining ten structures is shown to be in doubt. Thus, 46% of the present 52 inorganic structure types initially determined in the space group *R3* and 35% of those currently assigned to *R3* more likely exhibit an additional inversion center, mirror or glide plane, strongly exceeding the recently reported error rate of $\sim 11\%$ in organic structures.

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1. Introduction

1.1. Results reported previously in point group 3

A total of 21 inorganic crystal structures with the space group *P3* and a further 16 with the space groups *P3*₁ and *P3*₂ were shown to satisfy the structural criteria in §1.2, and hence were predicted to be new ferroelectrics (Abrahams, 2000, 2003). The validity of each such structural prediction rests upon the reliability of the underlying determination, hence the experimental determination of the characteristic properties of these materials is necessary before final acceptance. By comparison, a total of 201 ferroelectrics were reported in the most recent compilation (Landolt-Börnstein, 1990), of which approximately 38 appeared between 1978 and 1988. A comparable growth rate over the following decades would lead to *ca* 275 known ferroelectrics by 2008.

Release 2005/1 (FIZ Karlsruhe/ILL, 2005) of the Inorganic Crystal Structure Database (ICSD) contains a total of 158 entries under the space group *R3*. The space group *P3* had 57 entries with 62 more in the space group *P3*₁ and ten in the space group *P3*₂ when these inorganic structures in point

group 3 were examined (Abrahams, 2000, 2003). Analysis of the first 81 entries in the space group $R3$, together with 15 related entries, in the current release resulted in the 84 individual tables presented below. The remaining 71 entries will be analyzed later. The selection order follows the ICSD Collection Code sequence in each of the five sections below, except that subsequent entries for a given material are grouped with the initial entry, as are isostructural family members.

All entries below that were presented in a rhombohedral setting with lattice constants a_R and α are transformed to the hexagonal setting with lattice constants $a_H = 2a_R \sin(\alpha/2)$ and $c_H = a_R 3^{1/2}(1 + 2\cos \alpha)$. The corresponding atomic coordinates are transformed by the matrix

$$x_H, y_H, z_H = \begin{pmatrix} 2/3 & -1/3 & -1/3 \\ 1/3 & 1/3 & -2/3 \\ 1/3 & 1/3 & 1/3 \end{pmatrix} x_R, y_R, z_R.$$

1.2. Structural criteria for predicting ferroelectricity

The criteria used to determine if a structure reported in a polar space group is likely to be ferroelectric have been presented previously (e.g. Abrahams, 2003). In summary, they are:

(i) that the i th atom forming the shortest and least-ionic bonds in the unit cell undergoes no *polar* displacement $\Delta z_i \gtrsim 1.2 \text{ \AA}$ between the location reported at $x_i y_i z_i$ and that at which the resulting spontaneous polarization $P_S \rightarrow 0$ (i.e. for $z_i \rightarrow z_i^*$)¹ and

(ii) that $1.5 \gtrsim \Delta \xi_i \gtrsim 0.1 \text{ \AA}$ or u_i , the r.m.s. thermal or static displacement of that atom.

Since $|\Delta z_i|$ is origin dependent, that reported for each structure is translated along \mathbf{c} to minimize $\sum_i \Delta z_i$; the resulting z coordinates are termed z^* . The origin translation is stated in each table unless it is zero. Determinations in which the limit $\Delta \xi \lesssim 1.5 \text{ \AA}$ is exceeded by a small fraction only of the independent atoms in the structure may still be candidates for exhibiting ferroelectricity in view of possible atom misassignment or nonassignment, although any violation of this limit raises the uncertainty in the prediction.

The Curie temperature, T_C , may be predicted in structures with an i th atom that occupies an octahedron of O or F atoms and in which the cation is spherically symmetric by

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

where the force constant κ is $\sim 5.52 \text{ kPa}$, k is Boltzmann's constant, Δz_i is the largest displacement of the central i th atom along the polar c axis, as defined in criterion (i) and $\kappa/2k = 2.00 (9) \times 10^4 \text{ K \AA}^{-2}$ (Abrahams *et al.*, 1968). Equation (1) is applicable below only to the structures in §§2.11 and 2.13.

¹ Where each atom at x, y, z in the space group $R3$ is assumed as displaced to x'_i, y'_i, z'_i in a hypothetical supergroup with $\Delta \xi_i = [(x_i - x'_i)^2 + (y_i - y'_i)^2 + (z_i - z'_i)^2]^{1/2}$ in the hexagonal setting.

1.3. Space group–supergroup selection

The association of a structure with lower symmetry than justified in the course of a determination is not uncommon. This tendency in the determination of organic structures has been noted with increasingly frequency by critical observers, including Baur & Kassner (1992), Clemente & Marzotto (2004) and Marsh (2002, 2005). A similar tendency exists with inorganic structures; for example, $\Delta \xi_i$ in ten structures that were previously assigned to the space groups $P3_1$ or $P3_2$ have been identified in the search for new ferroelectrics as less than the corresponding static/thermal u_i displacement, and hence as more likely to belong to the space group $P3_121$, $P3_112$, $P3_221$ or $P3_212$ (Abrahams, 2003). It was noted by Marsh (2002) that $\sim 11\%$ of organic structure determinations 'described in the space group $R3$ are more properly described in higher symmetries'; the present study finds $\sim 46\%$ of the inorganic structure types initially determined in the space group $R3$ and $\sim 35\%$ of those currently assigned to $R3$ are more likely to belong to one of its supergroups. Literature searches for symmetry other than the $R3$ reported for the materials below were not made until all coordinate analyses were completed.

In the absence of thermal decomposition, T_C is generally the temperature at which $P_S \rightarrow 0$ as the ferroelectric crystal undergoes a transition to the paraelectric phase. Less frequently, a ferroelectric crystal may undergo a phase transition at T_{C1} to another ferroelectric phase in a supergroup that, with $T_{C2} > T_{C1}$, transforms at T_{C2} to the paraelectric phase in a higher-symmetry supergroup. Atomic arrangements capable of undergoing such reversible transitions are necessarily closely related to the structural arrangement in the other phase, *cf.* §1.5. The local structural free-energy minimum deepens in the course of the approach to centrosymmetry and, when the distance of each atom from a centrosymmetric location becomes comparable to or smaller than its thermal atomic displacement, the phase transition barrier to the higher symmetry form is likely to be overcome. The experimental thermal/static displacement u^i used in the analyses below substitutes for the unavailable static free component (*cf.* Trueblood *et al.*, 1996). If all but a small percentage of the independent atoms in a structure meet the conditions for ferroelectricity, it is thermodynamically likely that the apparent exceptions are associated with error. Accordingly, all noncentrosymmetric structure determinations that approach centrosymmetry should be examined for possible space-group misassignment or the presence of ferroelectricity.

1.4. Validation of the predicted ferroelectric state

The unique pyroelectric coefficient p_3 in a crystal with the space group $R3$ that undergoes a phase transition at T_C to form a minimal supergroup in the trigonal system, *viz.* $R\bar{3}$, $R32$, $R3m$ or $R3c$, becomes zero for classes $\bar{3}$ and 32 . This condition, which also causes P_S to become zero at $T \gtrsim T_C$, is necessary for the crystal to be ferroelectric below T_C , but not sufficient. Validation of the predicted ferroelectric state requires either the observation of ferroelectric hysteresis as the sense of P_S is reversed under an applied electric field or

Table 1

Atomic positions for $\text{Te}(\text{OH})_6\text{NaF}$ at room temperature (Allmann, 1976) with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz and u_{iso} displacements in Å.

$$a = 6.025 (3), c = 13.486 (5) \text{ \AA}. z^* = z + 0.0015; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position $R3, R\bar{3}$	x	y	z	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Te	$3(a), 3(a)$	0	0	0.0015	0	0	0	0	0	0.01	0.02	0.06
Na,F	$3(a)$ $6(c)^\dagger$	0	0	0.3770 (7)	0	0	0.4100	0	0	-0.45	0.45	0.13
F,Na	$3(a)$	0	0	0.5570 (9)	0	0	0.5900	0	0	-0.45	0.45	0.12
O1	$9(c)$ $18(f)$	0.267 (3)	0.007 (2)	0.0806 (9)	0.276	0.029	0.0798	-0.054	-0.13	0.01	0.16	0.15
O2	$9(c)$	-0.285 (3)	-0.050 (2)	-0.0789 (8)	-0.276	-0.029	-0.0798	-0.054	-0.13	0.01	0.16	0.10
H1	$9(c)$ $18(f)^\ddagger$	0.300	-0.163	0.061	0.304	-0.153	0.078	-0.02	-0.06	-0.23	0.25	0.28
H2	$9(c)$	0.691	0.142	0.904	0.696	0.153	0.922	-0.03	-0.07	-0.24	0.25	n/r

† Equal Na^+ and F^- ion occupancy is required in both $3(a)$ positions, on average. ‡ Allman's (1976) coordinates: H1 0.31 (5), 0.14 (5), 0.15 (2) with $u_{\text{iso}} = 0.28 \text{ \AA}^2$, H2 -0.3, 0.11, -0.09 with u_{iso} not reported (n/r).

the equivalent demonstration that the sense of p_3 is field reversible. All six independent d_{ij} piezoelectric moduli in $R\bar{3}$ reduce to zero in $R\bar{3}$, while two remain active in $R32$ with three each in $R3m$ and $R3c$. The dielectric permittivity ε_{ij} with $\varepsilon_{11} = \varepsilon_{22}$ and independent ε_{33} , is active both above and below T_C , but typically undergoes changes in magnitude at T_C . Characteristic variations in the permittivity at T_C , e.g. as determined calorimetrically, is also indicative of a ferroelectric-to-paraelectric phase transition in the event that dielectric breakdown prevents hysteresis measurement.

1.5. Atomic distribution and equivalent positions in supergroup

Each atom in a structure that can undergo a phase transition from ferroelectric to paraelectric is potentially related to a Wyckoff position in the resulting supergroup.² Supergroup coordinates, indicated by primes ($x'y'z'$) in the tables that follow, are either values of higher symmetry for atoms in special positions or else are obtained by averaging the related values of each xyz pair as modified to conform with the general position symmetry. Such relationships are often clearer if the xyz coordinates of one member of an atomic pair are transformed by an appropriate equivalency operation; appropriate transformations of this kind are used widely

² An atom in the general $9(b)$ position of the space group $R3$ has coordinates $(0, 0, 0)_+$, $(2/3, 2/3, 1/3)_+$ and $(1/3, 1/3, 2/3)_+$: (1) x, y, z ; (2) $\bar{y}, x - y, z$; (3) $\bar{x} + y, -x, z$. The only special position is $3(a)$ at $(0, 0, z)$. The general $18(f)$ position in supergroup $R\bar{3}$ includes the positions (1), (2) and (3) in $R3 + (4) \bar{x}, \bar{y}, \bar{z}$; (5) $y, \bar{x} + y, \bar{z}$; (6) $x - y, x, \bar{z}$; in addition, there are four sets of special positions with coordinates $3(a) 0, 0, 0$; $3(b) 0, 0, \frac{1}{2}$; $6(c) 0, 0, z$; $0, 0, \bar{z}$; $9(d) \frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$ and $9(e) \frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$, 0. The general $18(f)$ position in supergroup $R32$ also includes positions (1), (2) and (3) in $R3 + (4) y, x, \bar{z}$; (5) $x - y, \bar{y}, \bar{z}$; and (6) $\bar{x}, \bar{x} + y, \bar{z}$. $R32$ also has five sets of special positions with coordinates $3(a) 0, 0, 0$; $3(b) 0, 0, \frac{1}{2}$; $6(c) 0, 0, z$; $0, 0, \bar{z}$; $9(d) x, 0, 0$; $0, x, 0$; $\bar{x}, \bar{x}, 0$; and $9(e) x, 0, \frac{1}{2}$; $0, x, \frac{1}{2}$; $\bar{x}, \bar{x}, \frac{1}{2}$. The general $18(f)$ position in supergroup $R3m$ includes the positions (1), (2) and (3) in $R3 + (4) \bar{y}, \bar{x}, z$; (5) $\bar{x} + y, y, z$ and (6) $x, x - y, z$. $R3m$ also includes two sets of special positions with coordinates $3(a) 0, 0, z$; and $9(b) x, \bar{x}, z$; $x, 2x, z$; $2\bar{x}, \bar{x}, z$. The general $18(f)$ position in supergroup $R3c$ includes positions (1), (2) and (3) in $R3 + (4) \bar{y}, \bar{x}, z + \frac{1}{2}$; (5) $\bar{x} + y, y, z + \frac{1}{2}$; and (6) $x, x - y, z + \frac{1}{2}$; in addition, there is one set of special positions with coordinates $3(a) 0, 0, z$; $0, 0, z + \frac{1}{2}$ (ITA, 2005).

below. Footnote 2 facilitates the use of these operations without the need to consult ITA (2005). It is noted that P_S reversal at $T < T_C$ requires the z coordinate of each atom to undergo a total displacement of $2\Delta z$, reversing the sense of \mathbf{c} if all such coordinates thereby change sign. The values of $\Delta\xi$ are often strongly temperature dependent.

1.6. Presentation of structural analysis

The basic experimental information necessary to place the results for each material considered below in brief context is presented in the supplementary data.³ Unless noted otherwise, the sample was at ambient temperature and the F_{obs} were measured diffractometrically. No more than one table of atomic coordinates accompanies any analysis in §2 and then only if 9 or fewer unique atoms are present; all other tables are deposited in the supplementary data.

2. Predicted new inorganic ferroelectrics in space group $R3$

2.1. $\text{Te}(\text{OH})_6\text{NaF}$

Allmann (1976) determined H1 experimentally, but H2 was assumed to be 1.03 Å distant from O2 in the $d_{\text{O2}\dots\text{F}} = 2.50 \text{ \AA}$ bond. The other shortest contacts in $\text{Te}(\text{OH})_6\text{NaF}$ are $d_{\text{O1}\dots\text{Na}} = 2.33 \text{ \AA}$, the intra-octahedral $d_{\text{O1-O2}} = 2.56$ and $d_{\text{O1}\dots\text{O2}} = 2.76 \text{ \AA}$ with $\angle\text{O1-H1-O2} = 168.9^\circ$. Noting the closest 'Na' contacts are to 'F' at 2.43, three O1 at 2.33 Å and three O2 at 2.65 Å with closest 'F' contacts to 'Na' at 2.43, three O1 at 2.98 Å and three O2 at 2.50 Å, the two sites are rather comparable. Assuming the Na^+ and F^- sites are disordered over the two Wyckoff $3(a)$ positions, each with equal occupation, Table 1 shows that no atom deviates more than 0.45 Å from its corresponding location in the space group $R\bar{3}$,

³ All contextual experimental information and Tables S1-S48 have been deposited. Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5021). Services for accessing these data are described at the back of the journal.

Table 2

Atomic positions for $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ at 120 K (Bats *et al.*, 1986) with hypothetical $x'y'z'$ coordinates in the space group $R32$ and the Δx , Δy , Δz and u_{iso} displacements in Å.

Left-handed coordinates produced on conversion from rhombohedral to hexagonal axes were corrected by reversing the c_{hex} axis sense. Symmetry-equivalent coordinates were used for O1, Ow2, H2, H3 and H4.

$$a_{\text{H}} = 8.803 (2), c_{\text{H}} = 9.055 (2) \text{ \AA}. \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position $R3, R32$	x	y	z	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Mg	3(a),3(a)	0	0	0	0	0	0	0	0.9	0.9	0	0.08
S	3(a),3(b)	0	0	0.5028 (2)	0	0	0.5	0	0	0.03	0.03	0.09
O1	9(b),9(e)	0.1270 (1)	0.0504 (1)	0.4323 (1)	0.0887	0.0887	0.5	0.34	0.34	-0.61	0.85	0.10
Ow1	9(b)	-0.0031 (1)	-0.1910 (1)	0.1418(1)	-0.0998	-0.1945	0.1317	0.85	0.03	0.09	0.87	0.10
	18(f)											
Ow2	9(b)	-0.1980 (1)	-0.1964 (1)	-0.1216 (1)	-0.1945	-0.0998	-0.1317	-0.03	-0.85	0.09	0.87	0.11
H1	9(b)	0.9294 (2)	0.6810 (2)	0.1205 (2)	0.8642	0.6882	0.1427	0.57	-0.06	-0.20	0.58	0.15
	18(f)											
H4	9(b)	0.6954 (2)	0.7989 (2)	0.8352 (2)	0.6882	0.8642	0.8573	0.06	-0.57	-0.20	0.58	0.15
H2	9(b)	0.2290 (2)	0.8544 (2)	0.5036 (2)	0.3589	0.8514	0.4611	-1.14	0.03	0.38	1.19	0.16
	18(f)											
H3	9(b)	0.8485 (2)	0.4889 (2)	0.5814 (2)	0.8514	0.3589	0.5389	-0.03	1.14	0.38	1.19	0.15

Table 3

Atomic positions for $\text{Li}_3\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ at room temperature (Masse *et al.*, 1973) with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz and u_{iso} displacements in Å.

$$a = 12.511 (4), c = 5.594 (2) \text{ \AA}. z^* = z - 0.1110; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position $R3, R32$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}
Li†	9(b),9(d)	0.0743 (8)	0.4760 (8)	0.0670 (16)	0	0.4760	0	0.93	0	0.37	1.00	0.10 (2)
P	9(b),9(d)	0.14276 (7)	0.01839 (7)	-0.1110	0.14276	0	0	0	0.23	-0.62	0.66	0.12 (3)
O1	9(b)	0.1059 (2)	0.1219 (2)	-0.1647 (6)	0.0661	0.1501	-0.1542	0.50	-0.35	-0.06	0.45	0.12 (3)
	18(f)											
O3	9(b),9(e)	0.1783 (3)	0.0263 (3)	0.1436 (6)	0.1501	0.0661	0.1542	0.35	-0.50	-0.06	0.45	0.14 (3)
O2	9(b)	0.2308 (2)	0.0292 (2)	-0.3002 (6)	0.2409	0.1278	-0.3328	-0.13	-1.23	0.18	1.31	0.14 (3)
	18(f)											
O4	9(b)	0.2263 (3)	0.2511 (3)	0.3654 (16)	0.1278	0.2409	0.3328	1.23	0.13	0.18	1.31	0.14 (1)

† Reported coordinates for Li [0.4076 (8), 0.1427 (8), 0.7060 (16)] + $(\frac{2}{3}, \frac{1}{3}, \frac{2}{3})$.

consistent with a ferroelectric structure and suggestive of a location for H2 different from that reported. The only coordinates related to those of H1 through an inversion center place H2 about midway in the short O1...Na' contact. Table 1 hence takes H1 at the midpoint of the 2.50 Å contacts and H2 at the midpoint of the 2.33 Å contacts. Since hydrogen bonds do not form between O^{2-} and Na^+ , the Na^+ and F^- site disorder results in hydrogen bonds to half of all the fully occupied Na,F sites.

The resulting structure in Table 1 approaches the supergroup $R\bar{3}$ with maximum $\Delta\xi = 0.45$ Å. Since Na^+ and F^- ions appear nearly equal under X-ray diffraction, neutron diffraction would provide unambiguous determination of all site occupancies and the postulated H-atom positions. Shared occupancy of the Na^+ - and F^- -ion sites implies very small ionic contributions to the spontaneous polarization P_S and, with $z(\text{Te})$ almost exactly midway between $z(\text{O1})$ and $z(\text{O2})$, the $\text{Te}(\text{OH})_6$ octahedral contribution to P_S is also expected to be small. Nevertheless, $\text{Te}(\text{OH})_6 \cdot \text{NaF}$ satisfies the structural

criteria for ferroelectricity, see §1.2, for the site occupancies given.

2.2. $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ family

No atomic position in Table 2 determined by Bats *et al.* (1986) at 120 K is further than 1.2 Å from the corresponding location in the space group $R32$, hence the criteria for ferroelectricity are clearly satisfied, see §1.2. Andersen & Lindqvist's (1984) coordinates at ~298 K in Table S1 are comparable to those in Table 2, but with significantly smaller $\Delta\xi$ magnitudes, suggesting a strong thermal dependence. Although Mg^{2+} occupies an octahedron of O atoms, the major contribution to P_S by the SO_3^{2-} ion and bound H_2O makes (1) inapplicable. A combination of calorimetry and gravimetry would readily reveal if water of hydration were lost before T_C is reached. Confirmed family members including $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ are also expected to be ferroelectric. The structure of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$

Table 4

Atomic positions for NaZnBr₃·5H₂O at room temperature (Brehler & Rott, 1970), with hypothetical *x'y'z'* coordinates and the Δ*x*, Δ*y*, Δ*z* displacements in Å.

$$a_H = 7.273 (5), c_H = 17.844 (12) \text{ \AA}. z^* = z - 0.0429; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position <i>R3, R32</i>	<i>x</i>	<i>y</i>	<i>z</i> [*]	<i>x'</i>	<i>y'</i>	<i>z'</i>	Δ <i>x</i>	Δ <i>y</i>	Δ <i>z</i>	Δξ	<i>u</i> _{aniso} [†]
Zn‡	3(<i>a</i>), 3(<i>a</i>)	0	0	−0.0429	0.0	0.0	0.0	0.0	0.0	−0.76	0.76	n/r
Na	3(<i>a</i>), 3(<i>b</i>)	0	0	0.5554 (13)	0.0	0.0	0.5	0.0	0.0	0.99	0.99	n/r
Br	9(<i>b</i>), 9(<i>d</i>)	0.3228 (5)	0.0118 (5)	−0.0094 (8)	0.3228	0.0	0.0	0.0	0.09	−0.17	0.19	n/r
O1(H ₂)	9(<i>b</i>), 9(<i>e</i>)	−0.2693 (5)	−0.0007 (5)	0.4744 (8)	−0.2693	0	0.5	0.0	−0.01	−0.46	0.46	n/r
O2(H ₂)	3(<i>a</i>)	0	0	0.8411 (5)	0	0	0.829	0	0	0.22	0.22	n/r
	6(<i>c</i>)											
O3(H ₂)	3(<i>a</i>)	0	0	0.1831 (5)	0	0	0.171	0	0	0.22	0.22	n/r

[†] *u*_{aniso} values determined but not reported (n/r). ‡ *y*(Br) in the rhombohedral cell is replaced by *y*(Br) − 1 in deriving hexagonal coordinates.

and family members has also been studied by Klasens *et al.* (1935), Grandjean *et al.* (1962), Weiss *et al.* (1966), Baggio & Becka (1969), Flack (1973) and Andersen *et al.* (1984).

2.3. Li₃P₃O₉·3H₂O

The coordinates of no atom in Table 3 determined by Masse *et al.* (1973) are further than 1.3 Å from the corresponding location in the space group *R32*. With $1.3 \gtrsim \Delta\xi > u_{\text{iso}}$ Å for each atom, the criteria for this structure of corner-sharing LiO₄ and PO₄ tetrahedra being ferroelectric are fully satisfied.

2.4. SeNbF₉

The Se1, Nb1 and Se2, Nb2 pairs reported by Edwards & Jones (1970), see Table S2, are displaced less than 0.16 Å from the equivalent locations in the space group *R3̄*. Six F atoms have Δξ < 0.25 Å with $0.5 < \Delta\xi \lesssim 0.9$ Å for the remaining six F. If all displacements are confirmable, then both the less-distorted NbF₆ octahedra and the more strongly distorted SeF₆ octahedra together satisfy the criteria for ferroelectricity with a value of *T*_C that is unlikely to be much higher than ambient.

2.5. Al₂(H₂PO₄)₃PO₄·6H₂O

Table S3 shows that Δξ for all atoms except Al, P, O7 and O8 significantly exceed the assumed value of *u*_{iso} ≈ 0.1 Å. All remaining Δξ ≈ 1.4 Å. Hence, if the coordinates reported by Kniep & Wilms (1979) are confirmable, the structure satisfies the criteria for ferroelectricity.

2.6. [Cr(OCN₂H₄)₆]₃·[(Co(NH₃)₂(NO₂)₄)₃·(CCl₄)_{0.5}·(H₂O)]_{1.5}

All atoms, except Cl1 and O1, of the 52 determined by Rau *et al.* (1982) in the space group *R3* satisfy the criteria in §1.2 for ferroelectricity with Δξ ≈ 1.5 Å, see Table S4. Each Cl atom in the CCl₄ solvate is over 3.5 Å from its next-nearest neighbor, thus weakly bound; a 1.63 Å displacement that rotates a C—Cl2 bond to the *c* axis, thereby reversing the polar sense of the solvate, is hence possible. The O1 atom, with four O- and two N-atom neighbors within 3.05 Å, is identified as the H₂O postulated in the chemical formula; an inversion-related water atom was not reported, the absence of which would prevent

ferroelectricity. It is thermodynamically more likely, see §1.2, that such an atom as O22 exists within about 1 Å of the position noted in Table S4,⁴ with half-occupancy at both O1 and O22 sites. If CCl₄ rotation and atom O22 existence are each experimentally confirmable, then the criteria for ferroelectricity would be fully satisfied.

2.7. Mg₂Al₂SiO₅(OH)₄ (Amesite – 6R₂)

Steadman & Nuttall (1962) reported the amesite polytype is triclinic, but closely approximates the space group *R3*. The atomic coordinates determined by trial in Table S5 fully satisfy the criteria for ferroelectricity, but may be an artefact of the solution method and/or the rhombohedral approximation. Structural redetermination or dielectric measurement as appropriate is hence essential before the ferroelectric properties of this mineral can be inferred with confidence.

2.8. NaZnBr₃·5H₂O

Brehler & Rott's (1970) brief report contains few experimental details other than those given here and is without *u*_{aniso} values; it was not followed by a fuller report. The atomic coordinates in Table 4 closely approach the symmetry of supergroup *R32* with atomic displacements in the range $0.99 > \Delta\xi > 0.19$ Å. NaZnBr₃·5H₂O hence satisfies the structural criteria for ferroelectricity, assuming *u*_{aniso} ≈ 0.1 Å for all atoms and the structure determination is reliable.

2.9. III-Ag₃SI

The atomic coordinates in Table 5 (Hull *et al.*, 2001), and those in Table S6 (Perenthaler *et al.* (1981) with a rhombohedral unit-cell origin displacement of $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ for direct comparison with Table 5, are consistent with Δξ ≈ 0.3 Å for all atoms in the transition from phase III-(*R3*) to phase II-(*Pm3̄m*) at *T*_C = 156 (2) K. With Δξ comparable to but larger than *u* for Ag and S (I occupies a special position, with Δξ = 0), but much less than the maximum displacement in ferroelectric-to-paraelectric transitions, see §1.2, phase III satisfies the criteria for ferroelectricity, as previously suggested by Hull

⁴ Hypothetical atoms here and elsewhere in text or tables are in italic.

Table 5

Atomic positions for III-Ag₃IS at room temperature (Hull *et al.*, 2001), with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz displacements in Å. $a_R = 4.86728$ (2) Å, $\alpha = 90.00 \pm \delta^\circ$ with $\delta = 0.08$ (2)° at 5 K. $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z - z')c$.

	Wyckoff position $R3, Pm\bar{3}m$	x	y	z	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u^\dagger
Ag‡	3(<i>b</i>),12(<i>h</i>)	0.5300 (5)	0.8895 (4)	0.0175 (6)	0.5	0.8895	0.0	0.15	0	0.08	0.17	0.07
I	1(<i>a</i>),1(<i>b</i>)	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0	0	0.12
S	1(<i>a</i>),1(<i>a</i>)	0.0319 (5)	0.0319 (5)	0.0319 (5)	0	0	0.0	0.16	0.16	0.16	0.28	0.10

† Isotropic value for S and I, u_{33} for Ag; $\text{Ag}(u_{22}) = 0.16$ Å. ‡ Only one of the four locations in each of the three sets of tetrahedral sites in 12(*h*) is expected to be occupied, with random occupancy.

Table 6

Atomic positions for $(\text{LiTaO}_3)_9\cdot\text{Ta}_2\text{O}_5$ in space group $R3c \rightarrow R\bar{3}c$ (Santoro *et al.*, 1982).

$a = 5.1576$ (1), $c = 13.77842$ (2) Å. $z^* = z + 0.2044$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3c, R\bar{3}c$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}	Occ.
Li1, Li2†	6(<i>a</i>),6(<i>b</i>)	0	0	0.4961 (5)	0	0	0.5	0	0	−0.05	0.05	0.16	0.83
Ta1, Ta2	6(<i>a</i>),6(<i>a</i>)	0	0	0.2196	0	0	0.25	0	0	−0.42	0.42	0.08	1.0
Ta3, Ta4	6(<i>a</i>),6(<i>b</i>)	0	0	0.4926	0	0	0.5	0	0	−0.18	−0.10	0.08	0.03
O1, O2	18(<i>b</i>),18(<i>e</i>)	0.0498 (2)	0.3407 (4)	0.2916 (2)	0	0.3407	0.25	0.26	0.0	0.57	0.63	0.08	1.0
Li3	6(<i>a</i>),12(<i>c</i>)	0	0	0.84 (1)	0	0	~0.84	0	0	~0.0	~0.0	0.16	~0.015

† The xyz coordinates are those of Santoro *et al.* (1982) in Table S7 with allowance both for the origin shift and the implicit *c*-glide plane relation between Li1 and Li2, Ta1 and Ta2, Ta3 and Ta4, O1 and O2.

et al. (2001). The space group $Pm\bar{3}m$ is not a minimal supergroup of $R3$, but is reachable via $R\bar{3}$.

2.10. $(\text{LiTaO}_3)_9\cdot\text{Ta}_2\text{O}_5$

Ferroelectric LiTaO_3 has been widely studied since the first preparation by Ballman (1965). The stoichiometric composition melts incongruently leading to interest in nonstoichiometric crystals. Santoro *et al.*'s (1982) hypothesis testing of a model with nine independent atoms, for a strongly nonstoichiometric solid solution of Ta_2O_5 in LiTaO_3 , led to the assignment of the space group $R3$ rather than the $R3c$ group of stoichiometric LiTaO_3 , see Table S7. The symmetry of a ferroelectric material is expected to transform at T_C to that of its supergroup, *viz.* $R\bar{3}$ in the present case, see §1.3. The resulting displacements $2.46 > \Delta\xi > 1.93$ Å for O1, O2 and Li3 at T_C , however, exceed the criterion in §1.2. In addition, Li3 is required to occupy the filled Ta2 site while the model yields such distances as $d_{\text{Li2-Ta4}} = 0.05$ Å and $d_{\text{Li3-Ta2}} = 1.65$ Å. The *a* and *c* lattice constants of this unit cell, however, are each within 0.006 Å of their values in stoichiometric material (Barns & Carruthers, 1970).

Table 6 shows the structure in the alternative space group $R3c$, based on the experimental coordinates in Table S7 but with an origin shift that emphasizes the glide plane symmetry evidently present. A transition to $R\bar{3}c$ is thus possible with all $\Delta\xi$ well within the normal range for a transition from ferroelectric to paraelectric, as is the case for both stoichiometric and slightly nonstoichiometric LiTaO_3 compositions. In consequence, Li3 becomes distributed over 0, 0, *z* and 0, 0, \bar{z} ,

also over 0, 0, $\frac{1}{2} \pm z$. The resulting Curie temperature from (1) is 487 K.⁵ Experimentally, $T_C \simeq 875$ K from the congruent melt (*e.g.* Tomeno & Matsumura, 1988). The difference between measured and predicted T_C , together with the questionable $d_{\text{Li-Ta}}$ distances and the Li3 filled Ta2 sites noted above, suggests a need for further experimental investigation of this highly nonstoichiometric ferroelectric material.

2.11. Tl_2S (carlinite)

The atomic coordinates reported by Giester *et al.* (2002) in Table S8(*a*) generally resemble Man's (1970) in Table S8(*b*), but with major differences between the two sets of values for $z(\text{S})$. As a consequence, Giester *et al.*'s coordinates approach $R\bar{3}$ symmetry, whereas Man's approach $R3m$ in the absence of disorder, or $R\bar{3}m$ if two S atoms in the Wyckoff position 9(*b*) occupy a general 36(*f*) position with 50% occupancy, see Tables S8(*b*) and S8(*c*). Accepting the superior structural fit on which Table S8(*a*) is based, the largest displacement from centrosymmetry is $\Delta\xi(\text{S1}) = 0.67$ Å, clearly satisfying the structural criteria of §1.2 for ferroelectricity. It is noted that all the reported *z* coordinates may be subject to error related to the perfect cleavage in Tl_2S . The range $2.8 < d_{\text{Tl-S}} < 3.1$ Å in the highly distorted STl_6 octahedra may similarly be a cleavage-related artefact. Ketelaar & Gorter (1939) initially investigated Tl_2S by powder diffraction. Radke & Dickson

⁵ Taking the origin in $R3c$ at Ta1, Ta2, $\Delta z = z(\text{O1, O2}) - 1/12$ with equispaced O separated by $z/6$. The contribution to P_S by Li1, Li2 is reduced to zero if displaced to $00\frac{1}{2}$, neglecting the 3% occupancy attributed to Ta3, Ta4 and the 1.5% occupancy to Li3 sites.

Table 7

Atomic positions for Fe₁₂As₅ at room temperature (Maaref *et al.*, 1983), with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz displacements in Å. $a = 6.7855$ (5), $c = 16.301$ (2) Å. $z^* = z + 0.1274$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R32$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{33}
As1	3(a) 6(c)	0	0	0.1274	0	0	0.1459	0	0	-0.30	0.30	0.12
As2	3(a)	0	0	0.8356 (2)	0	0	0.8541	0	0	-0.30	0.30	0.10
As3	3(a) 18(f)	0.3144	0.3332	0.3148 (2)	0.3238	0.3771	0.2502	-0.06	-0.30	1.05	1.10	0.14
Fe6†	9(b)	0.6667 (5)	0.0972 (4)	0.8145 (4)	0.6762	0.0533	0.7498	-0.06	0.30	1.05	1.10	0.13
Fe1	3(a) 6(c)	0	0	0.3629 (3)	0	0	0.3816	0	0	-0.30	0.01	0.13
Fe2	3(a)	0	0	0.5996 (2)	0	0	0.6183			-0.30	0.01	0.14
Fe4‡	9(b) 18(f)	0.0570 (5)	0.4174 (4)	0.3998 (2)	0.0570	0.4175	0.4183	0	0	-0.30	0	0.12
Fe5§	9(b)	0.4176 (4)	0.0569 (5)	0.5633 (2)	0.4175	0.0569	0.5818	0	0	-0.30	0	0.12
Fe3	3(a),3(a)	0	0	-0.0178 (5)	0	0	0	0	0	-0.29	0.01	0.11

† As reported for Fe6 + (1/3, 2/3, 2/3). ‡ The Fe4 site composition in Fe_{10.3}Ru_{1.7}As₅ is assumed to be 0.15 Ru, 0.85 Fe, with the Fe5 site taken as occupied by 0.15 Ru, 0.857 Fe and the Fe3 site by 0.33 Ru, 0.67 Fe. § As reported for Fe5 + (2/3, 1/3, 1/3).

(1975) found no phase transition below $T_m = 722$ (5) K. Further structural as well as calorimetric investigation would be appropriate.

2.12. Ba₃Yb₄O₉ family

Krüger & Müller-Buschbaum (1983) reported coordinates for which no atom in Table S9(a) is further than 1.14 Å from the corresponding location in the supergroup $R\bar{3}$; with $0.14 > u_{\text{iso}} > 0.10$, the criteria for ferroelectricity in §1.2 are fully satisfied. All four independent Yb atoms are close to the centers of their distorted YbO₆ edge-sharing octahedra, but displaced 0.44–0.04 Å along the polar axis from the location at which $P_S = 0$. Structures with a single unique octahedron of O or F atoms have a predicted value of T_C given by (1); the wide spread in displacements among the four Yb octahedra gives an average $\delta[z(\text{O})] = 0.22$ (18) Å, hence $T_C \simeq 970$ (650) K.

Ba₃Ho₄O₉ and Ba₃Tm₄O₉, see Tables S9(b) and Table S9(c), are isostructural with Ba₃Yb₄O₉ (Müller-Buschbaum & Scheikowski, 1990), as are Ba₃Lu₄O₉ (Krüger & Müller-Buschbaum, 1984), see Table S9(d), and Ba₃Y₄O₉ (Szymanik *et al.*, 1998), see Table S9(e). Since these four Ba₃Ln₄O₉ compounds (Ln = lanthanide) similarly satisfy the ferroelectric criteria, they also are likely to be new ferroelectrics as would be any other isostructural lanthanides.

2.13. Fe₁₂As₅ family

Single crystals form at ambient pressure only if 15% of Fe is substituted by Ru but isomorphous polycrystalline Fe₁₂As₅ results at 1273 K under 30 kbars (Maaref *et al.*, 1983). All atoms in Fe_{10.7}Ru_{1.3}As₅ except the As3-Fe/Ru6 pair have locations that closely approach the symmetry of the space group $R32$, see Table 7. Although $u_{33}(\text{As3})$ is significantly larger than u_{33} (As1 or As2), the possible equivalence of the As3 and Fe6 sites has not yet been investigated. It is noted that As1 and As2 each have ten nearest neighbors in the range 2.4–

2.7 Å, As3 has nine between 2.3 and 2.8 Å with Fe6 having a comparable ten nearest neighbors between 2.5 and 2.8 Å. If the equivalency proposed in Table 7 proves correct, then Fe_{10.3}Ru_{1.7}As₅ satisfies the criteria for ferroelectricity (see §1.2). The family includes Fe_{10.3}Mo_{1.7}As₅, Fe_{10.3}Rh_{1.3}As₅ and Fe₁₂(Ge_{0.67}As_{0.33}).

2.14. Sr₁₇Ta₁₀S₄₂

Onoda *et al.* (1993) minimized parameter interactions by assuming rhombohedrally related local 2₁-screw axes between the two formulae in the asymmetric unit. Atomic displacements between the experimental coordinates in Table S10 and their likely values in the space group $R\bar{3}$ lie in the range $0.08 < \Delta\xi < 1.31$ Å. The structure as determined hence satisfies the criteria for ferroelectricity; reexamination of the assumption used in a single-crystal analysis would, however, improve the confidence level of this prediction (see ‘Note added in proof’).

2.15. Pd₈Sb₃

No atomic location determined by Man & Imamov (1979), the majority of which occupy the 3(a) positions at 00z in the space group $R3$, differs more than 0.60 Å from the corresponding location in the space group $R3c$, see Table S11(a). Further, the 12 resulting independent atomic locations in $R3c$ differ no more than 0.17 Å from the equivalent positions in $R\bar{3}c$, see Table S11(b). With all $u_{\text{iso}} \simeq 0.1$ Å, the structure is thus a candidate for ferroelectric behavior above the two inferred phase transitions, although the initial space group differs from that reported.

The $R\bar{3}c$ equivalents of the x and y coordinates determined by Wopersnow & Schubert (1976) agree with those of Man & Imanov (1979) within 0.5 Å, but only five of the 12 independent z coordinates agree within 1.3 Å. No atom in the former set has $\Delta\xi \geq 1.0$ Å, see Table S11(c), except for Pd1 and the Sb4/Pd4 pair at $\Delta\xi \simeq 1.6$ and 2.1 Å, respectively. Both

Table 8

Atomic positions for β -BaB₂O₄ at room temperature (Ito *et al.*, 1990) with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz displacements in Å.

Related to the coordinates in Tables S12(a), (b) and (c) by the appropriate symmetry operation.

$a = 12.5316$ (3), $c = 12.7285$ (9) Å. $z^* = z - 0.1236$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3c, R\bar{3}c$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{33}
Ba	18(f),18(e)	0.3608 (1)	0.0031 (1)	0.7564 (1)	0.3608	0.000	0.7500	0.00	0.04	0.08	0.09	0.13
B1	18(f) 36(f)	0.7683 (2)	0.4569 (2)	0.4517 (2)	0.7823	0.4317	0.4525	-0.18	0.32	-0.01	0.28	0.14
B2	18(f)	0.3758 (2)	0.7963 (2)	0.5467 (2)	0.3506	0.7823	0.5475	0.32	0.18	-0.01	0.44	0.13
O1	9(b) 18(f)	0.6453 (1)	0.4298 (1)	0.4540 (2)	0.5766	0.4245	0.4506	0.86	0.07	0.04	0.90	0.21
O2	9(b)	0.4192 (1)	0.9165 (1)	0.5528 (2)	0.4245	0.8479	0.5494	-0.07	0.86	0.04	0.83	0.18
O3	9(b) 18(f)	0.8591 (1)	0.5716 (1)	0.4448 (2)	0.7834	0.5522	0.4505	0.95	0.24	-0.07	1.09	0.21
O4	9(b)	0.2506 (1)	0.7077 (1)	0.5438 (1)	0.2312	0.7834	0.5495	0.24	-0.95	-0.07	0.86	0.15

determinations hence approach $R\bar{3}c$ symmetry, Wopersnow & Schubert's (1976) coordinates less closely. If the tendency toward centrosymmetry by Pd₈Sb₃ is confirmable, then the criteria for ferroelectricity are satisfied. The additional phase transition indicated by earlier work also remains open to investigation.

2.16. II-BaB₂O₄

Lu *et al.* (1982) rejected the choice of $R3c$ in favor of the better fit in $R3$ (see Xue & Zhang, 1998). However, all atoms in the space group $R3$ are related in pairs by a c glide such that none differ more than ~ 0.03 Å from the space group $R3c$ symmetry, see Table S12(a). Fröhlich's (1984) atomic coordinates in Table S12(b) show that no atomic position in II-BaB₂O₄ differs more than ~ 1.3 Å from those in centrosymmetric $R\bar{3}c$, except B2, for which $\Delta\xi \simeq 1.7$ Å. It is notable that no atom in a unit cell with $R3c$ symmetry, derived from Lu *et al.*'s (1982) determination, see Table S12(c), has $\Delta\xi \gtrsim 1.1$ Å with respect to $R\bar{3}c$ as is the case with the more accurate coordinates of Ito *et al.* (1990). The small polarization implied by the latter's $\Delta z \lesssim 0.08$ Å for all atoms in Table 8 is consistent with the small experimental $P_S \simeq 10^{-4}$ C m⁻² reported by Guo & Bhalla (1989), who also find $P \rightarrow 0$ at ~ 303 K. The structural criteria for ferroelectricity are hence well satisfied by II-BaB₂O₄.

A separate investigation by Eimerl *et al.* (1987) confirmed the Fröhlich (1984) structure without providing detailed information. Mighell *et al.* (1966) reported that the high-temperature phase I-BaB₂O₄ forms in the space group $R\bar{3}c$. Levin & McMurdie (1949) found the transition temperature from phase II to phase I ranged from 373 to 773 K. Liebertz (1988) confirmed the point group of phase II as $3m$ and also Mighell *et al.*'s (1966) finding that phase I does not generate second harmonics, and hence is centrosymmetric.

The coordinate sets in Tables 8, S12(b) and S12(c) are comparable but exhibit highly significant differences. Further measurement is necessary to determine whether such differ-

ences are confirmable; if so, they may be the cause of the wide range in Curie temperatures reported by Levin & McMurdie (1949). All three studies, however, are consistent both with the presence of ferroelectricity at room temperature, the high-intensity second- and third-harmonic generation, and the other nonlinear optical properties of II-BaB₂O₄ (Chen *et al.*, 1985; Banks *et al.*, 1999).

2.17. CsCd(NO₂)₃ family

The atomic coordinates in Table 9 (Himmelreich, 1998) show that CsCd(NO₂)₃ can exhibit $R\bar{3}$ symmetry with atomic displacements $\Delta\xi \lesssim 1.0$ Å, thereby satisfying the criteria for ferroelectricity in §1.2. The $x'y'z'$ coordinate center of the NO₂⁻ ion at 292 K is translated 0.12 Å in the table to coincide with the closest inversion center at 2/3, 5/6, 1/3 associated with the space group $R\bar{3}$. In consequence, the identity of $x'y'z'$ (O1) exchanges with that of $x'y'z'$ (O2) across the inversion center in the resulting disordered NO₂⁻ ion, with each site equally occupied. The rhombohedral angle dependence $\Delta\alpha \propto (T_C - T)^n$ for $n = 0.34$ (1) as $\alpha \rightarrow 90^\circ$ at T_C , with a symmetry change to $Pm\bar{3}$ above $T_C = 462$ (1) K; $R3$ symmetry was assumed over the range 273 K to T_C ,⁶ the temperature at which the birefringence also vanishes (Planta & Unruh, 1993).

The space group $Pm\bar{3}$ at $T > T_C$ is not a minimal supergroup of $R3$, but is of both $R\bar{3}$ and $P23$. The birefringence measured by Planta & Unruh (1993) changes sharply from linear between 290 and ~ 396 K to a power law function between ~ 396 K and T_C as $\Delta n \rightarrow 0$; Haussühl's (1994) elastic constants vary similarly, suggesting the formation of an additional phase between $R3$ and $Pm\bar{3}$. Himmelreich's (1998) data also reveals a small but unambiguous entropy anomaly at ~ 398 K, in addition to a function change in $\Delta\alpha$ comparable to that in Δn . Since $\Delta\alpha \simeq 0.15^\circ$ at 400 K, the choice of space group $P23$ may be eliminated leaving $R\bar{3}$ as a likely intermediate between the space groups $R3$ and $Pm\bar{3}$. An unequal

⁶ A copy of Himmelreich's (1998) dissertation was kindly provided by Professor H. Bärnighausen.

Table 9

Hexagonal system atomic coordinates for CsCd(NO₂)₃ (Himmelreich, 1998), with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz and u_{33} displacements in Å.

The coordinates in Himmelreich's (1998) dissertation used here (Bärnighausen, 2005) differ slightly from those in ICSD #56436, with those of N + $\frac{211}{333}$, of O1 + $\frac{122}{333}$ in the hexagonal setting of $R\bar{3}$. $a_H = 7.7334$ (2) Å; $c_H = 9.4170$ (3) Å. $z^* = z - 0.0069$, $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R\bar{3}$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta \xi$	u_{33}
Cs	3(a),3(a)	0	0	-0.0069	0	0	0	0	0	0.06	0.06	0.14
Cd	3(a),3(b)	0	0	0.5296	0	0	0.5	0	0	0.28	0.28	0.12
N	9(b),9(e)	0.7193 (2)	0.8451 (2)	0.3530 (2)	0.6141	0.8215	0.3136	0.81	0.18	0.37	0.98	0.15
O1	9(b)	0.5679 (2)	0.6772 (2)	0.3810 (2)	0.6255	0.7282	0.4163	-0.45	-0.39	-0.33	0.80	0.16
	18(f) [†]											
O2	9(b)	0.7079 (2)	0.9384 (2)	0.2503 (2)	0.7655	0.9894	0.2856	-0.45	-0.39	-0.33	0.80	0.16

[†] The coordinates of O1 and O2 reverse atomic identity across the inversion center at 2/3, 5/6, 1/3.

Table 10

Atomic positions for Sc₇I₁₂C at room temperature (Dudis *et al.*, 1986a,b), with hypothetical $x'y'z'$ coordinates and the Δx , Δy , Δz displacements in Å.

$a = 14.717$ (1), $c = 9.847$ (2) Å. $z^* = z + 0.0022$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R32$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta \xi$	u_{iso}
I1	9(b)	0.0773 (2)	0.3065 (2)	0.0008 (3)	0.1521	0.3064	-0.0013	-1.10	0.01	0.02	1.10	0.15
	18(f)											
I3	9(b)	0.3063 (2)	0.2269 (2)	0.0034 (3)	0.3064	0.1521	0.0013	-0.01	1.10	0.02	1.10	0.16
I2	9(b)	0.1759 (1)	0.051 (2)	0.66735	0.1824	0.0924	0.6678	-0.10	-0.61	-0.01	0.67	0.15
	18(f)											
I4	3(a)	0.1339 (2)	0.1888 (1)	0.3317 (1)	0.0924	0.1824	0.3322	0.61	0.09	-0.01	0.66	0.14
Sc1	3(a),3(b)	0	0	0.4752 (7)	0	0	0.5	0	0	-0.24	0.24	0.17
Sc2	9(b)	0.1045 (3)	0.1462 (3)	0.8708 (6)	0.0726	0.1441	0.8667	0.47	0.03	0.04	0.49	0.14
	18(f)											
Sc3	9(b)	0.1419 (3)	0.0406 (3)	0.1374 (6)	0.1441	0.0726	0.1333	-0.03	-0.47	0.04	0.49	0.14
C	3(a),3(a)	0	0	-0.004	0	0	0	0	0	-0.04	0.04	0.15

distribution of the Cd atom over three locations in the thermal range 292–462 K, with the NO₂ group unequally split over two other locations between 398 K and T_C , was also noted, based on $R3$. Hysteresis loops reported by Planta & Unruh (1993) between 454 and 463 K were unobservable below 454 K.

Smaller atomic displacements are required for a phase transition from $R3$ to $Pm\bar{3}$ than from $R3$ to $R\bar{3}$, see Tables 9 and S13(a), although the former transition requires each Cd atom to be distributed over eight sets of equivalent positions, the N and O atoms over two other sets. By contrast, disorder is required only of the NO₂⁻ ion in the transition from $R3$ to $R\bar{3}$, with a smaller potential barrier expected at the transition.

The $\Delta \xi$ range for a transition to $R\bar{3}$ symmetry in isostructural CsCa(NO₂)₃ is comparable to that in CsCd(NO₂)₃, see Table S13(b), hence CsCa(NO₂)₃ also satisfies the structural criteria for ferroelectricity. Notably, Himmelreich's (1998) calorimetric and $\Delta \alpha$ data for CsCa(NO₂)₃ reveal even clearer anomalies at ~ 392 K than those for CsCd(NO₂)₃ at ~ 398 K (Bärnighausen, 2005). Clarification of the phase transition(s) in this family awaits further investigation.

Avdeev & Kharton (2002) independently reported the structure of CsCd(NO₂)₃ together with that of $MCd(NO_2)_3$ for $M = K, Rb, Tl$ and NH_4 . All four nitrites are isostructural with

$M = Cs$, and hence are also most likely to be ferroelectric, although the setting used differs as noted in Table S13(c).

2.18. Sc₇I₁₂C family

Sc1 in Sc₇I₁₂C is bonded to six I with Sc2 and Sc3 each to four I and one C atom, with no atom reported by Dudis *et al.* (1986a,b) further than ~ 1.1 Å from its corresponding location in the space group $R32$, see Table 10. With $0.14 \lesssim u_{iso} \lesssim 0.17$ Å, Sc₇I₁₂C hence satisfies the criteria for ferroelectricity. Isostructural Sc₇Br₁₂C is similarly bonded and, with no atom further than ~ 1.0 Å from its corresponding location in space group $R32$, see Table S14, also satisfies the criteria for ferroelectricity. The relatively large $\Delta \xi$ (I, Br) magnitudes are indicative of correspondingly high T_C values in these two materials.

3. Structures reported in space group $R3$ that more likely belong to crystal class $3m$

A structure in space group $R3m$ or $R3c$ that does not approach $R\bar{3}m, R\bar{3}c$ or a higher centrosymmetric supergroup symmetry

is without symmetry restriction on P_S and hence is not a candidate for ferroelectricity.

3.1. CsGeCl₃ family

Christensen & Rasmussen (1965) reported a transition in ‘ferroelectric’ CsGeCl₃ from space group $R3$ to space group $Pm3m$ at $T \geq T_{PT} = 428$ K, without experimental verification of the ferroelectric property. The coordinates in Table S15(a) show that no atom is further than 0.06 Å from its location in the space group $R3m$; with each $\Delta\xi \ll u_{iso}$, the supergroup is clearly more likely than the proposed $R3$. Thiele *et al.* (1987) later reported the space group to be $R3m$ with atomic coordinates, see Table S15(b), which were subsequently confirmed by Yamada *et al.* (1994), see Table S15(c). Notably, the $x'y'z'$ coordinates in Table S15(a) differ less than ~ 0.2 Å from the experimental values in Tables S15(b) and (c). Both latter sets are also close to those expected in the space group $R\bar{3}m$, although the resulting 18(h) Wyckoff position for the disordered Cl atom would lead to half-occupancy in the x , $2x$, z locations. Phase I was reported by Thiele *et al.* (1987) to form in $Pm3m$ at 443 K through $R\bar{3}m$ as intermediate. The thermal dependence of the rhombohedral α angle through T_{PT} has not yet been reported conclusively; Yamada *et al.* (1994) find $\alpha = 89.71$ (1)° at 294 K, while Thiele *et al.* (1987) report 89.72 (3)° at 428 K. The definitive determination of phases I and II at temperatures close to T_{PT} requires further investigation. The structures of CsGeBr₃ and CsGeI₃ are isostructural with CsGeCl₃.

3.2. Sn₃PO₄F₃

The largest difference between an atomic position in the space group $R3$ reported by Berndt (1972) and that expected in the supergroup $R3m$ is ~ 0.5 Å in $x(F)$ and in $y(F)$, see Table S16. With $\Delta\xi(F) = 0.50$ Å and $u_{iso}(F) \simeq 0.19$ Å, the higher polar symmetry is likely to be more stable at or close to room temperature than the lower symmetry, *cf.* §1.3. The strongly distorted corner-sharing SnO₃F₃ octahedra differ notably from the rather regular PO₄ tetrahedra present.

3.3. Ag₈GeTe₆

The occupancies assigned by von Ünterrichter & Range (1978) to the 13 Ag sites range from 6 to 35% and sum to the requisite total. All atoms have $\Delta\xi \lesssim 0.10$ Å with respect to their corresponding locations in the space group $R3m$, see Table S17, except for the Ag8, Ag12 pair, each of which has $\Delta\xi = 0.47$ Å. One or other Ag atom in this pair may be misplaced, since $d_{Ag8-Ag12} = 0.89$ Å with $d_{Ag8-Agn}$ ranging from 1.16 to 2.29 Å for its $n = 7$ nearest Ag neighbors, whereas $d_{Ag12-Agn}$ ranges from 1.45 to 2.51 Å for its $n = 9$ nearest Ag neighbors. With thermal/static u_{33} displacements between 0.05 and 0.69 Å, the supergroup is likely to be more stable than the subgroup, see §1.3.

3.4. (Na₂CaZr(Si₆O₁₂(OH, O)₆)·H₂O (lovozerite)

The largest displacement by any atom reported by Yamnova *et al.* (2001) from its equivalent location in the space

group $R3m$ is that of O1 at $\Delta\xi = 0.26$ Å, with $u_{iso} = 0.24$ Å, see Table S18. All other atoms have $\Delta\xi < u_{iso}$ and hence, with no atom significantly displaced from the corresponding location in the space group $R3m$, all atoms are likely to be more stable in the supergroup.

3.5. BiCa₉(VO₄)₇

No atom determined by Evans *et al.* (2001) in the space group $R3$ at 120 K differs in position more than 0.04 Å from its equivalent location in the space group $R3c$, see Table S19(a), with room-temperature results stated to be ‘essentially identical’. If all sites were fully ordered, $R3c$ would be more probable than $R3$ since $0.19 \geq u_{iso} \geq 0.07$ Å, see §1.3. However, 20 $I(h\bar{h}0l)_{meas} > 3\sigma$ were observed with $l = 2n + 1$; this violation of the $R3c$ reflection conditions was shown not to result from a $\lambda/2$ component in the direct beam, but instead was attributed to incomplete Bi/Ca ordering. As reported, the Ca,Bi1–Ca,Bi3 pair with $\sim 54\%$ and the Ca,Bi2–Ca,Bi4 pair with $\sim 36\%$ occupancy are located at sites ~ 0.38 Å apart.

A second independent study was reported by Kim *et al.* (2002) who determined the space group to be $R3c$. A comparison of their coordinate set with Evans *et al.*’s (2001) in Table S19(b), using the equivalent positions noted therein, shows agreement within 0.06 Å except for the split Ca,Bi1_{Evans} and Ca,Bi3_{Evans} sites and the corresponding Ca3_{Kim} site. The differences between them, 0.10 and 0.25 Å, respectively, are related to the disorder identified in Evans *et al.*’s (2001) determination. The detection of $I(h\bar{h}0l)_{meas}$ was not reported by Kim *et al.* (2002) who grew their crystals from the melt at 1673 K by cooling to 573 K at 2 K h^{−1}, in contrast with Evans *et al.* (2001) who used ‘slow cooling’ from 1513 K. Growth condition differences may change the occupation of equivalent sites.

Both coordinate sets in the space group $R3c$ approach $R\bar{3}m$ symmetry, with $\Delta\xi_{max} \simeq 2.0$ Å, see Tables S19(c) and (d). The only rhombohedral minimal supergroups of $R3c$, however, are $R\bar{3}c$ and $R3m$, neither of which is realized. Since a transition to $R\bar{3}m$ would require $\Delta\xi$ to exceed the limit for either atomic coordinate set (see §1.2), leading to the conclusion that a transition to $R\bar{3}m$ symmetry cannot occur, BiCa₉(VO₄)₇ is hence not potentially ferroelectric.

4. Structures reported in space group $R3$ that are more likely nonpolar

4.1. Co₂Ge₃S₃ skudderite family

Partik *et al.*’s (1996) atomic coordinates in Table S20 reveal no differences larger than 0.07 Å from those expected in the space group $R\bar{3}$ or that are significantly larger than the corresponding u_{iso} . The centrosymmetric structure with a lower free-energy minimum is expected to be the more stable and hence the state actually occupied, see §1.3. Korenstein *et al.*’s (1977) coordinates are similarly close to $R\bar{3}$ symmetry. The atomic coordinates for Co₂Ge₃Se₃ are comparable to those of Co₂Ge₃S₃ and lead to the same inference that its symmetry is most likely $R\bar{3}$.

4.2. $\text{K}_2\text{Sn}_2\text{O}_3$

A note by Braun & Hoppe (1978) reported the formation of a perovskite structure variant at ~ 790 K in the space group $R\bar{3}$. No atomic coordinates reported, however, differ more than 0.15 \AA from $R\bar{3}m$ symmetry, see Table S21(a). A correction paper by Braun & Hoppe (1981) confirms the space group as $R\bar{3}m$; Sn1 and Sn2 may be independent as in Table S21(a) or more likely not as in S21(b); in either case, the coordinates agree well with the x', y', z' values in Table S21(a). Preparation at ~ 590 K gives a powder pattern with a total of six I_{obs} that match the pattern of the isotypic $\text{K}_2\text{Pb}_2\text{O}_3$ reported in the space group $I2_13$ (Hoppe & Nowitzki, 1984).

4.3. $[\text{Cr}(\text{H}_2\text{O})_6]\text{F}_3 \cdot (\text{H}_2\text{O})_3$

Epple & Massa's (1978) atomic coordinates in Table S22 correspond more likely to the space group $R\bar{3}$ than $R3$, since each $\Delta\xi \ll u_{33}$, except for the H1, H2 pair associated with O3; the H-atom locations had been assumed as occupying the $\text{O}\cdots\text{O}$ or $\text{O}\cdots\text{F}$ contacts of $\sim 2.6 \text{ \AA}$, with O—H taken as 0.80 \AA . Atoms O3 and F are equivalent in the supergroup structure, casting doubt on the choice of H1 and H2 as located close to O3, but $\sim 1.8 \text{ \AA}$ distant from F. The magnitudes of $\Delta\xi(\text{H1}, \text{H2})$ decrease strongly as the H atom is assumed closer to the $\text{O3}\cdots\text{F}$ bond center. Redetermination of all the atoms is not expected to show significant departures from centrosymmetry.

4.4. $\text{Cs}[\text{SbF}_5\text{OH}]$

Table S23(a) shows that Nolte and de Beer's (1979) coordinates have $\Delta\xi_{\text{max}} \leq 0.15 \text{ \AA}$ with respect to the equivalent values in $R\bar{3}$; since $u_{33} \lesssim 0.26 \text{ \AA}$, the centrosymmetric structure is hence more likely to be stable, see §1.3. The structure of CsSbF_6 , which is isostructural with $\text{Cs}[\text{SbF}_5\text{OH}]$, was refined successfully in $R\bar{3}$ (de Steyn *et al.*, 1984). The phase transition in CsSbF_6 at $T_C = 461 \text{ K}$ reported by de Beer *et al.* (1980) is consistent with a symmetry change at T_C from $R\bar{3}$ to $R\bar{3}m$, see Table S23(b), as the F atom is displaced $\sim 0.22 \text{ \AA}$.

4.5. $\text{B}_3\text{N}_3\text{Cl}_6$

Gopinathan *et al.* (1974) developed the preferred coordinate set in Table S24 on the basis of Haasnoot *et al.*'s (1972) diffraction data, see also Müller (1971). All four independent atoms have coordinates that satisfy the inversion-center relationship of the space group $R\bar{3}$ within 0.02 \AA . In view of the $\sim 0.2 \text{ \AA}$ r.m.s. thermal/static vibrational amplitude, the centrosymmetric structure is thermodynamically the more likely stable phase. The high correlation reported in the full-matrix least-squares refinements is consistent with the use of inappropriate symmetry.

4.6. Li_7SbO_6

Table S25, based on Hauck's (1969) brief report, shows that the only atom in $R3$ further than 0.8 \AA from its equivalent location in the space group $R\bar{3}$ is Li3 with $\Delta z = 2.56 \text{ \AA}$, unless it is disordered over $00z$ and $00\bar{z}$ in which case $\Delta z(\text{Li3}) =$

0.0 \AA . Sb is octahedrally coordinated, Li1 and Li2 tetrahedrally, while Li3 is octahedrally coordinated as reported. Redetermination by Mühle *et al.* (2004) shows that the symmetry for Li_7SbO_6 is actually $P\bar{1}$, confirming the structural centrosymmetry with a and c axes in the triclinic structure that are nearly identical in length to Hauck's (1969) values and $\beta = 119.6^\circ$.

4.7. $\text{Fe}_2\text{P}_2\text{Se}_6$ and family

Klingen *et al.*'s (1973) x, y, z coordinates in Table S26(a) reveal no atom to be further than 0.12 \AA from the corresponding location in the centrosymmetric space group. Assuming the unreported u_{iso} magnitudes are between 0.1 and 0.2 \AA , the $R\bar{3}$ structure is hence more likely. Wiedenmann *et al.* (1981) found the agreement in $R3$ to be no better than that in $R\bar{3}$; coordinates for the latter in Table S26(b) agree well with the derived $x'y'z'$ values in Table S26(a).

4.8. Ni_3TeO_6

Newnham & Meagher's (1967) atomic coordinates in Table S27 are identical to those in $R\bar{3}$, although with variable Ni/Te site occupancies; one distribution in $R\bar{3}$ was reported to give $R_f = 0.25$. All four $3(a)$ sites are chemically equivalent with each forming three Ni/Te—O bonds of 2.099 \AA , three of 1.985 \AA in a distorted octahedron. Any combination of site occupancies within the overall $3\text{Ni}:1\text{Te}$ composition is hence possible in principle. Thermodynamically, the phase is more likely to be stable in $R\bar{3}$ than in $R3$ on annealing, see §1.3, hence redetermination of the structure would be appropriate. Kasper (1967) reported that the spectral absorption of Mg_3TeO_6 , Ni_3TeN_6 and $\text{Mg}_2\text{InSbO}_6$ agrees with that of Ni_3TeO_6 , also that Mg_3TeO_6 forms in the space group $R\bar{3}$, but with a and c axes markedly different from those in Ni_3TeO_6 .

4.9. $2\text{CeFCO}_3 \cdot \text{CaCO}_3$ (parisite)

Displacing Donnay & Donnay's (1953) atomic z coordinates by 0.138 , with an additional displacement of $c/12$ by two C and six O atoms and an exchange of $yxz(\text{O}2)$ for $xyz(\text{O}2)$, results in a structure that conforms to $R32$ symmetry, see Table S28. Both CO_3 groups are thus closer to the plane occupied by Ca^{2+} ions instead of having the 2.35 \AA separation in the reported structure. Syntactic intergrowth among related phases delayed further progress until Ni *et al.*'s (2000) solution in a unit cell with $a_{\text{Ni}} \simeq a_{\text{Donnay}}$, $b_{\text{Ni}} \simeq 3^{1/2}b_{\text{Donnay}}$ and $c_{\text{Ni}} \simeq c_{\text{Donnay}}/3$ and space group Cc ; differing significantly from the earlier work, their coordinates may approach the space group $C2/c$.

4.10. $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$ (röntgenite)

Assuming the $z(\text{CO}_3)$ coordinates derived by Donnay & Donnay (1953) are misplaced by $\sim c/6$, then all differences between the coordinates reported and those satisfying the space group $R32$ become zero, except for $\Delta x(\text{C}) = -0.31$, $\Delta y(\text{C}) = 0.31$ and $\Delta x(\text{O}1) = 0.48 \text{ \AA}$, see Table S29. The latter three magnitudes are probably without significance in view of their provenance and the centrosymmetry of all other atoms in

the model, hence the space group is more likely to be $R32$ than $R3$, if the crystal system is indeed rhombohedral, *cf.* §4.9.

4.11. NiTiO₃ and CoTiO₃

Sullivan & Pavlovic's (1962) space group was stated to be $R3$ but, with atomic coordinates listed as either $\pm(0, 0, z)$ or $\pm(x, y, z)$ for all three independent atoms in both family members, the space group of each titanate is necessarily centrosymmetric, see Table S30. The $R\bar{3}$ centrosymmetric space group was confirmed by Boysen *et al.* (1995).

4.12. Er₁₃Ge₆O₃₁(OH)

Genkina *et al.* (1990) chose the structural solution in the space group $R3$ over that in $R\bar{3}$. The atomic coordinates in Table S31, however, show that $\Delta\xi < u_{\text{iso}}$ for all atoms except $\Delta\xi(\text{Er}1) = 0.29 \text{ \AA}$ and $\Delta\xi(\text{O}11, \text{O}12) = 0.21, 0.21 \text{ \AA}$. There are 16 of the 19 independent atoms determined that are hence more likely to satisfy $R\bar{3}$ than $R3$ symmetry, see §1.3. The remaining three $\Delta\xi$ magnitudes are strongly dependent on the accuracy of $z(\text{O}11)$ and $z(\text{O}12)$, as the closer each corresponds to the z' values in Table S31, the smaller are all three $\Delta\xi$. It is thus more likely that Er₁₃Ge₆O₃₁(OH) exhibits $R\bar{3}$ than $R3$ symmetry.

4.13. II-In₄(P₂Se₆)₃

No atom in Table S32(a) has $\Delta\xi > 0.02 \text{ \AA}$ with respect to the space group $R\bar{3}$, hence the structure as refined by Voroshilov *et al.* (1991) is indistinguishable from that expected in the centrosymmetric space group. A later ICSD entry #56891, see Table S32(b), updates the original entry #39536 and gives the space group as $R\bar{3}$, with coordinates virtually identical to the x', y', z' set derived in Table S32(a).

4.14. NaNi(AsO₄)

All atomic coordinates reported by Range & Meister (1984) in Table S33(a) are within 0.03 Å of their equivalents with $R\bar{3}$ symmetry. Subsequently, Jones *et al.* (1987, 1988) noted that the atomic coordinates indeed fit $R\bar{3}$ symmetry well within experimental error and gave $R = 0.044$ with reduced uncertainties. These coordinates, see Table S33(b), are virtually coincident with the x', y', z' set derived in Table S33(a).

4.15. Mg₃In

A shift of $c/8$ in Schubert *et al.*'s (1963) origin completely satisfies the 6(c) Wyckoff position relating pairs of 'independent' In atoms as well as the 18(f) Wyckoff position relating pairs of 'independent' Mg atoms in the space group $R\bar{3}$, see Table S34. The atomic coordinates hence correspond to a solution in the centrosymmetric space group $R\bar{3}$ rather than in $R3$ as reported.

4.16. AsTe₂I·0.5H₂O

The As1 and As2 bond distributions reported differ significantly (Stergiou, 1994). As1 has three bonds with $d_{\text{As}1-\text{Te}1} = 2.54 \text{ \AA}$ and three $d_{\text{As}1-\text{Te}2} = 3.55 \text{ \AA}$, whereas As2 has

three $d_{\text{As}2-\text{Te}1} = 3.34 \text{ \AA}$, three $d_{\text{As}2-\text{Te}2} = 2.65 \text{ \AA}$ and one $d_{\text{As}2-\text{O}1} = 2.53 \text{ \AA}$. If a previously undetected O2 atom occupies a site equivalent to $00\bar{z}(\text{O}1)$, as in Table S35, then an additional $d_{\text{As}1-\text{O}2} = 2.45 \text{ \AA}$ bond is present with the two As polyhedra closely comparable. Accepting the reported As:O ratio of 2:1, stoichiometry would be maintained with 25% occupancy at both O1 and O2 sites rather than the 50% occupancy previously proposed for O1 alone. Since $u_{\text{eq}}(\text{O}1) = 0.15 \text{ \AA}$ for the model with a single O atom, whereas $u_{\text{eq}}(\text{metal ions}) = 0.22\text{--}0.23 \text{ \AA}$, the occupancy of a second O-atom site could lead to a more realistic value for $u_{\text{eq}}(\text{O}1)$. Table S35 shows that all six independent atoms have $\Delta\xi \lesssim 0.08 \text{ \AA}$, with respect to $R\bar{3}$ symmetry. If the additional atom is confirmable, then the stable form of AsTe₂I·0.5H₂O is likely to be centrosymmetric since all $\Delta\xi \lesssim u_{\text{eq}}$.

4.17. Au₅Sn

The Au1–Au3 and Sn atomic coordinates reported in Wyckoff positions 3(a) and 9(b) for the space group $R3$ by Osada *et al.* (1974) are identical to those respectively in positions 6(c), 9(e) and 3(a) of the space group $R32$, see Table S36(a). The higher-symmetry space group hence provides a more appropriate description at room temperature. A displacement of 0.88 Å by Au3, but with no other atom displaced, may be seen in Table S36(b) to result in a transition to $R\bar{3}m$, consistent with the transition at $\sim 468 \text{ K}$ noted by Osada *et al.* (1974).

4.18. InBrI₂

Neither the atomic coordinates in $R3$ chosen by Kniep & Blee (1984) on the basis of the Hamilton significance test nor the u_{aniso} values are given in the brief publication, but ICSD entry #60001 provides both, see Table S37. Since all $\Delta\xi < u_{\text{eq}} \lesssim 0.19 \text{ \AA}$ with respect to $R\bar{3}$, the structure in the higher-symmetry space group is expected to be more stable, see §1.3.

4.19. H₃O⁺·Al₄SiP₃O₁₆[−]·*n*H₂O

Coordinates for the water atoms O9–O16 in this zeolite, with occupancies ranging from 0.03 to 0.25, are given by Ito *et al.* (1985) in a supplementary publication. Table S38 shows that all other atoms they reported refined to positions for which $\Delta\xi \lesssim 0.16 \text{ \AA} \lesssim u_{\text{eq}}$ with respect to $R\bar{3}$. The apparent departure from the space group $R\bar{3}$ symmetry by these seven water O atoms, each of which has an estimated uncertainty of at least 0.25 Å and an occupancy only $\sim 10\%$, is of doubtful validity. It is more likely that both the Al₄SiP₃O₁₆ component and its associated water conform to centrosymmetry. Experimental redetermination of the structure is appropriate.

5. Structures of lower predictability reported in the space group $R3$

5.1. (NH₄)₃Sc(SeO₄)₃

Eight of the 14 atoms in Table S39 determined by Valkonen & Niinistö (1978) are closely related in pairs by the super-

group $R\bar{3}c$ symmetry, with $0.01 < \Delta\xi < 0.35 \text{ \AA}$ for Se, Sc, O1 and O7, and with $\Delta\xi(\text{O3, O4}) \simeq 0.9 \text{ \AA}$. The remaining four O and two N atoms, however, have $1.70 < \Delta\xi < 2.15 \text{ \AA}$, a range that exceeds the displacement criteria in §1.2 which are well satisfied by the former eight atoms. The mixed result does not support property predictions. Further diffraction or calorimetric studies are hence necessary to determine whether or not the structural thermal dependence is consistent with a predicted phase transition.

5.2. $\text{Cu}_7\text{As}_6\text{Se}_{13}$

Differences (Δz) between $z(\text{Cu})$ and $z(\text{As})$ coordinate values determined by Takeuchi & Horiuchi (1972) in the space group $R3$ and the corresponding values in space group $R\bar{3}$, see Table S40(a), range from $1.0 \lesssim \Delta z(\text{S}) \lesssim 1.3 \text{ \AA}$, whereas $-1.0 \gtrsim \Delta z(\text{Se}) \gtrsim -1.3 \text{ \AA}$. If all coordinates are fully confirmable, then the structure is not a likely candidate either for higher symmetry or ferroelectricity, see §1.2. In the event, however, that the origin assigned to the Cu and As atoms differs from that of the Se atoms by $c/4$, as in Table S40(b), then each $\Delta\xi$ magnitude becomes comparable to its u_{iso} and $R\bar{3}$ would be the more likely space group. This partial shift in origin changes the tetragonal coordination of all atoms present to octahedral. Remeasurement may reveal further alternatives, but the present structure cannot support property prediction.

5.3. $\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$

All atoms determined by Powell *et al.* (1994) in Table S41(a) except for H1 differ less than $\sim 1.2 \text{ \AA}$ from the corresponding location in the nonpolar space group $R32$, hence ferroelectricity is strongly suggested with $0.25 > u_{\text{eq}} > 0.11 \text{ \AA}$. However, in the absence of an electric field or disorder, a 2.8 \AA displacement by H1 along the polar axis is unlikely although the O1 atoms in the PO_3^{3-} ion may be displaced 1.2 \AA for zero polarization. The neutron results in Table S41(b) are in agreement, see also Corbridge (1956). Ferroelectric characterization is thus indeterminate. Similarities between the present structure and that of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in §2.2 may be noted.

5.4. Cronstedtite-6R

The x and y atomic coordinates of this six-layer rhombohedral structure, taken by Steadman & Nuttal (1963) from a projection of (presumed) noncentrosymmetric single-layer cronstedtite-1T, were manually adjusted to decrease R . Assuming all four Si atom sites are shared equally with Fe, both Si/FeO_4 tetrahedra and Si/FeO_6 octahedra result, with Fe5 and Fe6 occupying octahedral sites. The difference between corresponding coordinates as reported and their equivalents in space group $R\bar{3}$ is zero for all Δx and Δy , with $12 \Delta z \lesssim 1.5 \text{ \AA}$; however, four O atoms have $2.1 \lesssim \Delta z \lesssim 2.5 \text{ \AA}$, see Table S42, well beyond the limit in §1.2. Structural remeasurement is hence necessary for reliable prediction of the properties of this polymorph; eight or more polymorphs of cronstedtite, a hydrous ferrosilicate, are known.

5.5. $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$ (aktashite) and $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$ (nowackiite)

The relationship between aktashite (A ; Kaplunnik *et al.*, 1980) and nowackiite (N ; Marumo, 1967) was examined by Nowacki (1982) in this 90th birthday tribute to Nikolai V. Belov. Each ordered Cu and Hg site in A is fully occupied, whereas the Cu and Zn sites in N are shared in various proportions, see Tables S43(a) and (b). Both atomic coordinates and $\Delta\xi$ displacements, with respect to equivalent locations in the space group $R32$, are closely comparable in the two minerals except that Hg in A occupies the site designated Cu2, Zn2 in N and the Cu2 site in A is the Cu3, Zn3 site in N . No Δz magnitude for any atom in either mineral exceeds $\sim 0.6 \text{ \AA}$, suggesting the possibility of ferroelectricity. However, $\Delta y(\text{As1}) \simeq 2.4 \text{ \AA}$ with both $\Delta x(\text{S4})$ and $\Delta y(\text{S4}) \simeq 1.9 \text{ \AA}$ in A , and $\sim 1.8 \text{ \AA}$ in N , significantly in excess of the limit in §1.2. The resulting predictive discrepancy is most readily resolved by structural remeasurement.

5.6. $\text{Na}_{0.55}\text{TiS}_2$

The $z(\text{Ti})$ and $z(\text{S})$ coordinates reported by Rouxel *et al.* (1971) differ less than 0.06 \AA from $R3m$ symmetry, although $z(\text{Na1})$ differs strongly, see Table S44. If, however, half the Na atom reported at a single $3(a)$ site with 55% occupancy were instead distributed over the $6(c)$ Wyckoff position pair of sites, each with 27.5% occupancy at room temperature, then the maximum structural divergence from $R\bar{3}m$ symmetry becomes 0.06 \AA . $\text{Na}_{0.55}\text{TiS}_2$ is isotypic with NaHF_2 (in $R\bar{3}m$). Cenozal *et al.* (1991) corrected the space group, given as $R3$, to $R3m$ with all atoms in Wyckoff position $3(b)$ and the reported value of $R = 0.10$ applicable to either space group. Definitive characterization awaits further structural or physical reinvestigation.

5.7. $\text{H}_6\text{As}_{6.3}\text{Cu}_{0.84}\text{FeMg}_{0.1}\text{Mn}_{13.9}\text{O}_{33}\text{Si}_{17}$ (dixenite)

All atoms reported by Araki & Moore (1981) except for Cu1, O7 and O11 are located within 1.5 \AA of the corresponding positions in the supergroup $R32$, see Table S45. The location of Cu1, however, is more than 5 \AA from the nearest site with symmetry 32 . If a previously undetected Cu3 atom were related within $\sim 1.0 \text{ \AA}$ to Cu1 by an inversion center while satisfying the mineral stoichiometry at both Cu1 and Cu3 sites, and if the location of the atom pair O7, O11 with $\Delta\xi \simeq 2.1 \text{ \AA}$ requires a correction resulting in smaller $\Delta\xi$, then the structure would meet the criteria for ferroelectricity. In that case, the previously reported occupation of several sites, see Table S45, would also change. Doubt associated with the 'missing' Cu3 atom, the unlikely 0.88 \AA separation between the locations reported for Cu1 and Cu2, and the possible misplacement of O7 or O11 as the remaining atoms approach centrosymmetry lead to a determination with reduced predictability. Additional structural investigation would be appropriate.

5.8. $[\text{C}(\text{NH}_2)_3]_6\text{As}_2\text{Mo}_{18}\text{O}_{62}\cdot 9\text{H}_2\text{O}$

Ichida & Sasaki's (1983) final refined coordinates for 36 of the 44 independent atoms in Table S46 are strikingly indicative of a structure close to centrosymmetry with maximum $\Delta z = 0.53 \text{ \AA}$ for these atoms and $0.25 > u_{\text{iso}} > 0.11 \text{ \AA}$. However, reversing the reported signs of x and y for O22, N6' and Ow3 in the table, as they otherwise violate such a conclusion, leads to close conformity with $R\bar{3}$ symmetry. In addition, atoms C3 and Ow1 with their large Δx , Δy magnitudes are noted to be nearly inversion-center related. The possibility that the $\Delta\xi$ magnitudes for these eight atoms are comparable to those of the remaining 36 atoms suggests the need for additional structural investigation before drawing definitive property conclusions.

5.9. $\text{H}_{0.8}\text{Ca}_{1.77}\text{Ce}_{2.1}\text{Cl}_{0.73}\text{Fe}_{1.41}\text{K}_{0.19}\text{Mn}_{3.7}\text{Na}_{13.61}\text{Nb}_{0.92}\text{O}_{76}\text{Si}_{25}\text{Y}_{0.25}\text{Zr}_{3.17}$ (oneillite)

The structure reported by Johnsen & Grice (1999*a,b*) approaches $R\bar{3}$ symmetry, with $\Delta\xi \lesssim 0.7 \text{ \AA}$ for all but four of the 44 independent atomic positions, see Table S47. The location of the Si2 atom is given close to the corresponding 6(*c*) position for Nb1, hence, if Si2 has been misidentified and is instead Nb2, and if the actual location of Si2 is related approximately to that of Si1 through a 6(*c*) Wyckoff position in $R\bar{3}$, then the Si1, Si2 pair becomes comparable to that of all other atoms in the structure, except for Na6 and O25. Atoms Na7 and O27 may similarly be postulated in locations related approximately to those of Na6 and O25 through 18(*f*) Wyckoff positions. If the relocated Nb2, the new location for Si2 and the introduction of Na7 and O27 are confirmable, then all atoms in the structure would approach $R\bar{3}$ symmetry. With about half the atomic $\Delta\xi$ magnitudes comparable to or less than u_{eq} and the remainder no larger than $\sim 3u_{\text{iso}}$, except for O26, the resulting structure is close to satisfying the criteria for ferroelectricity. The definitive structural prediction of the physical properties of oneillite requires the experimental confirmation or rejection of the coordinates in italic or alternatively, physical measurements capable of recognizing the properties of materials without inversion centers (*cf.* Abrahams *et al.*, 1998).

5.10. $\text{AlCa}_3\text{Cd}_{17}$

The coordinates of 51 of the 60 independent atoms in $\text{AlCa}_3\text{Cd}_{17}$ reported by Cordier *et al.* (1986) approach the symmetry of space group $R\bar{3}$ with $\Delta\xi < 1.5 \text{ \AA}$, see Table S48. Five Cd atoms, however, have $1.6 \lesssim \Delta\xi \lesssim 1.8 \text{ \AA}$ with four others at $2.0 \lesssim \Delta\xi \lesssim 3.1 \text{ \AA}$. In addition, two pairs of Al atoms are nearly related by a *c* glide plane. The uncertainty raised by $\Delta\xi$ magnitudes as large as $\sim 3.1 \text{ \AA}$ for some Cd locations together with a choice of symmetry elements among Al atoms suggests a need for additional structural investigation before the properties of this intermetallic compound can be predicted. $\text{AlCa}_3\text{Cd}_{17}$ is a variant of the YCd_6 structure with the space group $Im\bar{3}$ (Larson & Cromer, 1971).

Note added in proof: The $\text{Sr}_{17}\text{Ta}_{10}\text{S}_{42}$ atomic coordinates in §2.14 exhibit the transformation $\bar{x}, \bar{y}, \frac{1}{2} + z$ between atom pairs in addition to the symmetry previously noted, see Table S10(*a*). A slight departure from rhombohedral centering in the $\text{Sr}_{17}\text{Ta}_{10}\text{S}_{42}$ supercell would allow such a transformation in $P6_3$, also in several other hexagonal space groups. Table 10(*b*) shows that the hexagonal structure further satisfies the supergroup symmetry $P6_3/m$, with all $\Delta\xi < 1.2 \text{ \AA}$ except by S4 for which $\Delta\xi \simeq 1.85 \text{ \AA}$. If the latter displacement, reversing the orientation of TaS_4 tetrahedra, is achievable then a ferroelectric transition to this higher symmetry phase may be expected. Further investigation of $\text{Sr}_{17}\text{Ta}_{10}\text{S}_{42}$ is advisable.

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