

Systematic prediction of new ferroelectrics in space group $R3$. II

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Release 2006/1 of the Inorganic Crystal Structure Database contains 155 entries under space group $R3$. Atomic coordinate analysis of the first 81 structures, with 52 different structure types, in Part I [Abrahams (2006). *Acta Cryst.* **B62**, 26–41] identified a total of 18 new types that satisfy the structural criteria for ferroelectricity, five that are more likely to have or undergo a transition to $3m$ symmetry, 19 more likely to be or undergo a transition to nonpolar symmetry and ten with a lower property predictability. Coordinate analysis of the remaining 71 entries with 54 different structure types in Part II leads to 11 materials including $Al_4B_6O_{15}$, $PbTa_3(PO_4)(P_2O_7)_{3.5}$, the $KCd_4Ga_5S_{12}$ family, the $LiZnPO_4$ family, $Ca_3Nb_{1.95}O_8V_{0.05}$ and $Mn_4Ta_2O_9$ as new candidates which satisfy the structural criteria, together with the three known ferroelectrics $Na_3MoO_3F_3$, Pb_2ScTaO_6 , and $RbTi_2(PO_4)_3$ at 6.2 GPa. Two additional ferroelectric predictions are at a lower level of confidence. The analysis also reveals nine materials, two of which are isostructural, that more likely belong or are capable of undergoing a transition to crystal class $3m$. There are 14 additional structure types which are more likely to be nonpolar or undergo a transition to nonpolarity, ten have reduced predictive properties, with a further nine for which the space group is expected to remain $R3$ over the full thermal stability range. The increasing use of methods for identifying overlooked inversion centers in structural determinations may be extended by using coordinate analysis for detecting additional commonly overlooked symmetry elements.

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1. Introduction

1.1. Summary of present results for point group 3

The space group $P3$ has been shown to include 21 inorganic structures satisfying the structural criteria for ferroelectricity (Abrahams, 2000) with space groups $P3_1$ and $P3_2$ satisfying an additional 16 (Abrahams, 2003). Release 2006/1 (FIZ Karlsruhe/ILL, 2006) of the Inorganic Crystal Structure Database (ICSD) contains a total of 155 entries under the space group $R3$ with release 2005/1 listing 158 entries. The difference in totals is due to the elimination of nine duplicates and the addition of six new entries in the latest release (Allmann, 2006). Analysis of the first 81 entries in Part I (Abrahams, 2006) led to 18 new structure types that satisfy the structural criteria for ferroelectricity (Abrahams, 2000); analysis of the remaining 71 entries in Part II leads to 11 new ferroelectric candidates. In addition, nine materials of which two are isostructural more likely belong to, or are capable of undergoing a transition from, crystal class 3 to $3m$. There are 14 other materials which are more likely to have or are able to undergo a transition to nonpolar symmetry. The final eight

Table 1

Modified atomic positions in $\text{II-Al}_4\text{B}_6\text{O}_{15}$ (Ju *et al.*, 2004) with hypothetical x', y', z' coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [54854].

$a = 11.43398$ (9), $c = 6.48307$ (5) Å, $z^* = z - 0.0067$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$. The published z coordinates, modified by the given constant, result in the listed z^* coordinates here and in the other tables.

	Wyckoff position $R3, R32$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta \xi$	u_{eq}
A11	3(a), 3(a)	0	0	-0.0067	0	0	0	0	0	0.04	0.04	0.10
A12	9(b), 9(d)	0.9770 (4)	0.2344 (5)	0.9359 (10)	0	0.2344	0	-0.26	0	-0.42	0.49	0.10
O1	9(b)	0.7987 (6)	0.6256 (6)	0.0915 (12)	0.7236	0.6115	0.0118	0.86	0.16	0.52	1.08	0.08
	18(f)											
O5	9(b)	0.5973 (8)	0.6485 (7)	0.0680 (10)	0.6115	0.7236	-0.0118	-0.16	-0.86	0.52	1.08	0.07
O2	9(b), 9(e)	0.1360 (7)	0.1616 (6)	0.4639 (16)	0.1488	0.1488	0.5	-0.15	0.15	-0.23	0.27	0.07
O3	9(b)	0.4905 (7)	0.7666 (7)	0.4784 (11)	0.4914	0.7374	0.5071	-0.01	0.33	-0.19	0.38	0.07
	18(f)											
O4	9(b)	0.7081 (6)	0.4922 (7)	0.4642 (14)	0.7374	0.4914	0.4929	-0.34	0.01	-0.19	0.39	0.07
B1	9(b)	0.7235 (12)	0.5254 (11)	0.6639 (17)	0.7899	0.4999	0.6614	-0.76	0.29	0.02	0.66	0.10
	18(f)											
B2	9(b)	0.4745 (12)	0.8563 (12)	0.3411 (17)	0.4999	0.7899	0.3386	-0.29	0.76	0.02	0.66	0.10

Table 2

Modified atomic positions for $\text{Na}_3\text{MoO}_3\text{F}_3$ at 300 K (Brink *et al.*, 2003) with hypothetical x', y', z' coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [97452].

$a = 5.6248$ (1), $c = 14.5535$ (3) Å, $z^* = z + 0.0034$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R\bar{3}$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta \xi$	u_{iso}
Mo	3(a), 3(a)	0	0	0.0041	0	0	0	0	0	0.06	0.06	0.10
Na1	3(a)	0	0	0.2693 (7)	0	0	0.2463	0	0	0.36	0.36	0.09
	6(c)											
Na3	3(a)	0	0	0.7767 (7)	0	0	0.7537	0	0	0.36	0.36	0.12
Na2	3(a), 3(a)	0	0	0.494 (1)	0	0	0.5	0	0	-0.09	0.09	0.10
O	9(b)	-0.0763 (8)	0.2850 (7)	0.3886 (8)	-0.0801	0.2932	0.4104	0.02	-0.05	-0.34	0.34	0.12
	18(f)											
F	9(b)	0.0838 (8)	-0.3044 (7)	0.5678 (9)	0.0801	-0.2932	0.5896	0.02	-0.06	-0.34	0.34	0.11

structures are more likely to remain stable in the space group $R3$ throughout their thermal stability range. All unit cells reported in a rhombohedral setting are converted to the hexagonal setting by means of the relations $a_{\text{H}} = 2a_{\text{R}} \sin(\alpha/2)$ and $c_{\text{H}} = a_{\text{R}} 3^{1/2} (1 + 2 \cos \alpha R)^{1/2}$.

1.2. Structural criteria for predicting ferroelectricity

The structural criteria used in this paper, as discussed more fully in Part I (Abrahams, 2006), are:

(i) that $1.5 \gtrsim \Delta \xi_i \gtrsim 0.1$ Å or u_i , the r.m.s. thermal or static displacement of the i th atom, and

(ii) that the i th atom forming the shortest least-ionic bonds in the unit cell undergoes no polar displacement $\Delta z_i \gtrsim 1.2$ Å 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

1.3. Pseudosymmetry element detection

The proportion of materials reported in $R3$ or other noncentrosymmetric space groups that more likely are

¹ Where each atom at x, y, z in the space group $R3$ is considered as displaced from the location x', y', z' 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 a hexagonal setting.

nonpolar, see §4 for examples, is expected to decrease as the use of methods for detecting pseudosymmetry, such as those used by Flack *et al.* (2006) and Marsh (2005), increases. Detection of the second harmonics generated by materials without inversion centers under laser (*e.g.* Nd:YAG) irradiation on the basis of Kurtz & Perry's (1968) design (see also Abrahams, 1972) is also in steady use and may become more common as laser power output continues to increase. Coordinate analysis, by contrast, is capable of distinguishing between structures with inversion centers and those close to but not yet centrosymmetric, as is typical of ferroelectrics. Such analysis can also detect the presence of other symmetry elements, including mirror planes or rotation axes, see §3 for example. It is striking that of the total 155 current entries assigned to space group $R3$, 21.6% are more likely to be nonpolar, with another 4.7% containing undetected mirror planes. In addition, 14.2% of the entries are likely to undergo phase transitions to space groups of higher symmetry such as $R\bar{3}, R3m$ or $R32$ on heating.

1.4. Space group–supergroup selection

Parts I and II of space group $R3$ together contain 155 entries, of which 29 fulfil the structural criteria for ferroelec-

Table 3

Modified atomic positions.

(a) For $\text{KCa}_4\text{Ga}_5\text{S}_{12}$ at ~ 295 K (Schwer *et al.*, 1993) with hypothetical x', y', z' coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [67945]. $a = 13.782$ (3), $c = 9.329$ (3) Å, $z^* = z - 0.0339$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R\bar{3}$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{33}	Occ.†
K1	3(a), 3(a)	0	0	-0.0300	0	0	0	0	0	-0.28	0.28	0.24	1
Cd1,Ga1	9(b) 18(f)	0.3589 (9)	0.1014 (1)	0.0499 (6)	0.4227	0.1597	-0.0025	-0.88	-0.80	0.49	1.54	0.13	1/3,2/3
Cd3,Ga3	9(b)	0.20468 (4)	0.4865 (6)	0.0548 (6)	0.2630	0.4227	0.0025	-0.80	0.88	0.49	0.97	0.14	1/2,1/2
Cd2,Ga2	9(b)	0.5904 (1)	0.02121 (9)	0.0497 (6)	0.5	0	0	1.25	0.29	0.46	1.49	0.15	1/2,1/2
S1	9(b) 18(f)	0.2987 (2)	0.2236 (2)	-0.0272 (5)	0.2991	0.2235	0.0004	-0.01	0.00	-0.26	0.26	0.17	1
S4	9(b)	0.0757 (1)	0.2994 (2)	-0.0279 (5)	0.0756	0.2991	-0.0004	0.00	0.01	-0.26	0.26	0.18	1
S2	9(b) 18(f)	0.5444 (1)	0.1629 (1)	-0.0220 (6)	0.5419	0.1608	0.0129	0.03	0.03	-0.33	0.33	0.18	1
S3	9(b)	0.3833 (2)	0.5395 (1)	-0.0477 (6)	0.3812	0.5419	-0.0129	0.03	-0.03	-0.33	0.33	0.16	1

(b) For $\text{CsHg}_4\text{Ga}_5\text{Se}_{12}$ at ~ 295 K (Krauß *et al.*, 1996) with hypothetical $x'y'z'$ coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [67945]. $a = 14.380$ (4), $c = 9.758$ (6) Å, $z^* = z - 0.0294$; $\Delta x = (x - x')a$, $\Delta y = (y - y')a$, $\Delta z = (z^* - z')c$.

	Wyckoff position $R3, R\bar{3}$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{33}	Occ.†
Cs1	3(a), 3(a)	0	0	-0.0294 (3)	0	0	0	0	0	-0.29	0.29	0.12	1
Hg1,Ga1	9(b) 18(f)	0.3601 (2)	0.0996 (2)	0.0477 (2)	0.4234	0.1591	-0.0041	-0.91	-0.87	0.51	1.62	0.11	1/3,2/3
Hg3,Ga3	9(b)	0.20480 (11)	0.48668 (13)	0.0558 (2)	0.2643	0.4234	0.0041	-0.86	0.91	0.50	1.02	0.12	1/2,1/2
Hg2,Ga2	9(b)	0.5876 (2)	0.0202 (2)	0.0525 (1)	0.5	0	0	1.26	0.29	0.51	1.52	0.12	1/2,1/2
Se1	9(b) 18(f)	0.2976 (2)	0.2253 (3)	-0.0244 (3)	0.2972	0.2225	0.0026	0.01	0.04	-0.26	0.27	0.13	1
Se4	9(b)	0.0776 (2)	0.2968 (2)	-0.0295 (3)	0.0748	0.2972	-0.0026	0.08	-0.01	-0.26	0.27	0.14	1
Se2	9(b) 18(f)	0.5484 (2)	0.1664 (2)	-0.0199 (2)	0.5440	0.1628	0.0165	0.06	-0.05	-0.36	0.36	0.13	1
Se3	9(b)	0.3849 (2)	0.5395 (2)	-0.0529 (2)	0.3821	0.5440	-0.0165	0.04	-0.06	-0.36	0.36	0.12	1

† The unequal Cd and Ga occupancies of sites 1 and 3, proposed as equivalent, suggests the 1/3, 2/3 site occupancy is more likely associated with Cd2,Ga2.

tricity at a confidence level ranging from high (*e.g.* $\text{Na}_3\text{MoO}_3\text{F}_3$) to moderate (*e.g.* $\text{Na}(\text{H}_3\text{O})[\text{I}(\text{OH})_3\text{O}_3]$), 13 are likely to belong in or undergo a phase transition to crystal classes $3m$ or $31m$, 33 are likely to be in or undergo a phase transition to a nonpolar class, 20 have reduced property predictability and only nine are likely to remain in space group $R3$ without a phase change at higher temperatures. The confidence level of each assignment depends upon the structure determination, the possibilities for symmetry change and the extent, if any, to which structural problems associated with a possible symmetry change have been investigated. An experimental summary, with an indication of confidence level, is provided for each entry in §2; the corresponding summaries for §§3–6 may be found in the supplementary materials.² Reduced confidence levels may, however, lead to classification ambiguity as in the case of $\text{Na}(\text{H}_3\text{O})[\text{I}(\text{OH})_3\text{O}_3]$ which, if appreciably lower, would be assigned to §5.

² Supplementary data, including Tables S1–S6 referred to in §2 and further discussion of each structure noted in Tables 6–9, together with the corresponding Tables S7–S48, for this paper are available from the IUCr electronic archives (Reference: BK5048). Services for accessing these data are described at the back of the journal.

1.5. Validation of the predicted ferroelectric state

As is the case for all predictions, validation rests upon the presentation of acceptable experimental proof, see Part I (Abrahams, 2006) for details.

1.6. Atomic distribution and equivalent positions in the supergroup

In addition to the equivalent coordinates enumerated in Part I for supergroups $R\bar{3}, R32, R3m$ and $R3c$ with respect to the space group $R3$, six additional space groups may be supergroups in Part II, *viz.* $R\bar{3}c$ [§2.6, Table S3(a,b)], $R\bar{3}m$ [§5.5.2, Tables 8 and S33(b)], $P31m$ [§3.7, Tables 6 and S13(a,b)], $P312$ [§6.4, Tables 9 and S44], $P6_3/mcm$ (Table 7 and §4.10) and $Fm\bar{3}m$ [Table S2(d)]. Atomic coordinates for all Wyckoff positions utilized in each of these supergroups have been deposited to facilitate their use without a need to consult *International Tables for Crystallography* (2005, Vol. A, 5th ed.).³

³ Atomic coordinates used only by the six supergroups in Part II are deposited in the supplementary materials (108 pp), see footnote 2. Coordinates for all Wyckoff positions in space groups $R3, R\bar{3}, R32, R3m$ and $R3c$ are presented in footnote 2 of Part I (Abrahams, 2006).

Table 4

Modified atomic positions in Na(H₃O)[I(OH)₃O₃] (Abrahams & Bernstein, 1978) with hypothetical x', y', z' coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [200568].

$$a = 6.04272(6), c = 13.23165(2) \text{ \AA}, z^* = z - 0.0023; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position $R3, R\bar{3}$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{eq}
I	3(<i>a</i>)	0	0	-0.0023	0	0	0	0	0	-0.03	0.03	0.09
Na	3(<i>a</i>) 6(<i>c</i>)	0	0	0.6308 (1)	0	0	0.5946	0	0	0.48	0.48	0.14
O1	3(<i>a</i>)	0	0	0.4415 (2)	0	0	0.4054	0	0	0.48	0.48	0.13
O2	9(<i>b</i>) 18(<i>f</i>)	0.0178 (2)	0.7523 (2)	0.9124 (1)	0.0346	0.7610	0.9208	-0.10	-0.05	-0.11	0.17	0.13
O3	9(<i>b</i>)	0.9486 (2)	0.2303 (2)	0.0709 (1)	0.9654	0.2390	0.0792	-0.10	-0.05	-0.11	0.17	0.12
H1	9(<i>b</i>) 18(<i>f</i>)	0.76 (3)	0.72 (3)	0.413 (11)	0.65	0.595	0.440	0.66	0.75	-0.35	1.27	0.16
H2	9(<i>b</i>)	0.459 (12)	0.529 (13)	0.534 (3)	0.350	0.405	0.560	0.66	0.75	-0.35	1.27	0.16

Table 5

Modified atomic positions in Mn₄Ta₂O₉ (Esmailzadeh & Grins, 2002) with hypothetical x', y', z' coordinates and the $\Delta x, \Delta y, \Delta z$ and u_{iso} displacements in Å [411944].

$$a = 5.360(3), c = 14.30(1) \text{ \AA}, z^* = z - 0.0073; \Delta x = (x - x')a, \Delta y = (y - y')a, \Delta z = (z^* - z')c.$$

	Wyckoff position $R3, R32$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$\Delta\xi$	u_{iso}	Occ.
Mn1, Ta1	3(<i>a</i>), 3(<i>a</i>)	0	0	-0.0073	0	0	0	0	0	-0.10	0.10	0.11	11/12, 1/12
Ta2, Mn2	3(<i>a</i>) 6(<i>c</i>)	0	0	0.2100 (7)	0	0	0.2516	0	0	-0.59	0.59	0.13	11/12, 1/12
Mn4, Ta4	3(<i>a</i>)	0	0	0.7069 (12)	0	0	0.7484	0	0	-0.59	0.59	0.12	11/12, 1/12
Mn3, Ta3	3(<i>a</i>), 3(<i>b</i>)	0	0	0.5061 (8)	0	0	0.5	0	0	0.09	0.09	0.12	3/4, 1/4
O1	9(<i>b</i>) 18(<i>f</i>)	0.984 (7)	0.344 (7)	0.460 (2)	0.008	0.330	0.4175	-0.13	0.08	0.61	0.62	0.15	1
O2	9(<i>b</i>)	0.702 (9)	0.684 (9)	0.625 (3)	0.678	0.670	0.5825	0.13	0.08	0.61	0.64	0.20	1

1.7. Presentation of structural analysis

The discussion of all ferroelectric materials predicted in §2, based on ICSD release 2006/1 for space group $R3$ Part II and analysis of each set of atomic coordinates, is presented below in full unless the structure has more than ten independent atoms in which case the coordinate analysis table is deposited. In contrast with Part I, however, the results for the remaining structures considered in Part II are given in Tables 6–9 with minimal background. Fuller discussion of each structure in §§3–6, together with the corresponding coordinate analyses, may be found in the supplementary material.

2. Predicted inorganic ferroelectrics in second half of space group $R3$ entries

2.1. Al₄B₆O₁₅ [54854] (Ju *et al.*, 2004)

Cu $K\alpha$, Ge monochromator; $T \simeq 295$ K; powder diffraction, Rietveld analysis, B_{eq} varied for each atom; $R_p = 0.025, R_{\text{wp}} = 0.032$; nine independent atoms. All atoms in Al₄B₆O₁₅ at ~ 300 K, with $u_{\text{eq}} \simeq 0.10$ Å, approach the symmetry of the nonpolar space group $R32$ with $0.04 \lesssim \Delta\xi \lesssim 1.08$ Å, see

Table 1. Assuming the structural solution is fully reliable, the criteria for ferroelectricity in §1.2 are well satisfied.

2.2. Na₃MoO₃F₃ [97452] (Brink *et al.*, 2003)

Electron diffraction indicates triclinic symmetry with space group $P1$, but Cu $K\alpha$ X-ray and neutron (1.493 Å) powder diffraction led to the metric assignment of rhombohedral $R3$ symmetry; X-ray powder pattern, 57 I_{obs} visually estimated; neutron pattern, 218 $I_{\text{obs}} > n\sigma(I_{\text{obs}})$ at 10 K and 224 I_{obs} at 300 K, n not reported; Rietveld refinement, $R_p = 0.054, R_{\text{wp}} = 0.067$ at 10 K, 0.053 and 0.064 at 300 K; six independent atoms. Ferroelectric hysteresis, spontaneous polarization $P_s \simeq 2 \times 10^{-4} \text{ C m}^{-2}$; relative permittivity ϵ_r with linear thermal dependence between 293 and 433 K. Refinement results in $\Delta\xi_{\text{max}} \lesssim 3u_{\text{iso}}$ with respect to the symmetry of $R\bar{3}$ at 300 K, see Table 2, hence the structural criteria are fulfilled. Confirmation is provided by the experimental evidence for ferroelectricity. The O and F sites in Na₃MoO₃F₃ are necessarily occupied identically since $R\bar{3}$ symmetry occurs in the course of polarization reversal. The magnitude of $\Delta\xi_{\text{max}}$ is consistent with $T_C > 433$ K, but is probably well under the preparation temperature of ~ 925 K. The thermal dependence of $\Delta\xi$ in the

Table 6

Survey of materials reported in space group $R3$ that more likely are in or may undergo a transition to crystal class $3m$ or $31m$.

§†	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Phase transition restrictions
3.1	$\text{Li}_2(\text{Zr},\text{Nb},\text{Te})_2\text{O}_6$	Archaimbault <i>et al.</i> (1992)	71488	S7(a)–S7(d)	$0.04 \lesssim \Delta\xi \lesssim 0.15$	$0.10 \lesssim u_{\text{iso}} \lesssim 0.12$	$R3c$	$T_{\text{transition}} \lesssim T_{\text{ambient}}$ for Zr/Te sites with identical composition ⁽¹⁾
		Choisnet <i>et al.</i> (1988)	202648	S7(e)	$0.04 \lesssim \Delta\xi \lesssim 0.21$	$0.10 \lesssim u_{\text{iso}} \lesssim 0.12$	$R3c$	
3.2	$[\text{Cl-P}(\text{NPCI}_3)_3]^+\cdot\text{Cl}^-$	Belaj (1992)	71913	S8	$0 \lesssim \Delta\xi \lesssim 0.32$	All $u_{\text{iso}} \simeq 0.15$	$R3m$	Above 100 K ⁽²⁾
3.3	$\text{Ba}_{2.7}\text{Ga}_{5.4}\text{Ge}_{3.6}\text{S}_{18}$	Häuseler & Schmidt (1994)	75002	S9	$0 \lesssim \Delta\xi \lesssim 1.2$	$0.09 \lesssim u_{\text{iso}} \lesssim 0.13$	$R3m$	At elevated T ⁽³⁾
3.4	$\text{K}_2\text{Ca}_2(\text{CO}_3)_3$	Winbo <i>et al.</i> (1997)	83431	S10	All $\Delta\xi \gtrsim 0.9$ except $\Delta\xi(\text{O}3) \simeq 1.5$	$0.10 \lesssim u_{\text{iso}} \lesssim 0.18$	$R3c$	At elevated T and pressure ⁽⁴⁾
3.5	$\text{Li}_{0.27}\text{Ni}_{0.75}\text{O}$	Monge <i>et al.</i> (2000)	89958	S11	All $\Delta\xi \lesssim 0.02$	$0.03 \lesssim u_{\text{iso}} \lesssim 0.28$	$R3m$	At $T \gtrsim 153$ K ⁽⁵⁾
3.6	$\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$	Kaplunnik <i>et al.</i> (1980)	200785	S12	All $\Delta\xi \lesssim 1.11$	$0.05 \lesssim u_{\text{iso}} \lesssim 0.16$	$R3m$	At T well above ambient ⁽⁶⁾
3.7.1	$\text{Cs}_4\text{BaTi}_6\text{Se}_{27}$	Huang & Ibers (2001)	280562	S13(a)	$0 \lesssim \Delta\xi \lesssim 1.20$	$0.11 \lesssim u_{\text{eq}} \lesssim 0.18$	$P31m$	Between 153 and 873 K ^(7a)
3.7.2	$\text{Cs}_6\text{Ti}_6\text{S}_{27}$	Huang & Ibers (2001)	280564	S13(b)	$0 \lesssim \Delta\xi \lesssim 1.16$	$0.11 \lesssim u_{\text{eq}} \lesssim 0.16$	$P31m$	Between 153 and 873 K ^(7b)
3.8	$\text{H}_2\text{Hg}_7\text{Se}_3\text{O}_{13}$	Weil (2004)	414035	S14	$0 \lesssim \Delta\xi \lesssim 0.08$ except $\Delta\xi(\text{Hg}1) \simeq 0.55$	$0.11 \lesssim u_{\text{eq}} \lesssim 0.27$	$R3m$	At $T > 295$ K ⁽⁸⁾

† Section number in the supplementary data. (1) Choisnet *et al.*'s (1988) results in Table S7(e) do not differ significantly from those in Table S7(b). $\text{Li}_2\text{ZrTeO}_6$ is likely to undergo a transition to $R3c$ if well annealed, $\text{Li}_{1.75}\text{Zr}_{0.75}\text{Nb}_{0.25}\text{Te}_3\text{O}_6$ probably remains in $R3$ with $\text{Li}_{1.75}\text{Nb}_{1.75}\text{Te}_{0.25}\text{O}_6$ in $R3c$. (2) Structure determined at 100 K leads to smaller u_{iso} . Higher temperatures may result in $\Delta\xi_{\text{max}} \lesssim u_{\text{iso}}$ and hence a phase transition to $R3m$. (3) Prepared at ~ 1600 K, increasing values of u_{iso} at temperatures above ambient enhance the likelihood of a higher-temperature phase transition to $R3m$ at $T \gg 300$ K. (4) $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ decomposes at 785 K under 1 bar, but remains stable to 1080 K at 10 kbar. (5) Grown from a $\text{LiBO}_2/\text{Nd}_2\text{O}_3/\text{NiO}$ mix at 1473 K, structure determination at 153 K. Other space groups reported for $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with $0.01 \lesssim x \lesssim 0.49$ include $R\bar{3}m$, $Fm\bar{3}m$ and $C2/c$. (6) Melting or decomposition temperature for the mineral Aktashite not reported. (7a) The coordinates reported at 153 K are consistent with a transition from a higher-temperature phase in space group $P31m$, given the preparation $T \simeq 873$ K. Although $P31m$ is not a supergroup of $R3$, it is of $R3m$ which may be an intermediate phase. $d_{\text{Se-S}}$ here and in $\alpha\text{-Se}_8$ (Maaninen *et al.*, 2001) does not differ significantly. $\Delta\xi$ values assume any change owing to rhombohedral centering relaxation is minor. (7b) Temperatures as in footnote (7a); $d_{\text{S-S}}$ here and in orthorhombic S_8 (Abrahams, 1955; Caron & Donohue, 1965) does not differ significantly. See footnote (7a) on $\Delta\xi$ values. (8) Grown from aqueous solution, with $T_{\text{decomposition}}$ unreported. A phase transition to $R3m$ is expected if $\Delta\xi(\text{Hg}1)$ approaches u_{iso} as T increases. Attempted refinement of the hypothetical coordinates in $R3m$, including the unequally split $\text{Hg}2,\text{Hg}3$ pair, proved unsuccessful (Weil, 2006), lending support to the original assignment of $R3$ symmetry at 295 K.

range 10–300 K is low, with no atomic coordinate change as large as u_{iso} .

2.3. $\text{KCd}_4\text{Ga}_5\text{S}_{12}$ family [67945, 402222]

2.3.1. $\text{KCd}_4\text{Ga}_5\text{S}_{12}$ (Schwer *et al.*, 1993). Mo $K\alpha$; graphite monochromator; absorption corrections; 1568 independent F_{obs} including 1442 superstructure reflections, u_{aniso} ; $R_{\text{all}(F_{\text{obs}})} = 0.0304$, $R_{\text{superstructure}} = 0.034$; four independent metal sites (three shared by Ga and Cd), four independent S atoms. Polarization reversal in this chalcogenide, with its oppositely oriented corner-sharing XS_4 and YS_4 tetrahedra ($X = \text{Cd}, \text{Ga}$; $Y = 0$), is readily achievable since $\Delta z \lesssim 0.5$ Å for all atoms with respect to $R\bar{3}$ symmetry, see Table 3(a), although $\Delta\xi_{\text{(max)}} \simeq 1.5$ Å. The cooperative movement of Cd, Ga and S atoms allows the exchange of all X and empty Y sites with $\langle d_{\text{Cd}, \text{Ga-S}} \rangle = 2.383$ Å and $d_{\text{S-S}} = 3.61\text{--}3.96$ Å in the S–S–S faces.

2.3.2. $\text{CsHg}_4\text{Ga}_5\text{Se}_{12}$ (Krauß *et al.*, 1996). Isotypic $\text{CsHg}_4\text{Ga}_5\text{Se}_{12}$; preliminary publication. Mo $K\alpha$, graphite monochromator, $T = 293$ K; 2269 independent $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, absorption corrections not reported, U^{ij} for all atoms, $R = 0.064$, $wR(F^2) = 0.161$; three of four independent metal sites shared by Ga and Hg, four independent Se atoms. The site shared by $\text{Hg}2,\text{Ga}2$ has $\Delta\xi \simeq 1.6$ Å, but for all other atoms $0.3 \lesssim \Delta\xi \lesssim 1.5$ Å with respect to $R\bar{3}$ symmetry, see Table 3(b). The criteria for ferroelectricity are very nearly satisfied, hence $\text{CsHg}_4\text{Ga}_5\text{Se}_{12}$ is also a candidate, but experimental

confirmation, as that of $\text{KCd}_4\text{Ga}_5\text{S}_{12}$, is particularly advisable. Twinning is frequent and suggestive of a higher-temperature phase transition; several related isotypic Hg compounds decompose before melting, at ~ 975 K (Krämer, 2006).

2.4. $\text{RbTi}_2(\text{PO}_4)_3$ at 6.2 GPa [78428] (Hazen *et al.*, 1994)

Mo $K\alpha$, Ni-filtered; absorption corrections both for crystal and high-pressure cell; ω step scans; 6.21 (5) GPa at ambient temperature; six independent metal, two P and eight O atoms, $R = 0.089$, $wR = 0.049$ for all 504 independent F_{obs} with $R = 0.061$, $wR = 0.046$ for 394 $F_{\text{obs}} > 2\sigma(F_{\text{obs}})$. The present structure is among the few that have been determined in both the ferroelectric and the paraelectric states. The $R\bar{3}c$ space group at ambient pressure (100 kPa) and temperature (Masse, 1970) persists to ~ 1.7 GPa, with violations of the glide plane becoming apparent at higher pressure. A reduction of $\sim 9.8\%$ in unit-cell volume at 6.2 GPa, compared with that at 100 kPa, is reported as both glide plane and inversion centers are lost in the transition to $R3$. The experimental coordinate shifts of $0.02 \lesssim \Delta\xi \lesssim 1.09$ Å between 6.2 GPa and 100 kPa in Table S1(a) agree with those of $0.03 \lesssim \Delta\xi \lesssim 1.34$ Å in Table S1(b), based on the shifts between the xyz coordinates at 6.2 GPa and the hypothetical x', y', z' coordinates; unweighted averages in the latter can however give larger values of $\Delta\xi$. The atomic arrangement in $\text{RbTi}_2(\text{PO}_4)_3$ at 6.2 GPa clearly satisfies the structural if not the practical criteria for ferroelectricity.

Table 7
Survey of structures reported in space group $R\bar{3}$ that more likely are nonpolar.

§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Phase transition restriction
4.1	Mg_9Sn_5	Range <i>et al.</i> (1996)	55577	S15	$0.05 \lesssim \Delta\xi \lesssim 0.16$, all $\Delta\xi_i \lesssim u_{\text{eq}(i)}$	$0.12 \lesssim u_{\text{eq}} \lesssim 0.21$	$R\bar{3}$	Space group most likely misassigned ⁽¹⁾
4.2	$\text{Al}_{4.2}\text{Cu}_{3.2}\text{Zn}_{0.7}$	Murphy (1975)	57730	S16	All $\Delta\xi = 0$	Not determined	$R\bar{3}$, $R32$	Space group most likely misassigned ⁽²⁾
4.3	$\text{Gd}_{13}\text{Ge}_6\text{O}_{31}\text{F}$	Mamin <i>et al.</i> (1987)	62329	S17	$0.02 \lesssim \Delta\xi \lesssim 0.18$ for all atoms except O9 and O10	$0.05 \lesssim u_{\text{iso}} \lesssim 0.16$	$R\bar{3}$	A negative sign for $x(\text{O}9)$ may be missing ⁽³⁾
4.4	$\text{Cr}_2\text{Si}_2\text{Te}_6$	Ouvrard <i>et al.</i> (1988)	62379	S18a	All $\Delta\xi \lesssim 0.02$	$0.11 \lesssim u_{\text{iso}} \lesssim 0.12$	$R\bar{3}$	Space group most likely misassigned ⁽⁴⁾
		Marsh (1988)	71020	S18b	–	–	–	Confirms centrosymmetric space group
4.5	$(\text{NH}_4)_6\text{NiMo}_9\text{O}_{32}\cdot 6\text{H}_2\text{O}$	Dunne <i>et al.</i> (1992)	72710	S19a	$0.01 \lesssim \Delta\xi \lesssim 0.18$ for all atoms except O13 and O14 with $\Delta\xi = 1.13$	u amplitudes not reported. $0.10 \lesssim u_{\text{eq}} \lesssim 0.33$	$R32$	All atoms conform to $R32$ symmetry
		Weakley (1987)	49909	–	–	–	$R32$	Determined space group as $R32$
		Stratemeier <i>et al.</i> (1992)	67576	S19b	–	–	$R32$	Table S19b independently confirms space group as $R32$ ⁽⁵⁾
4.6	$\text{Sr}(\text{BH})_{12}\cdot 7\text{H}_2\text{O}$	Solntsev <i>et al.</i> (1977)	94431	S20a	$0.04 \lesssim \Delta\xi \lesssim 0.15$ for all atoms except O3	$0.13 \lesssim u_{\text{iso}} \lesssim 0.25$	$R\bar{3}$	Atom O3 conforms with $R\bar{3}$ symmetry, if atom O4 with $z = -z(\text{O}3)$ were previously overlooked ⁽⁶⁾
		Tiritiris & Schleid (2001)	200016	S20b	–	–	$R\bar{3}$	
4.7	MgSiO_3 (ilmenite type)	Horiuchi <i>et al.</i> (1988)	31176	S21a	Found space group $R\bar{3}$	$u_{\text{iso}} \simeq 0.08$	$R\bar{3}$	
		d'Arco <i>et al.</i> (1994)	75738	S21b	Calculations used $R\bar{3}$	–	–	Reported as in space group $R3$ or $R3c$, but space group used was $R\bar{3}$ ⁽⁷⁾
		Karki <i>et al.</i> (2000)	89805	S21c	Stated as $R3c$, with all $\Delta\xi_{\text{exp}} \lesssim 0.03$, but used $R\bar{3}$	–	–	
4.8	CdPS_3	Boucher <i>et al.</i> (1995); Covino & Lowe-Ma (1986); Ouvrard <i>et al.</i> (1985)	80875	S22	All $\Delta\xi \lesssim 0.03$	$0.08 \lesssim u_{\text{iso}} \lesssim 0.10$	$R\bar{3}$	Phase transition from $C2/m$ on cooling through $T \simeq 228$ K to $R\bar{3}$ ⁽⁸⁾
			61393	–	–	–	–	
4.9.1	Eudialyte-type minerals	Ekimenkova <i>et al.</i> (2000)	90835	S23a	$0.01 \lesssim \Delta\xi \lesssim 0.17$ for all 34 framework atoms	$0.13 \lesssim u_{\text{eq}} \lesssim 0.32$	$R32$	Thermodynamically, $R32$ is more likely than $R3$ in either eudialyte variant ⁽⁹⁾
4.9.2	Eudialyte-type minerals	Rastsvetaeva & Khomyakov (2000)	91548	S23b	$0.01 \lesssim \Delta\xi \lesssim 0.16$ for 35 of 36 independent framework atoms	$0.13 \lesssim u_{\text{eq}} \lesssim 0.34$	$R32$	
4.10	$\text{ZrCr}_2\text{D}_{3.8}$	Irodova & Suard (2000)	90289	S24	All $\Delta\xi = 0$	$0.07 \lesssim u_{\text{iso}} \lesssim 0.13$	$P6_3/mcm$	Measured at 100 K, space group most likely misassigned ⁽¹⁰⁾
4.11	$\text{Cs}_2\text{SO}_4\text{Te}(\text{OH})_6$	Dammak <i>et al.</i> (2001)	93016	S25	$0.07 \lesssim \Delta\xi \lesssim 0.19$ for all except the H atoms at 0.58 Å and O4	$0.13 \lesssim u_{\text{eq}} \lesssim 0.31$	$R32$	The anomalous O4 at 0,0,z is satisfied if O5 is present ⁽¹¹⁾

Table 7 (continued)

§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Phase transition restriction
4.12	Ga ₄ Pd ₇ Zn ₃	Subrahmanyam & Schubert (1973)	103911	S26	$0.13 \lesssim \Delta\xi \lesssim 0.22$ for all atoms	$0.08 \lesssim u_{\text{iso}} \lesssim 0.14$	$R\bar{3}$	Sites presently identified as occupied either by Zn or Ga ₂ are more likely half-occupied by both ⁽¹²⁾
4.13	K ₆ MnMo ₉ O ₃₂ ·6H ₂ O	Weakley (1977)	200048	S27a	$0.04 \lesssim \Delta\xi \lesssim 0.15$ for all but three atoms	$0.06 \lesssim u_{\text{eq}} \lesssim 0.23$	R32	Atoms K2, O13 and O14 are each likely in error ⁽¹³⁾
		Dunne <i>et al.</i> (1992)	71885	S27b	–	$0.09 \lesssim u_{\text{eq}} \lesssim 0.38$	R32	
4.14	Pd ₇ P ₃	Matković & Schubert (1977)	200055	S28	$0.10 \lesssim \Delta\xi \lesssim 0.34$ for all atoms	$0.33 \lesssim u_{\text{iso}} \lesssim 0.44$	$R\bar{3}$	Space group most likely misassigned ⁽¹⁴⁾

(1) Since all $\Delta\xi_i \lesssim u_{\text{eq}(i)}$ the supergroup is, thermodynamically, more likely to be the stable phase. (2) All atoms, taken as partly or fully occupying eight out of ten equispaced locations along the *c* axis excluding 000 and 00 $\frac{1}{2}$, exactly satisfy both $R\bar{3}$ and R32. The previous assignment of ICSD #57730 to the space group R3 has been changed to $R\bar{3}$ (Allmann, 2006). (3) Sign reversal of *x*(O9) eliminates the exception and leads to $d_{\text{Ga1-O9}} = 2.28$ Å; the missing negative sign may be a typographic error. (4) Comparison of the *x'*, *y'*, *z'* coordinates in Table S18(a) with Marsh's (1988) *x*, *y*, *z* values in Table S18(b), as refined in the space group $R\bar{3}$, shows agreement to within 0.003 Å. (5) Stratemeier *et al.*'s (1992) coordinates generally agree well with those of Dunne, Burns & Lawrance (1992) after the latter are averaged in space group R32. Only one of the two independent H₂O was located in Dunne *et al.*'s report, see Tables S19(a,b). (6) The more reliable redetermination by Tiritiris & Schleid (2001) in the space group $R\bar{3}$, see Table S20(b), confirms the atomic coordinates for Sr and both independent O atoms, including O4 in Table S20(a). The earlier coordinates for B are shown to be in substantial error and both independent H atoms are now located. (7) Karki *et al.* (2000) reported the space group as R3c, but used $R\bar{3}$ symmetry, d'Arco *et al.* (1994) used R3 symmetry, both with atomic coordinates that differ less than 0.03 Å from those of Horiuchi *et al.* (1988) in $R\bar{3}$. (8) Reported as in space group R3, but no atomic coordinates depart more than 0.03 Å from $R\bar{3}$ symmetry, which is hence the most likely space group. (9) Nonframework atoms in Table S23a have $0.01 \lesssim \Delta\xi \lesssim 0.33$ Å from R32 symmetry. In the second variant, Table S23b shows 22 of the 33 nonframework atoms with $0.01 \lesssim \Delta\xi \lesssim 0.16$ Å under R32 symmetry. Final space-group assignment awaits independent redetermination of the nonconforming nonframework atoms, many of which may be disordered. (10) A phase transition to space group $P6_3/mmc$ occurs at 250 K. The four independent Zr and 12 Cr atoms at 100 K have coordinates that exactly match the symmetry of supergroup $R\bar{3}c$, but those of the 28 occupied D atom sites do not; all sites exactly fulfil the symmetry of the space group $P6_3/mcm$ (Table S24) in a cell with relaxed rhombohedral centering assumed. (11) If a half-occupied previously undetected O5 site were located at 0,0, \bar{z} , a distance of 1.399 Å from S, where O4 is at 0,0, *z*, then all atoms would satisfy the space group R32. In that case, three new H1...O5 bonds of 2.295 Å would exist, comparable to those formed by O4. (12) Zn and Ga, with atomic numbers 30 and 31, are indistinguishable by the X-ray powder technique used. (13) Atoms K2, O13w and O14w in Table S27a have $\Delta\xi = 0.51, 3.11$ and 3.11 Å, respectively. Since the coordinates of O13w in Table S27a are within 0.74 Å of that in S27b, it is likely the O14w coordinates in Table S27a are in substantial error. Table S27b confirms the space group is indeed R32. (14) Space group $R\bar{3}$ is more likely thermodynamically than R3. Physical properties for Pd₇P₃ have not been reported.

2.5. LiABO₄ (phenakite/eucryptite) family [83652, 86184]

2.5.1. LiZnPO₄ (Bu *et al.*, 1996). Mo *Kα*, graphite monochromator; ψ -scan absorption, extinction corrections; 428 independent I_{obs} at 293 K with $424 I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, U_{iso} , $R = 0.024$, $wR = 0.034$; four metal, two P and eight independent O atoms in R3. All independent atoms in LiZnPO₄ are related in like-pairs such that each is displaced from an equivalent location in the space group $R\bar{3}$ by $0.18 \lesssim \Delta\xi \lesssim 1.26$ Å, thus satisfying the criteria for ferroelectricity at an acceptable confidence level, see Table S2(a).

2.5.2. α -LiZnAsO₄ (Jensen *et al.*, 1998). Synchrotron radiation with $\lambda = 0.9540$ Å; no absorption corrections; 917 independent F_{obs}^2 , $677 F_{\text{obs}}^2 > 2\sigma(F_{\text{obs}}^2)$; strongly correlated pairs of Li and O atoms prevented refinement of U^{ij} except for As and Zn, $R = 0.0698$, $wR(F^2) = 0.182$; Flack factor, 0.16 (4); 14 independent atoms; phase transition at ~ 682 K. Table S2(b) shows no Δx or $\Delta y > 0.06$ Å with respect to the space group $R\bar{3}$ in α -LiZnAsO₄ and all $\Delta z \lesssim 0.29$ Å except for $z(\text{Zn}) \simeq 1.35$ Å; all atoms form like pairs in $R\bar{3}$ and, apart from $z(\text{Zn})$ which slightly violates one of the criteria for ferroelectricity, see also §2.5.1, the latter are otherwise satisfied. The reversible phase transition reported at ~ 955 K is consistent with a transition from R3 to $R\bar{3}$. Several related phenakite-like structures such as Be₂SiO₄ form in the space group $R\bar{3}$, while many minerals and synthetics of LiABO₄-type composition with corner-sharing tetrahedra form in the space group R3. See also §6.2, Table 9.

2.6. RbSb_{0.33}Te₆U [93834] (Choi & Kanatzidis, 2001)

Substructure space group $P3$, $a = 9.0925$ (14), $c = 8.129$ (2) Å; superstructure space group R3, $a = 15.741$ (2), $c = 24.382$ (4) Å; Mo *Kα*, graphite monochromator; absorption, extinction but not anomalous dispersion corrections; 4095 unique $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, $R = 0.070$, $wR^2 = 0.097$ with 4 restraints, 184 variables; conductive, with $\kappa \simeq 40$ S cm⁻¹. Assuming the location of all 20 independent atoms as reported in Table S3, then $0.13 \lesssim \Delta\xi \lesssim 1.32$ Å with respect to R32; since $0.10 \lesssim u_{\text{eq}} \lesssim 0.36$ Å the structural criteria for ferroelectricity are satisfied. The confidence level is, however, reduced by the four nominal pairs of Rb atoms with $0.80 \lesssim d_{\text{Rb-Rb}} \lesssim 0.99$ Å; the unusually short $d_{\text{Rb-Sb}} \simeq 2.14$ Å and $d_{\text{Sb3-Sb4}} \simeq 2.33$ Å also indicate a need for further investigation. It is noted that all $\Delta\xi(\text{Te}) \gg \Delta\xi(\text{U, Sb or Rb})$, whereas $\Delta\xi \lesssim u_{\text{eq}}$ for U, Rb and Sb while all $\Delta\xi(\text{Te}) \gg u_{\text{eq}}(\text{Te})$.

2.7. Ca₃Nb_{1.95}O₈V_{0.05} [96423] (Cranswick *et al.*, 2003)

Mo *Kα*, graphite monochromator; 9058 independent $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$, no corrections stated, U^{ij} , $R = 0.047$; all 10 902 F_{obs} gave $R = 0.065$, $wR(F^2) = 0.11$; 42 independent metal, 56 O atoms. The maximum values of $\Delta\xi$ in this perovskite-related structure are 0.12 Å for the sole V atom, 0.07 Å for the 15 independent Nb and 0.19 Å for the 26 independent Ca atoms, with respect to the space group $R\bar{3}$, see Table S4. All metal atoms hence very nearly achieve $R\bar{3}$ symmetry, since $0.04 \lesssim$

Table 8
Structures reported in space group $R\bar{3}$ with reduced predictive property.

§	Formula	Reference	ICSD	Table	$\Delta\xi$ range (Å)	u_{eq} range (Å)	Likely space group	Structural problems
5.1	$\text{Sn}_{4.2}\text{Si}_9\text{P}_{16}$	Pivan <i>et al.</i> (1988)	68123	S29	$0.02 \lesssim \Delta\xi \lesssim 0.14$ for seven atoms, $0.37 \lesssim \Delta\xi \lesssim 0.60$ for the five remaining atoms	$0.09 \lesssim u_{\text{eq}} \lesssim 0.18$	$R\bar{3}$	Equivalence of P and Sn, also that of P and Si atoms at T_C in satisfying the ferroelectric criteria ⁽¹⁾
5.2	$\text{Li}_4\text{Rh}(\text{SO}_3)\cdot 3\text{H}_2\text{O}\cdot\text{OH}$	Mäurer <i>et al.</i> (1993)	67921	S30	$0.21 \lesssim \Delta\xi \lesssim 1.42$ for all atoms	$0.09 \lesssim u_{\text{eq}} \lesssim 0.29$	$R32$	Structural uncertainties that reduce the confidence of property prediction ⁽²⁾
5.3	$\text{Cs}_3[(\text{UO}_2)_{12}\text{O}_7(\text{OH})_{13}]\cdot 3\text{H}_2\text{O}$	Hill & Burns (1999)	87737	S31	$0.20 \lesssim \Delta\xi \lesssim 1.34$ for all atoms except Cs and O7	$0.07 \lesssim u_{\text{iso}} \lesssim 0.20$	$R32$	Possible distribution of CsA and $O7A$ atoms over both x,y,z and y,x,\bar{z} sites ⁽³⁾
5.4	$\text{Li}_2\text{GeTeO}_6$ family	Woodward <i>et al.</i> (1999)	88785	S32	$0.01 \lesssim \Delta\xi \lesssim 0.12$ for all atoms	$0.07 \lesssim u_{\text{iso}} \lesssim 0.20$	$R\bar{3}$	Equal occupancy of the Ge/Te sites required to achieve centrosymmetry ⁽⁴⁾
5.5.1	Eudialyte-type mineral variants	Rastsvetaeva <i>et al.</i> (1999)	88895	S33a	$0.01 \lesssim \Delta\xi \lesssim 0.27$ for all 36 framework atoms, $0.02 \lesssim \Delta\xi \lesssim 1.00$ for 25 of 26 non-framework atoms	$0.14 \lesssim u_{\text{eq}} \lesssim 0.27$	$R32$	The close structural approach to nonpolarity, assuming a previously undetected $Na4A$ atom ^(5a)
5.5.2	Eudialyte-type mineral variants	Rastsvetaeva & Khomyakov (2001)	93950	S33b	$0.02 \lesssim \Delta\xi \lesssim 0.11$ for 68 of 70 framework atoms, $0.02 \lesssim \Delta\xi \lesssim 1.00$ for 33 of 39 non-framework atoms	$0.09 \lesssim u_{\text{eq}} \lesssim 0.26$	$R\bar{3}m$	The comparable approach to centrosymmetry, see §5.5.1, if two Ca and six other atoms are assumed present ^(5b)
5.6	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	Marosi <i>et al.</i> (2000)	90636	S34	$0.18 \lesssim \Delta\xi \lesssim 0.43$ for the eight independent Mo atoms	u_{eq} not reported	$R\bar{3}$	One or both independent $z(\text{P})$ are in doubt and the H and O atoms undetermined ⁽⁶⁾
5.7	$\text{Ca}_4(\text{Ca}_{0.7}\text{Na}_{0.3})_3\text{Na}_{0.7}\text{Li}_5(\text{B}_{22}\text{O}_{39}(\text{OH})_3)(\text{CO}_3)(\text{OH})(\text{OH})_{0.8}(\text{H}_2\text{O})_{0.2}$	Yamnova <i>et al.</i> (2002)	97107	S35	$0.2 \lesssim \Delta\xi \lesssim 1.2$ for all atoms except Li1 and Li3	$0.08 \lesssim u_{\text{iso}} \lesssim 0.17$	$R32$	If $z(\text{Li}1) \simeq 0.035$ instead of the reported 0.085 and $z(\text{Li}4) \simeq -z(\text{Li}3)$, then no $\Delta\xi > 1.4 \text{ \AA}$ ⁽⁷⁾
5.8	$\text{Ga}_2\text{Cr}_{1.33}\text{Se}_5$	Okońska-Kozłowska <i>et al.</i> (2004)	99119	S36a, S36b	$0.42 \leq \Delta\xi \leq 1.56$	$0.08 \lesssim u_{\text{iso}} \lesssim 0.29$	$R32$	The possibility of Se and Ga, Cr; also Cr and Ga, becoming equivalent ⁽⁸⁾
5.9	$[\text{Zn}(\text{H}_2\text{O})_4]_2[\text{H}_2\text{As}_6\text{V}_{15}\text{O}_{42}\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$	Cui <i>et al.</i> (2003)	99351	S37a	$0.03 \lesssim \Delta\xi \lesssim 1.55$ for 29 of 31 atoms	$0.13 \lesssim u_{\text{iso}} \lesssim 0.44$	$R\bar{3}$	AsO_4 tetrahedral and 'square' pyramidal VO_5 distortion. Site occupancies ⁽⁹⁾
				S37b	$0.03 \lesssim \Delta\xi \lesssim 1.55$ for all atoms		$R\bar{3}m$	
5.10	$\text{Bi}_{11.23}\text{IrCl}_{12.23}$ family $\text{Bi}_{11.7}\text{RhCl}_{12.7}$ $\text{Bi}_{11.28}\text{RhBr}_{12.28}$	Ruck & Hampel (2002)	412014	S38a S38b S38c	$0.09 \lesssim \Delta\xi \lesssim 0.32$ for all atoms except $\Delta\xi(\text{Cl}6) \simeq 3.70 \text{ \AA}$	$0.09 \lesssim u_{\text{eq}} \lesssim 0.23$	$R\bar{3}$	The possible presence of a previously undetected $Cl6A$ resulting in a close approach to centrosymmetry ⁽¹⁰⁾

(1) The structure is close to supergroup $R\bar{3}$ symmetry, but a model with full equivalence leads to excess positive and negative residual electron densities (Guerin, 2006). In addition, nearest neighbors of 'equivalent' pairs exhibit characteristically different interatomic distances, indicative of a need for further investigation. Uncertainty in structure too high for property prediction. (2) Coordination differences about the two independent Li atoms, also the tetrahedral coordination of three Li and H3 about O5 with $d_{\text{O5-H3}} = 0.60 \text{ \AA}$, where $\sim 1.00 \text{ \AA}$ is normal, *e.g.* Ricci *et al.* (2005), reduce the confidence level required for property prediction. (3) Occupation of both Cs and O7 sets of x,y,z and y,x,\bar{z} sites would satisfy the criteria for ferroelectricity. A typographic error in the sign of $x(\text{Cs})$ that would have independently satisfied the criteria was possible but eliminated by Burns (2000). Previously uninvestigated site occupancies and resulting nearest-neighbor inequivalencies suggest the advisability of further investigation. (4) The Ge/Te site occupancies, reported as unequal, are supported by the 0.06 \AA increase in average $d_{\text{Ge}2,\text{Te}2-\text{O}} = 1.892, 1.986 \text{ \AA}$ compared with $d_{\text{Ge}1,\text{Te}1-\text{O}} = 1.878, 1.881 \text{ \AA}$ unless this effect is a result of refinement in $R\bar{3}$. Shannon's (1976) radii are $\text{Ge}^{4+}(\text{VI}) = 0.67, \text{Te}^{6+}(\text{VI}) = 0.70 \text{ \AA}$. Further investigation is indicated. (5a) The exception in §5.5.1, Table 8, is the half-occupied site at Na4; if an undetected $Na4A$ atom with coordinates $x, y, z = -x, -y, -z$ (Na4) were postulated, then all atoms present would approach $R\bar{3}2$ symmetry and hence satisfy the criteria for ferroelectricity. However, eight pairs of metal atoms reported less than 0.95 \AA apart (with $d_{\text{Mn}2-\text{Zr}2}, d_{\text{Na}1-\text{Na}2}, d_{\text{Na}3-\text{Na}4}, d_{\text{Sr}1-\text{Na}5}, d_{\text{Zr}2-\text{Na}6}, d_{\text{Na}7-\text{Na}8}, d_{\text{Na}9-\text{Na}10}, d_{\text{Na}9-\text{Na}11} \lesssim 0.95 \text{ \AA}$) with $d_{\text{O}25-\text{O}24} = 0.50 \text{ \AA}$, introduces sufficient uncertainty to prevent property prediction. (5b) The exceptions in §5.5.2, Table 8, are the Ca1 and Ca2 framework atoms, also the Na5, Na9, Na14, O51, Cl3 and Cl4 nonframework atoms; if each such atom at x, y, z were paired, approximately, with an undetected like atom at $-x, -y, -z$ then the symmetry $R\bar{3}m$ would be nearly satisfied as would the criteria for ferroelectricity. The present structural uncertainties, as in §5.5.1, Table 8, do not allow property prediction. The eudialytes have been reviewed by Johnson & Grice (1999). (6)

Table 8 (continued)

All eight independent Mo atoms have negative Δz , but both P atoms have positive and much larger Δz with respect to the space group $R\bar{3}$. The space group of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is hence likely to be centrosymmetric, but at least one $z(\text{P})$ coordinate is open to question. A full structural investigation is appropriate. (7) $R32$ symmetry and hence the criteria for ferroelectricity would be fully satisfied with $\Delta\xi \lesssim 1.4 \text{ \AA}$ for all atoms if $z(\text{Li}1)$ were ~ 0.05 less than stated and $Li4$ assumed to be related centrosymmetrically to $Li3$. Both proposed $Li1$ and $Li4$ sites have environments comparable to those of $Li2$ and $Li3$. Further investigation is necessary before physical property prediction is appropriate. (8) If two Se and two Cr atoms occupying octahedra could exchange with the remaining three Se and all three Ga that occupy tetrahedra, then the structural criteria for ferroelectricity would be satisfied. Such exchange, however, is unlikely as, hence, is a transition to the supergroup. Both polar origin uncertainty and bond distance variability suggest the need for additional structural investigation prior to property prediction. (9) The two exceptions are $\Delta\xi(\text{O}22, \text{V}5) \simeq 2.07, 2.65 \text{ \AA}$. If the transition were to $R\bar{3}m$ via $R32$ or $R3m$, then $\Delta\xi(\text{V}5)$ would reduce to 0.76 \AA with no $\Delta\xi \gtrsim 1.55 \text{ \AA}$, see Table 37(b); however, the resulting reduction in each site occupancy by a factor of 2 renders such a transition unlikely. Further structural investigation is necessary prior to property prediction. (10) Uncertainty associated with $Cl6A$ and several site occupancies indicate a need for additional investigation before physical properties may be predicted. Both isomorphous $\text{Bi}_{11.7}\text{RhCl}_{12.7}$, with $0.09 \lesssim \Delta\xi \lesssim 0.36 \text{ \AA}$ for all atoms, see Table 38(b), and $\text{Bi}_{11.28}\text{RhBr}_{12.28}$ with $0.04 \lesssim \Delta\xi \lesssim 0.35 \text{ \AA}$ for all atoms, see Table 38(c), are very similar to $\text{Bi}_{11.23}\text{IrCl}_{12.23}$ assuming the equivalent presence of $Cl6A$ in the former, $Br6A$ in the latter.

$u_{\text{eq}} \lesssim 0.16 \text{ \AA}$, in a unit cell close to cubic with $c \simeq a^{2/3}3^{1/2}$. The O atoms have $\Delta\xi \lesssim 0.67 \text{ \AA}$ with $u_{\text{iso}} \lesssim 0.14 \text{ \AA}$, except for the half-occupied O53 and O54 sites which have the largest $\Delta\xi$ at $\sim 1.18 \text{ \AA}$. All 56 independent O atoms are thus also capable of achieving $R\bar{3}$ symmetry at higher temperatures, hence the structure as determined satisfies the criteria for ferroelectricity. Calorimetric investigation will show if the phase transition occurs as expected well below the preparation temperature of 1773 K.

2.8. $\text{Na}(\text{H}_3\text{O})[\text{I}(\text{OH})_3\text{O}_3]$ [200568] (Abrahams & Bernstein, 1978)

Mo $K\alpha$, Nb filter; 1102 independent $F_{\text{obs}} > 3\sigma(F_{\text{obs}})$ at 298 K, spherically ground crystal, absorption and extinction corrections, U^{ij} for I, Na and O, U_{iso} for H atoms,⁴ $R = 0.0150$, $wR = 0.0192$; seven independent atoms. Pyroelectric $\mu_3 = 4.3 \times 10^{-6} \text{ C m}^{-2} \text{ K}^{-1}$, piezoelectric $d_{33} = 4.3 \times 10^{-12} \text{ CN}^{-1}$ at 298 K (Abrahams *et al.*, 1979) eliminate the possibility of ambient centrosymmetry. Occupancy of the nominal Na and O1 sites by 50% of both atoms would lead to $0.03 \lesssim \Delta\xi \lesssim 0.48 \text{ \AA}$, with respect to $R\bar{3}$ symmetry, see Table 4, and hence meet the criteria for ferroelectricity since $0.09 \lesssim u_{\text{eq}} \lesssim 0.16 \text{ \AA}$. The possibility of mixed Na and O1 site occupancy, together with the resulting H1 bonding rearrangement required in an approach to supergroup symmetry, has not been investigated experimentally and is not expected to be high unless as a product of the domain distribution at 298 K. Both nominal $d_{\text{Na-O}}$ and $d_{\text{O-O,Na}}$ are $2.50 (5) \text{ \AA}$, the former with CN = 7, the latter with CN = 5. The steady polarization increase of $\sim 1.5 \times 10^{-3} \text{ C m}^{-2}$ on cooling the crystal from 298 K (Abrahams *et al.*, 1979) is typical of ferroelectrics, although a maximum is reached at 137 K with ΔP decreasing at lower T . Since neither ΔP nor the change in d_{33} has been reported above ambient T , no information on T_C is available; dehydration is likely to initiate at $T \gtrsim 400 \text{ K}$.

2.9. $\text{PbTa}_3(\text{PO}_4)(\text{P}_2\text{O}_7)_{3.5}$ [250098] (Murashova *et al.*, 2003)

Mo $K\alpha$, graphite monochromator; $T = 295 \text{ K}$; rhombohedral cell with $\alpha_R = 89.72^\circ$; 936 independent $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, U^{ij} , $R = 0.044$, $wR(F^2) = 0.134$; 25 independent sites including all eight P, seven O atoms with $\sim 50\%$ occupancy. All atoms in $\text{PbTa}_3(\text{PO}_4)(\text{P}_2\text{O}_7)_{3.5}$ at $\sim 300 \text{ K}$ have $\Delta\xi \lesssim 0.4 \text{ \AA}$ with

respect to $R\bar{3}$ symmetry and $0.1 \lesssim u_{\text{iso}} \lesssim 0.3 \text{ \AA}$, except for six O with $0.7 \lesssim \Delta\xi \lesssim 1.2 \text{ \AA}$ of which four are half-occupied, see Table S5. Taking the present structure as reliable, the criteria for ferroelectricity are clearly fulfilled.

2.10. $\text{Pb}_2\text{ScTaO}_6$ [281087] (Woodward & Baba-Kishi, 2002)

Time-of-flight neutron powder diffraction data (31–122 ms) at 4.2 K; first-order paraelectric to ferroelectric phase transition at $T_C \simeq 295 \text{ K}$; Rietveld refinement in space group $R3$, $R_{\text{exp}} = 0.065$; nine independent metal, eight O atoms with 1487 $F_{\text{obs}} \geq n\sigma(F_{\text{obs}})$, n not stated. The paraelectric structure at 400 K was refined similarly in space group $Fm\bar{3}m$. Analysis of the atomic coordinates at 4.2 K in a rhombohedral setting, since $\alpha_R = 89.849^\circ$, shows $0 \lesssim \Delta\xi \lesssim 0.30 \text{ \AA}$ and $0.09 \lesssim u_{\text{iso}} \lesssim 0.13 \text{ \AA}$ with respect either to $Fm\bar{3}m$ or $F\bar{3}m$ symmetry, see Table S6(a). The criteria for ferroelectricity are hence well satisfied, in agreement with Woodward & Baba-Kishi's (2002) and Baba-Kishi *et al.*'s (1992) reports of a phase transition over the range 283–296 K to the paraelectric state with space group $Fm\bar{3}m$. The latter is not a supergroup of $R3$ or of $R\bar{3}$, but $Fm\bar{3}$ is a supergroup of $R\bar{3}$; further, both $Fm\bar{3}m$ and $Fm\bar{3}$ have identical coordinates in the 4(a), 4(b), 8(c) and 24(e) Wyckoff positions. The phase transition could hence occur in two stages, from space group $R3$ to supergroup $R\bar{3}$, then at a slightly higher temperature to supergroup $Fm\bar{3}$. The potential barrier separating the structure in space group $R3$ from that in $R\bar{3}$ is necessarily lower than between $R3$ and $Fm\bar{3}$; thermodynamically, such a process is hence not unlikely. The 13–14 K gap in the only temperature-dependent study, see above, is unable to distinguish between a one-stage and a closely separated two-stage transition. A transition from space group $R3$ to $R\bar{3}$ has $0 \lesssim \Delta\xi \lesssim 0.28 \text{ \AA}$, see Table S6(b), that from $R\bar{3}$ to $Fm\bar{3}$ has $0 \lesssim \Delta\xi \lesssim 0.11 \text{ \AA}$, see Table S6(c). The average $0.144 (14) \text{ \AA}$ displacement by each Ta/Sc atom from the center of its octahedron corresponds to $T_C = 415 (85) \text{ K}$, not significantly different from the experimental T_C . Calorimetric studies combined with single-crystal structural redetermination would clarify these phase and bonding relationships.

2.11. $\text{II-Mn}_4\text{Ta}_2\text{O}_9$ [411944] (Esmailzadeh & Grins, 2002)

Mo $K\alpha$, graphite monochromator, rotating anode; 121 independent $F_{\text{obs}} > n\sigma(F_{\text{obs}})$, n not reported, absorption corrections, U_{iso} for all atoms, $R = 0.066$, $wR(F^2) = 0.154$; 4 independent metal and 2 O atoms, metastable phase II, crystal quality characterized as poor. Mixed occupancies are reported

⁴ B refined only for H2 with $B(\text{H}1)$ set equal to $B(\text{H}2)$; the occupancy factor for H1 refined to 0.41 (10).

Table 9

Structures most likely to remain in space group $R\bar{3}$ without phase change.

§	Formula	Reference	ICSD	Table	Polarity reversal	Conclusions and Footnotes
6.1	$\text{Na}_3\text{VO}_4 \cdot 3\text{H}_2\text{O}$	Kato & Takayama-Muromachi (1987)	62533	S39	Reorientation of VO_4^{3-} tetrahedra required, with $\Delta\xi(\text{O1}) \approx 2.3 \text{ \AA}$	Atomic coordinates do not approach supergroup symmetry within acceptable limits ⁽¹⁾
6.2.1	LiGaSiO ₄ family	Fleet (1987)	65125	S40	$0.05 \lesssim \Delta\xi \lesssim 0.30 \text{ \AA}$, with $0.07 \lesssim u_{\text{iso}} \lesssim 0.10 \text{ \AA}$	Criteria for ferroelectricity are satisfied only if all equivalent 9(b) Wyckoff sites are equally occupied ^(2a)
6.2.2	LiAlSiO ₄	Daniels & Fyfe (2001)	92708	S41	$0.0 \lesssim \Delta\xi \lesssim 0.13 \text{ \AA}$, with $0.09 \lesssim u_{\text{iso}} \lesssim 0.12 \text{ \AA}$	As in §6.2.1 ^(2b)
6.3	$\text{Co}(\text{CO})_4\text{SnCl}_3$	Klüfers (1991)	69685	S42	The linear Sn–Co–C–O group along the <i>c</i> axis does not allow polarization reversal	The remaining three Cl, three C and three O atoms are nearly in a plane \perp to the linear group along <i>c</i> ⁽³⁾
6.4	$\text{Sn}_{1.008}\text{P}_2\text{S}_6$	Wang <i>et al.</i> (1995)	79818	S43	Minor SHG temperature dependence at 225–425 K precludes a transition to nonpolar within that range	The major difference in occupation between the two Sn sites and $\Delta\xi \approx 2.2 \text{ \AA}$ for both S shows the structure must remain polar ⁽⁴⁾
6.5	$\text{KNi}(\text{PO}_3)_3$	Kapshuk <i>et al.</i> (2000)	91527	S44	$0.07 \lesssim \Delta\xi \lesssim 1.49 \text{ \AA}$, with $0.08 \lesssim u_{\text{eq}} \lesssim 0.13 \text{ \AA}$	K, Ni, O1 and O3 closely approach $R\bar{3}$ symmetry, but P and O2 cannot be interchangeable in an 18(<i>f</i>) site ⁽⁵⁾
6.6	$\text{La}_2\text{MgGeO}_6$	Swaffer <i>et al.</i> (2002)	97016	S45	$0.02 \lesssim \Delta\xi \lesssim 0.11 \text{ \AA}$ for all atoms, with $0.04 \lesssim u_{\text{eq}} \lesssim 0.08 \text{ \AA}$	Mg and Ge sites are clearly ordered, hence $R\bar{3}$ is the more likely symmetry over the thermal stability range ⁽⁶⁾
6.7	$\text{Ti}_2(\text{MoO}_3)_3(\text{PO}_3(\text{CH}_3))$	Harrison <i>et al.</i> (1998)	150170	S46	$0.16 \lesssim \Delta\xi \lesssim 1.28 \text{ \AA}$ if P and C occupy equivalent sites and Mo is neglected	With equivalence unlikely and $\Delta\xi(\text{Mo}) \approx 2.79 \text{ \AA}$, the structure necessarily remains polar ⁽⁷⁾
6.8	$\text{Cs}_4\text{SrSn}_3\text{Se}_9$	Almsick & Sheldrick (2005)	171013	S47	$0 \lesssim \Delta\xi \lesssim 0.80 \text{ \AA}$ for four of the atoms but the remaining three have $1.6 \lesssim \Delta\xi \lesssim 2.0 \text{ \AA}$	The three large $\Delta\xi$ at 293 K are unlikely to vanish at a transition to $R\bar{3}m$ with the low T_{prep} of 463 K ⁽⁸⁾
6.9	$\text{Mn}_{10.39}\text{Mg}_{2.53}\text{Al}_{1.89}\text{Fe}_{0.19}(\text{OH})_{23}(\text{AsO}_3)(\text{AsO}_4)_2$ (Hematolite)	Moore & Araki (1978)	200324	S48a S48b	$0.18 \lesssim \Delta\xi \lesssim 1.13 \text{ \AA}$ except for four O and an Al,Fe,Mn atom with $\Delta\xi \approx 1.9, 2.96 \text{ \AA}$	A possibly overlooked second Al ₂ Fe ₁ Mn site, eliminating this $\Delta\xi$ range, has four rather than six O n.n. ⁽⁹⁾

(1) The apex atom O1 of the VO_4^{3-} tetrahedron lies on, with the equilateral O2–O2–O2 base normal to, the trigonal axis. P_3 reversal also requires new O···H bonds to be broken and made. (2a) The close match between $\langle d_{\text{Li-O}} \rangle - \langle d_{\text{Si-O}} \rangle = 0.34 \text{ \AA}$ in space group $R\bar{3}$ and the 0.33 Å difference between Shannon's (1976) ionic radii for Li^+ and Si^{4+} strongly indicates full ordering by the highly stable SiO_4^{4-} ion, hence LiGaSiO₄ is expected to remain polar over its thermal stability range. (2b) The difference $\langle d_{\text{Li-O}} \rangle - \langle d_{\text{Al-O}} \rangle = 0.13 \text{ \AA}$ and the 0.20 Å difference between Shannon's (1976) radii for $\text{Li}^+(\text{IV})$ and $\text{Al}^{3+}(\text{IV})$ is also indicative of full ordering, hence of LiAlSiO₄ remaining polar, cf. §2.5. (3) The combination of the linear Sn–Co–C–O array aligned along the polar $R\bar{3}$ axis in $\text{SnCl}_3\text{Co}(\text{CO})_4$, with Cl, C and O atoms nearly in a plane normal to *c*, precludes the possibility of reversing the *c*-axis sense, see Table S42. (4) Second harmonic observation to 425 K by Cleary (2006) and the major difference in occupation of the Sn sites together eliminate the possibility of any tendency toward $P312$ symmetry through $R32$ as the rhombohedral centering relaxes, see Table S43. Ferroelectricity in $\text{Sn}_2\text{P}_2\text{S}_6$ was reported by Carpentier & Nitsche (1974) with $T_c = 339$ (2) K. Cleary *et al.* (1993) reported the transition in $\text{Sn}_2\text{P}_2\text{S}_6$ from space group Pn to $P2_1/n$; Gamernyk *et al.* (2006) determined $T_c \approx 337$ K. (5) P forms a PO_4 tetrahedron in which O2 is bonded to P with $d_{\text{P-O2}} = 1.49 \text{ \AA}$. Although the coordinates numerically satisfy the criteria for a transition to centrosymmetry, the P and O2 atoms cannot occupy the same 18(*f*) Wyckoff site in $R\bar{3}$ under normal conditions. The symmetry of $\text{KNi}(\text{PO}_3)_3$, hence most likely remains $R\bar{3}$ throughout the thermal stability range. (6) The $\sim 0.20 \text{ \AA}$ difference between average metal–oxygen bond lengths at the nominal Mg and Ge sites determined by Swaffer *et al.* (2002), see Table S45, is indistinguishable from that expected from Shannon's (1976) atomic radii, hence the Mg and Ge sites are most likely fully ordered and correspond to the space group $R\bar{3}$. It is not known whether annealing results in fully disordered Mg/Ge sites or not but if it does, then the space group would more likely be $R3c$, cf. §6.2, Table 9. (7) The approach of all atoms except Mo to $R\bar{3}$ symmetry would be satisfied, with $0.11 \lesssim u_{\text{eq}} \lesssim 0.23 \text{ \AA}$, in the unlikely event that the tetrahedral P and C atoms could become equivalent. However, the strong deviation by Mo from centrosymmetry clearly prevents such a phase transition. (8) Unless $\text{Cs}_4\text{SrSn}_3\text{Se}_9$ remains stable to $T \gg 463 \text{ K}$, the preparation temperature, the magnitudes $\Delta\xi(\text{Se1}) \approx 2.04 \text{ \AA}$, as also the 1.65 and 1.61 Å at 293 K for the two other independent $\Delta\xi(\text{Se})$, are unlikely to become comparable to u_{eq} in an approach to a hypothetical phase transition to $R\bar{3}m$. (9) The possible location of a comparable but overlooked Al, Fe, Mn atom (*Al2a*) at $0,0,\bar{z}$ in the 1978 determination that would reduce $\Delta\xi(\text{Al2a})$ to zero is eliminated by its resulting number of nearest O-atom neighbors. The structure most likely remains in space group $R\bar{3}$ over its stability range.

for all metal atom sites in this second rhombohedral phase, with two as containing 11/12 Mn, 1/12 Ta, one with 3/4 Mn, 1/4 Ta and the fourth 11/12 Ta, 1/12 Mn. The resulting structure has $0.09 \lesssim \Delta\xi \lesssim 0.64 \text{ \AA}$ with respect to space group $R32$, see Table 5. Assuming the structure is reliable, the conditions for ferroelectricity are fully satisfied since $0.11 \lesssim u_{\text{eq}} \lesssim 0.20 \text{ \AA}$. A corundum-related phase of $\text{Mn}_4\text{Ta}_2\text{O}_9$ with $a = 5.3306(2)$, $c = 14.336(1) \text{ \AA}$ was reported in space group $P\bar{3}c$ by Grins & Tyutyunnik (1998); it has a structure that differs from Esmailzadeh & Grins' (2002) phase I with $a = 5.4308(1)$, $c = 14.1194(5) \text{ \AA}$ and space group $R3c$. Calorimetric data for $\text{Mn}_4\text{Ta}_2\text{O}_9$ have not yet been published. Clarification of the phase relationships in this system would illuminate the present structures.

3. Structures reported in space group $R3$ that are more likely in, or may undergo a transition to, crystal class $3m$ or $31m$

All nine materials surveyed in Table 6 were refined in the space group $R3$. The structure of each, however, is characterized by maximum i th atom deviations $\Delta\xi_i$, from corresponding locations in a supergroup containing an additional mirror or glide plane, that are less than or comparable with the corresponding u_{eq}^i . The thermodynamic stability of such a structure in a supergroup identified in Table 6 as $R3m$, $R3c$ or $P31m$ hence either exceeds that of the structure in $R3$ and corresponds to the stable phase or, in the event some $\Delta\xi_i$ are greater than the corresponding thermal amplitudes at the measurement temperature, a pyroelectric-to-pyroelectric phase transition to that supergroup is more likely at a characteristic temperature $T(\text{transition}) > T(\text{structure determination})$.

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

Each of the 15 materials surveyed in Table 7 was refined in space group $R3$. All but one have maximum atomic deviations $\Delta\xi_i$ from locations that correspond to the symmetry of either supergroup $R\bar{3}$ or $R32$ that are less than the corresponding u_{eq}^i for that i th atom and hence are more likely to be nonpolar. The exception is $\text{ZrCr}_2\text{D}_{3.8}$, see §4.10 in Table 7, which was measured at 100 K and differs by fully satisfying the symmetry of space group $P6_3/mcm$, a supergroup related to $R3$ through a sequence such as $R3m$, $P31m$ and $P\bar{3}1m$. Additional uncertainties are associated with the structures analyzed in §§4.3,⁵ 4.11, 4.12 and 4.13, as noted in Table 7.

5. Structures reported in space group $R3$ with reduced predictive qualities

All 12 refined structures in the survey presented in Table 8 approach supergroup symmetry, but have one or more major characteristic uncertainties that lower the confidence of any

property prediction. The structure of $\text{Sn}_{4.2}\text{Si}_9\text{P}_{16}$ in §5.1, Table 8, is typical; it contains a pair of atoms identified as P and Sn that are required to become equivalent in $R\bar{3}$. In addition, the equivalency of three P and Si pairs of atoms is also required. Although both are possible, neither set of equivalences is likely.

6. Structures most likely to remain in space group $R3$ without phase change

Either the atomic deviations from higher symmetry required in the nine structure types surveyed in Table 9 are so large or polarization reversal is impossible because of atomic ordering, as in the case of §6.2, Table 9, that each type may be characterized as most likely to remain in space group $R3$ without the likelihood of a phase change at higher temperatures. The structure of $\text{Na}_3\text{VO}_4 \cdot 3\text{H}_2\text{O}$ is typical, with polarization reversal requiring the unlikely reorientation of all VO_4 tetrahedra with a resulting displacement by O1 of $\sim 2.3 \text{ \AA}$ as $\text{O} \cdots \text{H}$ bonds are broken and made, see §6.1, Table 9.

Note added in proof. It is notable that the structural results on orthorhombic sulfur obtained in 1955 cited in §3.7.2 do not differ significantly from those recently reported by David, W. I. F., Ibberson, R. M., Cox, S. F. J. & Wood, P. T. (2006), *Acta Cryst.* **B62**, 952–959. The latter inadvertently omitted the reference to the earlier work, Ibberson (2006).

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