Inorganic structures in space group $P31m$; coordinate analysis and systematic prediction of new ferroelectrics

S. C. Abrahams


Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see http://journals.iucr.org/services/authorrights.html

Acta Crystallographica Section B: Structural Science publishes papers in structural chemistry and solid-state physics in which structure is the primary focus of the work reported. The central themes are the acquisition of structural knowledge from novel experimental observations or from existing data, the correlation of structural knowledge with physico-chemical and other properties, and the application of this knowledge to solve problems in the structural domain. The journal covers metals and alloys, inorganics and minerals, metal-organics and purely organic compounds.

Crystallography Journals Online is available from journals.iucr.org
Inorganic structures in space group $P31m$; coordinate analysis and systematic prediction of new ferroelectrics

The 62 entries listed in ICSD release 2009/1 under polar space group $P31m$ correspond to 31 families of inorganic crystal structures, some with only one member. Coordinate analysis reveals, over a wide confidence range, 11 of these families as ferroelectric candidates. One includes the well known improper ferroelectric GASH (guanidinium aluminum sulfate hexahydrate), \((\text{C(NH}_2)_3\text{Al(SO}_4)_2\text{H}_2\text{O})_6\); another the previously predicted ferroelectric CsNO$_3$ phase II. Those remaining include K$_3$Nb$_3$B$_2$O$_{12}$, the minerals schairerite, galeite and lizardite 1T, LaNi$_3$D$_6$ and $\gamma$-CaNi$_3$D$_6$, Ca(OCl)$_2$. Ca(OH)$_2$, \([\text{N(CH}_3)_4]_2\text{Mo}_3\text{S}_13\), Li$_{17}$Ag$_3$Sn$_6$ and Cs$_3$As$_5$O$_9$. Candidate selection is based upon detecting an approach by the reported atomic arrangement to the symmetry of a corresponding nonpolar supergroup. A further 13 families are typified by their reduced predictive properties, with four others likely to remain polar at higher temperatures and the remaining three noted as having a unit cell larger than reported or a misassigned space group. The primary sources of uncertainty in structurally based predictions of ferroelectricity are the reliability of the underlying structural determination and the upper limit assigned to the cationic displacement magnitudes required to achieve supergroup symmetry.

1. Introduction

1.1. Ferroelectric phase transitions

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

$^1$The highest phase-transition temperatures from ferroelectric to nonpolar presently reported are $\sim 1773$ K for La$_3$Ti$_2$O$_7$ (Nanamatsu et al., 1974) and $\sim 1615$ K for Sr$_2$Nb$_2$O$_7$ (Nanamatsu et al., 1972), cf. equation (1).
The present series of systematic studies, seeking to examine all known polar inorganic crystal structures for indications of possible ferroelectricity, began with those listed in the highest symmetry polar space group, viz. $P_{63}cm$ (Abrahams, 1988), followed by those studied in space groups of successively lower symmetry. Examination of the structures reported in the space group $P31m$, directly after that for structures with space group $P3m1$ (Abrahams, 2008), departs from the standard International Tables for Crystallography sequence to allow a ready contrast between the structural characteristics of materials in space groups exhibiting an apparently minor symmetry change. In the present case, the fivefold decrease in number of ICSD entries from 328 in space group $P3m1$, to 62 in the space group $P31m$, is notable.

1.2. Prior and present results for point group 3

A total of 21 single-member inorganic structural families with the space group $P3$ have been shown to satisfy the structural criteria for ferroelectricity, with 16 families identified in space groups $P3_1$ or $P3_3$, of which five contain two members, 29 families in the space group $R3$, of which two include two members, and 12 in space group $P31m$, of which four families contain a total of 13 members (Abrahams, 2000, 2003, 2006, 2007, 2008); the structures in space groups $P31c$, $P3c1$, $R3m$ and $R3c$ within the trigonal system remain examined. The coordinate analysis reported below for the structures reported in space group $P31m$ reveals 32 families of which 11 are ferroelectric candidates; one is GASH (guanidinium aluminum sulfate hexahydrate), [(C(NH$_2$)$_3$)Al(SO$_4$)$_2$(H$_2$O)$_6$], a known ferroelectric since 1956, another is CsNO$_3$, phase II predicted in 2003 to be ferroelectric. Only one family contains two members viz. LaNi$_5$D$_6$ and $\gamma$-CaNi$_5$D$_6$, with none presently containing more.

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

A total of 163 CdI$_2$, 69 ZnS and 10 SiC structures, among the 311 entries reported under space group $P3m1$ in ICSD Release 2007/1, are polytypes.$^2$ By contrast, not a single polytype appears among the 62 entries listed under symorphic space group $P31m$ in the 2009/1 release of ICSD, in accordance with Iglesias’ (2006) sapient observation that presently containing more.

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

3 Fenooitte is the only mineral reported in $P3m1$, whereas scharite, galeite, lizardite 1T and 9T, crozstidite, holtedahlite, satterlyite and langbanite form in $P31m$.

group. By contrast, no structure with $P3m1$ symmetry has been reported more than twice.

1.4. $P31m$ space group—supergroup relationships

A structure with the space group $P31m$, on heating, may undergo a transition to a phase with minimal nonisomorphic supergroup symmetry $P31m$, $P62m$, $P6_{3}cm$ or $P6mm$. In the present investigation, the experimental atomic coordinates of members in 11 different families are found to approach either $P31m$ or $P6_{3}cm$ symmetry closely enough to be indicative of such a phase transition; no such approach was detected either to $P6_{3}cm$ or $P6mm$. Although the supergroup coordinates thus derived are not necessarily identical to those that subsequently may be determined experimentally, they are expected to be close. In the tables that follow, the Wyckoff position of each independent atom is given both in the space group $P31m$ and in the expected supergroup.$^4$ Unit-cell axes without integral change of length are assumed at the predicted phase transitions.

1.5. Structural criteria for predicting ferroelectricity

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

(i) that the structure determination is fundamentally correct,

(ii) that the total i-th cation displacement ($\Delta \xi_i$),$^5$ between a reported $x_i,y_i,z_i$ location and that in the assumed paraelectric phase, is $1.5 \geq \Delta \xi_i \geq 0.05$ Å with $\Delta \xi_i$ not less than the r.m.s. thermal or static displacement of the i-th cation $u_i$, and

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

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

$$T_C = (k/2\kappa) (\Delta z_i)^2 K,$$

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

Application of (1) to the ferroelectric crystal with the highest $T_C$ presently reported, i.e. La$_2$Ti$_3$O$_7$ with $T_C \simeq 1773$ K (see footnote 1), gives $\Delta z_{Ti} \simeq 0.30$ Å; higher displacements are possible in principle, as suggested in (iii) above, but as yet have not been reported. The well known ferroelectric BaTiO$_3$, which is considered displaced from its

4 Multiplicity, Wyckoff letters and the corresponding coordinates for all positions in the space group $P3m1$ and in supergroups $P31m$ and $P62m$ may be found conveniently listed in International Tables for Crystallography, Vol. A (2002).

5 With $\Delta \xi_i$ defined as $[(\Delta x))^2 + (\Delta y))^2 + (\Delta z))^2 + (\Delta z$) in space group $P31m$, where the i-th atom located at $x_i,y_i,z_i$ is considered displaced from its $x'_i,y'_i,z'_i$ location in the hypothetical (nonpolar) supergroup, and $\Delta x = (x_i - x'_i)$, $\Delta y = (y_i - y'_i)$, $\Delta z = (z_i - z'_i)$.

6 The applicability of (1) is now widely demonstrable. A modified approach was offered by Kroumova et al. (2002).
with experimental $T_c = 393$ K, corresponds to $\Delta z_{Ti} = 0.14$ Å by (1) and has reported $\Delta z_{Ti}$ values ranging from 0.10 to 0.12 Å, see the summary in Abrahams (2009). With coordinate uncertainties $\sim 0.02$ Å, the determined and predicted $\Delta z_{Ti}$ values for BaTiO$_3$ are without significant disagreement.

1.6. Origin choice in space group $P31m$ and algorithmic analysis

The $c$ axis may be identified with any threefold axis in the space group $P31m$ and may be assigned $x, y$ coordinates 0; 1/3, 2/3; or 2/3, 1/3. The choice of $z$ coordinate origin is arbitrary but, although discretionary, care is required in making it to avoid the generation of related but unrecognized pairs of atoms approaching supergroup equivalence.

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

1.7. Confidence in and validation of predicted ferroelectric structures

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

1.8. Presentation of structural analysis

All families reported in the ICSD release 2009/1 as forming in the space group $P31m$ and identified by atomic coordinate analysis in §2 as new potential ferroelectric candidates are presented below in full, unless the structure contains more than ten independent atoms or requires more than a single table. In each such case, the accompanying larger and/or additional tables, together with those for structures not meeting the criteria in §1.5, are provided as supplementary material. The presentation order follows that of the ICSD accession number, given in bold type within square parentheses for each determination. Structures with reduced predictive properties are presented in §3; structures more likely to remain polar at higher temperatures in §4, and those considered misassigned to space group $P31m$ in §5.

---

2. Predicted/possible new inorganic ferroelectrics in the space group $P31m$

2.1. $K_4Nb_6B_2O_{12}$, sub- and full-cell [968, 969]\(^a\)

Choisnet et al. (1977) measured a total of 410 anomalous dispersion-corrected subcell $I_{obs}$ using graphite-monochromated Mo $K\alpha$, refining them to $R = 0.12$ in the space group $P31m$. Coordinate analysis shows $\Delta \xi < h_{max}$ for all resulting atomic locations, see Table S1(a), hence the structure is indistinguishable in principle from that expected in the centrosymmetric supergroup $P62m$. A total of 1500 superstructure $F_{obs} \geq 0.08F_{max}$, mostly described as very weak and with measurement precision reduced by the strong substructure reflections present, were refined in the space group $P31m$ to $R = 0.08$ for the 62 independent atoms in a unit cell with $V_{full cell} \approx 3V_{subcell}$ and Laue symmetry no higher than 6$\overline{3}mmm$. Coordinate analysis, see Table S1(b), shows that no cation location in the full cell differs more than $\sim 0.19$ Å, nor any O location more than $\sim 0.26$ Å, from satisfying $P62m$ symmetry. Hence, although the subcell structure appears not to differ significantly from centrosymmetry, acceptance of the present full cell structure would satisfy the criteria for ferroelectricity. The confidence level for physical property prediction on the basis of the present structural determination is not high; it is, however, capable of being raised sharply by redetermination with greater accuracy. Second harmonic detection, dielectric or calorimetric investigation would also enhance the confidence level.

2.2. $Na_{22}(SO_4)_2F_6Cl$, Schaierite [4289]

Fanfani et al. (1975) used 2536 $I_{obs} > 3\sigma(I_{obs})$ of a total 2921 independent graphite-monochromated $I_{obs}$ for the structural refinement of schaierite in the space group $P31m$, reaching a final $R = 0.070$. Coordinate analysis, see Table S2, shows that all 14 Na, 10 S, both independent Cl and the six F anions present satisfy the conditions in §1.5 for ferroelectricity, with no cation displaced more than 0.21 Å and no Cl, S or F anion further than $\sim 0.42$ Å from satisfying $P31m$ supergroup symmetry. Three single and one pair of O atoms, however, appear unacceptably far from such symmetry. If three matching O atoms had inadvertently been overlooked and a fourth either mislocated or overlooked, then the conditions of §1.5 would be met and schaierite could be predicted as a new ferroelectric. Higher accuracy measurement is clearly advisable. It may be noted that all O-atom positions are not necessarily fully occupied.

2.3. $Na_{13}(SO_4)_5F_4Cl$, Galeite [4290]

Structural refinement of 2078 independent $I_{obs} > 3\sigma(I_{obs})$ for the mineral galeite, measured with graphite-monochromated Mo $K\alpha$ in the space group $P31m$, led Fanfani et al. (1975) to their lowest $R = 0.070$. The formula

---

* Supplementary data, including tables containing the atomic coordinates of structures with more than ten independent atoms in the space group $P31m$, together with any extra tables, and all tables with structures not meeting the criteria in §1.5, designated by the letter ‘$\star$’ for this paper, are available from the IUCr electronic archives (Reference: BK5094). Services for accessing these data are described at the back of the journal.

* Family includes $K_2Ta_3B_2O_{12}$.

* See footnote to Table S2; with $\sim 95\%$ of all other atoms present in acceptable conformity with centrosymmetry, such locational errors for some of the lightest atoms are not implausible.
Table 1
Averaged, modified lizardite 1T-atomic positions (see Table S4 for all experimental coordinates) with hypothetical x’y’z’ coordinates and the Δx, Δy, Δz, Δξ and u_iso displacements in Å [17046, 67332, 67333, 75933, 75934, 81102, 82411, 87436, 87437, 87438, 87506, 202358, 245887] (see footnote 4).

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>P31m</th>
<th>P62m</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(z*)</th>
<th>x’</th>
<th>y’</th>
<th>z’</th>
<th>Δx</th>
<th>Δy</th>
<th>Δz</th>
<th>Δξ</th>
<th>u_iso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>3c</td>
<td>3g</td>
<td>0.3325</td>
<td>0.0</td>
<td>0.4520</td>
<td>0.4430</td>
<td>0.3325</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.41</td>
<td>0.41</td>
<td>0.11</td>
</tr>
<tr>
<td>Si</td>
<td>2b</td>
<td>2c</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0704</td>
<td>0.6614</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>O1</td>
<td>2b</td>
<td>2d</td>
<td>1/3</td>
<td>2/3</td>
<td>0.2901</td>
<td>0.2811</td>
<td>1/3</td>
<td>2/3</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.58</td>
<td>1.58</td>
<td>0.10</td>
</tr>
<tr>
<td>O2</td>
<td>3c</td>
<td>3f</td>
<td>0.5054</td>
<td>0.0</td>
<td>-0.0114</td>
<td>-0.2024</td>
<td>0.5054</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.15</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>O3</td>
<td>3c</td>
<td>3g</td>
<td>0.6655</td>
<td>0.0</td>
<td>0.5850</td>
<td>0.5760</td>
<td>0.6655</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>0.55</td>
<td>0.55</td>
<td>0.12</td>
</tr>
<tr>
<td>O4</td>
<td>1a</td>
<td>1b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2951</td>
<td>0.2861</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.55</td>
<td>1.55</td>
<td>0.09</td>
</tr>
<tr>
<td>H1</td>
<td>3c</td>
<td>3g</td>
<td>0.6278</td>
<td>0.0</td>
<td>0.716</td>
<td>0.7070</td>
<td>0.6278</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>1.50</td>
<td>1.50</td>
<td>0.16</td>
</tr>
<tr>
<td>H2</td>
<td>1a</td>
<td>1a</td>
<td>-0.0042</td>
<td>0.0</td>
<td>0.175</td>
<td>0.166</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.02</td>
<td>0.12</td>
<td>1.20</td>
<td>1.20</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 2
Modified atomic positions for LaNi5D6.5 based on Noréus et al. (1983) neutron scattering data [38402] with hypothetical x’y’z’ coordinates and the Δx, Δy, Δz, Δξ and u_iso displacements in Å (see Table S4 for all five independently measured sets of coordinates [20188, 38402, 200242, 638253, 638254] (see also footnote 4).

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>P31m</th>
<th>P62m</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>z*</th>
<th>x’</th>
<th>y’</th>
<th>z’</th>
<th>Δx</th>
<th>Δy</th>
<th>Δz</th>
<th>Δξ</th>
<th>u_iso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1a</td>
<td>1a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.0012</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.0252</td>
<td>0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni1</td>
<td>2b</td>
<td>2c</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.980 (5)</td>
<td>0.9678</td>
<td>0.3333</td>
<td>0.0667</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.137</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>Ni2</td>
<td>3c</td>
<td>3g</td>
<td>0.499 (1)</td>
<td>0.0</td>
<td>0.496 (5)</td>
<td>0.4838</td>
<td>0.499</td>
<td>0.00</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.069</td>
<td>0.07</td>
<td>0.16</td>
</tr>
<tr>
<td>D1</td>
<td>3c</td>
<td>3f</td>
<td>0.470 (1)</td>
<td>0.0</td>
<td>0.092 (5)</td>
<td>0.0798</td>
<td>0.47</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.340</td>
<td>0.34</td>
<td>0.15</td>
</tr>
<tr>
<td>D2</td>
<td>6d</td>
<td>6k</td>
<td>0.189 (2)</td>
<td>0.864 (3)</td>
<td>0.493 (4)</td>
<td>0.4808</td>
<td>0.189</td>
<td>0.864</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.082</td>
<td>0.08</td>
<td>0.17</td>
</tr>
</tbody>
</table>

n(Na2SO4)·(nNaF·nCl) is shared by schairerite, see §2.2 with n = 7, and galeite with n = 5. Coordinate analysis shows that all Na, S and Cl ions in galeite, and also 12 of the 17 independent O ions, satisfy the conditions for ferroelectricity with acceptable displacements from P62m symmetry, see Table S3. At least three O atoms, however, appear misplaced, cf. schairerite, resulting in apparent Δξ(O) magnitudes ranging from ~1.6 to 1.7 Å. Should structural redetermination find either that the reported positions for these three O atoms are in error, or locate the related but overlooked atoms, then galeite and also schairerite would be predicted as most likely ferroelectric.

2.4. Mg3Si2O5(OH)4, lizardite 1T [17046, 67332, 67333, 75933, 75934, 81102, 82411, 87436, 87437, 87438, 87506, 202358, 245887]

Thirteen separate crystal structure studies of the mineral lizardite 1T, with the basic composition Mg3Si2O5(OH)4, have been reported. Following ICSD order, the first two by Mellini & Zanazzi (1989), two by Mellini & Viti (1994), one by Krstanovic & Karanovic (1995), one by Gregorkiewitz et al. (1996), three by Guggenheim & Zhan (1998), one by Zhukhlistov & Zvyagin (1998), one by Mellini & Zanazzi (1987), with the last Mercier & Le Page’s (2008) ‘ideal’ structure. Analysis of the coordinates in Table 1, using the fully averaged set in Table S4, reveals the Mg cation departs ~0.41 Å, the Si ion ~0.44 Å from supergroup P62m symmetry with O and H ionic departures ranging from ~0.15 to ~1.55 Å. The Mg2+ and two O2− ionic displacements approach the upper bound in §1.1(iii), the former corresponding to TC ~3400 K by (1), a temperature that is likely well above decomposition. The possibility that Lizardite 1T might prove capable of dielectric poling at temperatures well below ambient and decomposition is worthy of investigation: if so, it would be a new ferroelectric; if not, it would more appropriately fall within the category of §3.

2.5. LaNi5D6 [20188, 38402, 87127, 200242, 638240, 638253, 638254]; γ-CaNi5D6.5 [54478]

Bowman et al. (1973) used X-ray powder diffraction to derive a set of coordinates for LaNi5D6 with R ~0.26. Both Fischer et al. (1977) and Andresen (1977) refined the structure of LaNi5D6 by neutron powder diffraction, reporting final R values of 0.054 and 0.04, respectively, while Burnasheva et al. (1978), also using neutron powder diffraction, reported R = 0.124. Noréus et al. (1983) refined the LaNi5D6 structure to R = 0.083 using the intensities of 92 neutron diffraction powder lines, while Furrer et al. (1977) used similar techniques to obtain R = 0.064. The results of all six analyses, see Table S5, show several coordinates that depart from average, but nevertheless exhibit pseudosymmetric near-identities with D2y[20188] ≈ D2y[all other reports] and NiIz[200242, 638254] ≈ NiIz[all other reports] + ½. No analysis, however, results in atomic positions that depart more than ~0.3 Å from P31m symmetry; additionally, the coordinates of all atoms including D2 are closer to P62m than P31m symmetry.
Table 3
Modified atomic positions for γ-CaNi₅D₆.₁ based on Yoshikawa et al. (1998) [54478] with hypothetical x’ y’ z’ coordinates and the Δx, Δy, Δz, Δξ and uiso displacements in Å (isomorphous with LaNi₅H₆₀ structure); see footnote 4.

\[ a = 5.333 \ (1), \ c = 4.262 \ (1) \ \AA; \ z^* = z + 0.033 \text{ based on Ca(z) and Ni(z) only.} \]

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>P31m</th>
<th>P62m</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>z^*</th>
<th>x’</th>
<th>y’</th>
<th>z’</th>
<th>Δx</th>
<th>Δy</th>
<th>Δz</th>
<th>Δξ</th>
<th>uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca 1a</td>
<td>1a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.033</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.141</td>
<td>0.14</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni1 3c</td>
<td>3g</td>
<td>0.508 (4)</td>
<td>0.0</td>
<td>0.45 (1)</td>
<td>0.483</td>
<td>0.508</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.072</td>
<td>0.09</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni2 2b</td>
<td>2c</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.05 (1)</td>
<td>0.017</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.0</td>
<td>0.0</td>
<td>0.072</td>
<td>0.07</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1 3c</td>
<td>3f</td>
<td>0.52 (1)</td>
<td>0.0</td>
<td>0.06 (1)</td>
<td>0.093</td>
<td>0.52</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.396</td>
<td>0.40</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2 6d</td>
<td>6k</td>
<td>0.18 (1)</td>
<td>0.82 (1)</td>
<td>0.6 (1)</td>
<td>0.633</td>
<td>0.18</td>
<td>0.82</td>
<td>0.5</td>
<td>0.0</td>
<td>0.567</td>
<td>0.57</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Not determined or reported.

Table 4
Modified atomic positions for Ca(OCl)₂(Ca(OH)₂)₂ based on Aleksandrova et al. (1968) [20283] with hypothetical x’ y’ z’ coordinates and the Δx, Δy, Δz, Δξ and uiso displacements in Å (see footnote 4).

\[ a = 6.31 (20), \ c = 6.49 (2) \ \AA; \ z^* = z - 0.018 \text{ based on Ca(z) and Cl(z) only.} \]

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>P31m</th>
<th>P62m</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>z^*</th>
<th>x’</th>
<th>y’</th>
<th>z’</th>
<th>Δx</th>
<th>Δy</th>
<th>Δz</th>
<th>Δξ</th>
<th>uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca 3c</td>
<td>3f</td>
<td>0.6667</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.12</td>
<td>0.12</td>
<td>n/d†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl 2b</td>
<td>2d</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.536</td>
<td>0.518</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.12</td>
<td>0.12</td>
<td>n/d</td>
<td></td>
</tr>
<tr>
<td>O₁ 1a</td>
<td>1a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.213</td>
<td>0.195</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.27</td>
<td>1.27</td>
<td>n/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ 2b</td>
<td>2c</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.213</td>
<td>0.195</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.0</td>
<td>0.0</td>
<td>1.27</td>
<td>1.27</td>
<td>n/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃ 3c</td>
<td>3g</td>
<td>0.3333</td>
<td>0.787</td>
<td>0.769</td>
<td>0.3333</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>1.75</td>
<td>1.75</td>
<td>n/d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Not determined or reported.

al.’s (1983) elastic and inelastic neutron scattering measurements as both typical and among the most reliable in Table S5, the maximum departure by La or Ni from P62m symmetry, viz. \( \sim 0.14 \) Å, corresponds to \( T_{C} \geq 390 \) K, see Table 2. LaNi₅D₆₀ as also isomorphous LaNi₅H₆₀, hence meets the criteria for ferroelectricity.

Comparable results for the isostructural \( \gamma \)-phase of CaNi₅D₆.₁ have been reported by Yoshikawa et al. (1998), who refined their neutron diffraction powder data to \( R = 0.0226 \), see Table 3. The largest departure by a metal ion in \( \gamma \)-CaNi₅D₆.₁ from P31m or P62m symmetry is \( \Delta z(Ca) \geq 0.14 \) Å, identical to \( \Delta z(Ni1) \) in LaNi₅D₆₀ if the \( D(z) \) values in the former are neglected in scaling; the criteria in §1.5 are hence met by both deuterides.

2.6. Ca(OCl)₂(Ca(OH)₂)₂ [20283]

The ‘probable’ structure for Ca(OCl)₂(Ca(OH)₂)₂ as determined by Aleksandrova et al. (1968), on the basis of 23 X-ray powder diffraction intensities, was neither refined nor were the H atoms located; no subsequent study has been reported. The model, however, shows both Ca and Cl ions apparently displaced \( \sim 0.12 \) Å, with O₁ and O₂ each displaced \( \sim 1.27 \) Å, from supergroup P62m symmetry assuming O₃ occupies Wyckoff position 3g above such a hypothetical transition. The resulting ambient displacement of O₃ is then \( \sim 1.75 \) Å as in Table 4, with all O(z) positions neglected in origin scaling. The resulting Ca and Cl ion-displacement magnitudes correspond to \( T_{C} \geq 288 \) K, and hence are suggestive of ferroelectricity; all three independent O displacements, however, are questionably large. Structural rede-

termination, calorimetry and/or dielectric measurements are thus necessary in order to clarify the properties of Ca(OCl)₂(Ca(OH)₂)₂.

2.7. CsNO₃ phase II [29392]

Ferroni et al. (1957) characterized ambient CsNO₃ as exhibiting trigonal symmetry, with \( Z = 1 \) and space group P31m, undergoing a transition at \( \sim 434 \) K to cubic symmetry. DeLacy & Kennard (1971), however, determined the ambient space group to be P3₁ with \( Z = 9 \), a result independently confirmed by others including Pohl & Gross (1993), Liu et al. (2001), and Zhou et al. (2005). Based on the 1993 determination, CsNO₃ phase II had previously been shown (Abrahams, 2003) to satisfy the structural criteria required for ferroelectricity. Although ambient CsNO₃ may also be assigned to §5, the positive property prediction suggests the present assignment as more appropriate.

2.8. (C(NH₂)₃)Al(SO₄)₂(H₂O)₆ [30566, 34261]

GASH was experimentally discovered to be ferroelectric by Holden et al. (1956). Based on 882 diffraactomically measured \( F_{obs} \) and previously published coordinates, Schein et al. (1967) reduced \( R \) to 0.035 by least-squares refinement. Very similar results, presented in the same paper, were also obtained for the isomorphic Cr compound GCrS₃H. Previous refinements by Geller & Katz (1962), and also Lingafelter et al. (1980) of the GASH structure have been reported.

GASH is the guanidinium aluminum sulfate hexahydrate compound; it is a common material due to its piezoelectric properties. Its high Curie temperature makes it useful in applications requiring ferroelectricity at room temperature.

\[ \text{Guadininium aluminum sulfate hexahydrate is commonly referred to as GASH.} \]

\[ \text{Reference to Geller & Katz (1962) is missing from ICSD release 2009/1.} \]
al. (1966), reported that their least-squares refinement produced large parameter interactions, possible origins for which gave rise to vigorous discussion in the literature. Anomalously, all atomic locations determined by Schein et al. (1967) approach $P62m$ supergroup symmetry within the criteria of §1.5, as may be seen in Table S6, except for S and O in both sulfate groups which instead approach $P31m$ supergroup symmetry.

GASH decomposes at $\sim 475$ K, i.e. below a Curie temperature that is hence undeterminable at ambient pressure. The hypothetical phase transition to higher symmetry may thus be regarded as improper, see e.g. Ishibashi & Takagi (1976) and Kobayashi et al. (1972). In addition to the anomalous symmetry relationships noted above, with its possible connection to the relative rigidity of the C(NH$_3$)$_4^+$ and SO$_4^{2-}$ ions, the structurally related, ambient, spontaneous polarization magnitude $P_s = 3.5 \times 10^{-3}$ C m$^{-2}$ is unusually low; further study of the structure and properties of both GASH and GaCrS$_3$ is clearly appropriate.

### 2.9. [N(CH$_3$)$_4$]$_2$Mo$_3$S$_{13}$ [56429, 110357]

A total of 1268 [N(CH$_3$)$_4$]$_2$Mo$_3$S$_{13}$ $I_{obs}$ > 2$\sigma$I$_{obs}$ measured diffractometrically by Bensch & Schur (1998) using graphite-monochromated Mo K$\alpha$ were fully corrected and refined to include all H atom locations for a final $R(F) = 0.036$. A polar axis origin based only on the $z$ coordinates of Mo and the five S atoms, see Table 5, shows Mo to be within 0.27 Å of Wyckoff position 3f in the supergroup $P62m$, all S atoms within 0.66–1.10 Å, and the N and C atoms within 1.44 Å of comparable positions. (N(CH$_3$)$_4$)$_2$Mo$_3$S$_{13}$ hence approaches and possibly exceeds the presently undetermined upper displacement limits for ferroelectricity, see §1.5(iii). A material with identical formula and comparable lattice constants was reported by Lu et al. (2002) in the space group $P3$ and refined to $R(F) = 0.0667$; the resulting atomic coordinates are unrelated to those above, to which reference was not made. Examination of Lu et al.’s experimental intensity data by means of PLATON (Bensch, 2009) revealed the presence of the mirror-symmetry plane expected in space group $P31m$, hence the 2002 structure appears inappropriate. The possibility of ferroelectricity in (N(CH$_3$)$_4$)$_2$Mo$_3$S$_{13}$ is sufficient to warrant dielectric investigation.

### 2.10. Li$_7$Ag$_3$Sn$_6$ [170571]

A total of 2972 reflections attributed to the Zintl phase Li$_7$Ag$_3$Sn$_6$, of which 801 are independent, were measured diffractometrically by Lupu et al. (2004) using Mo K$\alpha$; initial refinement led to the formula Li$_{13}$Ag$_3$Sn$_6$, but one Li with a large $U_{eq}$ value was rejected in the final refinement, giving $R = 0.0446$ for $I > 2\sigma(I)$ and the atomic coordinates in Table S7.\textsuperscript{12} The remaining Li7 located at 0, 0, −0.132 is the only atom that fails to fulfill the criteria for ferroelectricity, with all other atoms less than 0.2 Å from satisfying the symmetry of the supergroup $P62m$. If an Li8 atom, with coordinates as in footnote 12, were overlooked then both the supergroup symmetry and the initial chemical formula would be satisfied; the resulting 11 nearest neighbors around Li8 would be closely comparable to those about all other Li sites except Li7, which is too close at $d_{Li7-Li8} = 2.25$ Å. Alternative equal-occupancy locations for atoms Li7 and Li8 at 0, 0, ±0.174 would eliminate this problem, with all other interatomic distances remaining

\textsuperscript{12} The initial coordinates used for Li8 were not given, but are predicted to be 0, 0, −0.132.
acceptable; it is noted that the occupancy sum of both Li sites may be less than 2.

The resistivity $\rho$ of intermetallic Li$_{17/18}$Ag$_3$Sn$_6$ is presently unknown. Han et al. (2005) report the ‘polar intermetallic’ Tb$_2$Zn$_{3.6}$Al$_{7.4}$ has $\rho \approx 26 \mu \Omega$ cm at 2 K, increasing linearly to $\sim 50 \mu \Omega$ cm at ambiance. The resistivity of doped ferroelectrics is not comparable, with $\rho_{\text{BaTiO}_3} \approx 10^{10} \Omega$ cm for pure BaTiO$_3$ reportedly reduced to $\sim 4 \times 10^2 \Omega$ cm for samples doped with 0.05 atom % La$^{3+}$ (Brutchey et al., 2008); Li$_{17/18}$Ag$_3$Sn$_6$ may hence be an attractive candidate for current device applications.

2.11. Cs$_3$As$_5$O$_9$ [413151]

Emmerling & Röhr (2003) measured a total of 2668 $F_{\text{obs}}$(Cs$_3$As$_5$O$_9$) > 2$\sigma$(I$_{\text{obs}}$) diffractometrically, refining them to a final $R = 0.0316$ for the atomic coordinates in Table 6. Materials of such compositions were not previously known. A scale factor based only on the metal atom $z$ coordinates results in no cationic displacement larger than 0.12 Å from supergroup $P62m$ symmetry, with $O$ displacements of $\sim 0.8$ and 1.5 Å; a $z$-coordinate correction based on all atoms increases the cation displacements to $\sim 0.4$ Å, but reduces that of $O$ to less than $\sim 1$ Å. Either model, or an intermediate, clearly approaches the criteria for ferroelectricity. Calorimetric, second harmonic and/or dielectric study would hence be particularly appropriate in view of the possibility that, should the expected $T_C$ be observed not far above ambience, Cs$_3$As$_5$O$_9$ might have dielectric properties comparable with BaTiO$_3$.

3. Structures with reduced ferroelectric predictive properties

3.1. [Fe$_2$(Si$_{0.685}$Fe$_{0.315}$)$_2$O$_5$(OH)$_4$], cronstedtite 1T [18193, 89909, 89910, 158233, 158234, 158235, 158236]

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

3.2. Yb$_2$SO$_4$ [23583, 109335]

Ballestracci & Rossat-Mignod’s (1969) refinement of the Yb$_2$SO$_4$ neutron diffraction powder pattern measured at room temperature assumed the space group ‘$P3m$’ and led to $R \approx 0.03$ for the atomic coordinates in Table S9; cooling to 1.5 K revealed unit-cell doubling owing to antiferromagnetic array formation. The structure of Yb$_2$SO$_4$ at ambience, as also that of Tb$_2$O$_2$S, Dy$_2$O$_2$S and Ho$_2$O$_2$S, had been reported previously in the space group ‘$P3m$’ by Eick (1958) following Zachariasen’s (1949) assignment of the centrosymmetric space group to isomorphous Ce$_2$O$_2$S, La$_2$O$_2$S and Pu$_2$SO$_2$. Table S9 shows that, with $z^*$ values based on the predominant Yb neutron scattering, all three independent atoms approach either supergroup $P31m$ or $P62m$ symmetry, both of which have identical one- and twofold Wyckoff positions, within 1.4 Å; the lack of coordinate uncertainties may be noted. If Yb$_2$SO$_4$ were confirmed to be acentric at ambience, it would then be a candidate for exhibiting ferroelectricity, but space-group assignment uncertainty, together with the low structural precision ($\sim 0.07$ Å), indicates the need for further study before property prediction is appropriate.

3.3. K$_3$V$_2$O$_4$ [24068, 75219]

Bystro¨m & Evans (1959) refined 63 visually estimated $I(hk0)$, 51 $I(hk1)$ and 93 $I(hh0)$ to obtain an overall $R \approx 0.14$ for the atomic coordinates in Table S10(a); $Z$ was not listed. Analysis shows no cation to be further than $\sim 0.17$ Å, nor any O ion than $\sim 0.84$ Å, from satisfying $P62m$ symmetry, i.e. this structure appears to offer a strong case for exhibiting ferroelectricity, with an estimated $T_C$ not far above ambience. However, Evans & Brusewitz (1994) subsequently measured...
3.4. \( \text{Na}_2\text{ZnCl}_4(\text{H}_2\text{O})_3 \) [24269]

Brehler (1960) measured 35 \( I_{\text{obs}} \) by \( \text{Cu} \ K\alpha_1 \) powder diffractometry in order to determine the five coordinate-variables in \( \text{Na}_2\text{ZnCl}_4(\text{H}_2\text{O})_3 \), reporting \( R = 0.16 \). No atom in the resulting structure approaches the symmetry of any relevant supergroup closely, as may be seen in Table S11. Remeasurement and redetermination with higher structural accuracy would be appropriate.

3.5. \( \text{H}_4\text{Al}_{12}\text{FeO}_4\text{Mg}_2\text{O}_3\text{Si}_1\text{Al}_4 \), lizardite 9T [24427]

A total of 149 1T \( F(hk\ell) \), measured diffractometrically by Jahanbagloo & Zoltai (1968) using \( \text{Cu} \ K\alpha_1 \), refined to \( R = 0.102 \) for the 3m diffraction symmetry observed in a unit cell with \( a = 5.295 \) (4), \( c = 63.99 \) (6) \( \text{Å} \) and \( I(001) \) with \( l = 3n \) (cf. lizardite 1T with \( a \approx 5.332 \), \( c \approx 7.233 \) \( \text{Å} \) in §2.4). The resulting 1T subcell coordinates, see Table S12, approach supergroup \( \text{P}6\text{2}m \) symmetry with \( \Delta \xi > 0.24 \) \( \text{Å} \), suggestive of ferroelectricity in this Al-serpentinite if the nine-layer unit-cell structure retains the one-layer symmetry. The authors, however, suggested the symmetry of the full 18-layer structure is more closely approximated by \( \text{P}3\text{I}c \). A definitive study of this mineral is hence still awaited.

3.6. \( \text{AuCd} \) [58408]

Alasafi & Schubert’s (1977) refinement of their 287 diffractometrically measured \( F(hk\ell) \) using Mo Ka led to \( R = 0.08 \) for the coordinates in Table S13. Although all atoms as reported are within \( \sim 0.5 \) \( \text{Å} \) of \( \text{P}3\text{I}m \) symmetry, Au and Cd displacements of such magnitude are unlikely; the 301 K martensitic transformation reported by Noda et al. (1988) increases such improbability further. The \( \sim 8 \mu\text{Ω} \) cm electrical resistivity observed at 300 K, with a maximum at \( \sim 595 \) K (Mukherjee et al., 1984), eliminates AuCd from consideration as a practical ferroelectric candidate. AuCd alloy martensitic transformations have been studied extensively with alloys having atomic ratios \( \sim 1.1 \) reported to undergo such transitions as \( \beta_1 \) (\( \text{P}3\text{m} \)) to \( \beta'_1 \) (\( \text{Pmn}a \)) phase at \( \sim 353 \) K and, with slightly smaller Cd content, to the \( \beta''_1 \) (\( \text{P}3\text{Im} \)) phase at \( \sim 575 \) K, see Wallace et al. (1968). Structural redetermination would be appropriate.

3.7. \( \text{Mg}_{12}(\text{PO}_3\text{OH})(\text{PO}_4)_6(\text{OH},\text{O})_6 \), holtedahlite [64769, 67048] and \( \text{(Fe,Mg)}_{12}(\text{PO}_3\text{OH})(\text{PO}_4)_6(\text{OH},\text{O})_6 \), satterlyite [94842]

The structures of both synthetic and natural holtedahlite were determined by Rømming & Raade (1989) on the basis of 718 diffractometrically measured \( I_{\text{obs}} > 3\sigma(I_{\text{obs}}) \) for the former, 1202 for the latter, with \( R = 0.033 \) and 0.031. Partial substitution of the P1 site in natural holtedahlite by the C atom of a \( \text{CO}_3^- \) group led to the present selection of results only for synthetic holtedahlite. Coordinate analysis, see Table S14, shows many atomic positions in synthetic holtedahlite far from meeting the structural requirements for ferroelectricity, with displacement magnitudes of \( \sim 0.4 \) \( \text{Å} \) for Mg and \( \sim 0.7 \) \( \text{Å} \) for P; the displacements in natural holtedahlite are closely comparable. The mineral holtedahlite is hence not a ferroelectric candidate.

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

3.8. \( [(\text{CH}_3)_2\text{N}]_2\text{Mo}_3\text{Se}_{13} \) [66870]

Liao et al. (1995) refined 438 diffractometrically measured \( I_{\text{obs}} > 3\sigma(I_{\text{obs}}) \) by the use of graphite-monochromated Mo Ka. The resulting atomic coordinates, see Table S16, have \( R = 0.060 \) in a space group noted both as No. 157 and as ‘\( \text{P}3\text{I}m \)’. Coordinate analysis shows that all five independent Se ions require displacements ranging from 0.6 to 1.2 \( \text{Å} \) in order to satisfy the symmetry of supergroup \( \text{P}6\text{2}m \), although \( \Delta\xi(\text{Mo}) \) is only 0.05 \( \text{Å} \). Such required displacement magnitudes by Se effectively eliminate the possibility that \( [(\text{CH}_3)_2\text{N}]_2\text{Mo}_3\text{Se}_{13} \) might be ferroelectric.

3.9. \( \text{TiO}_{0.3}\text{D}_{0.1} \) [71816]

Kajitani et al. (1991) measured 612 \( F_{\text{obs}} \) with Mo Ka radiation, discarding all \( F_{\text{obs}} \) with \( 20 < 66^\circ \) because of ‘possible overlap of reflections’; in addition to 120 \( F_{\text{obs}} > 0 \) determined by the use of neutron radiation with \( \lambda = 1.019 \) \( \text{Å} \). Refinement gave \( R = 0.102 \) and 0.150, with atomic coordinates for the former listed in Table S17.4 Displacement magnitudes of \( \sim 0.31 \) \( \text{Å} \) by both independent Ti ions, required for a ferroelectric phase transition with a transition temperature of \( \sim 1800 \) K, are unlikely in a unit cell with volume as small as \( \sim 111 \) \( \text{Å}^3 \); \( \text{TiO}_{0.3}\text{D}_{0.1} \) is hence not predicted to be ferroelectric.

---

4 The satterlyite \( x, y, z \) coordinates are reported in place of Table S15 by \( 1-x, y, 1-z \) to simplify comparison with those of holtedahlite in Table S14.

4 The refined neutron study coordinates were not presented. The O4 atom in the X-ray study is listed as sharing Wyckoff position 1(a) with D2.
3.10. Cs$_2$Au$_5$S$_5$ [82557]

A total of 453 fully corrected $F_{\text{obs}} > 3\sigma(F_{\text{obs}})$, measured diffractometrically with graphite-monochromated Mo $K\alpha$ by Klepp & Weithaler (1996), led on refinement to $R = 0.048$ for the coordinates in Table S18. The possibility of an Au cation undergoing an $\sim 0.8$ Å displacement in a phase transition approaches zero, hence Cs$_2$Au$_5$S$_5$ is not expected to be ferroelectric.

3.11. Ba$_{10}$Cl$_3$F$_{31.3}$Fe$_3$Mn$_3$ [82861]

Darriet et al.’s (1996) refinement of 1384 independent $F_{\text{obs}}$ with $I_{\text{obs}} > 3\sigma(I_{\text{obs}})$, resulted in $R = 0.0275$ for the coordinates in Table S19. The strongly disordered structure was solved and refined assuming a Ba$_{10}$(MnFeF$_{10}$Cl)$_3$FCl:Ba$_{10}$(MnFeF$_{11}$)Cl$_2$ ratio of 17:3. As a consequence, eight pairs of atoms exhibit averaged separations as small as $\sim 0.55$ Å between Ba4 and Ba5, $\sim 0.72$ Å between Mn1 and Mn2, $\sim 0.67$ Å between two F7 atoms, and $\sim 1.09$ Å between F9 and Cl3, with other pairs of atoms also apparently very close. Uncertainties associated with the nature of this disorder, including its possible heat treatment dependence, effectively eliminates confidence in any present structurally based prediction of Ba$_{10}$Cl$_3$F$_{31.3}$Fe$_3$Mn$_3$ properties.

3.12. NiTi [156442]

The structure of NiTi, a shape memory alloy, has been widely investigated. Gong et al.’s (2006) ab initio study of the premartensitic rhombohedral NiTi phase proposed $P31m$ as the lowest energy space group at 0 K. Krishnan et al. (2008), Strutt et al. (2008), Goryczka & Morawiec (2004) and Sitepu (2003) among others have proposed space groups $P3$ or $P3_1$, $P3\bar{2}$, and $P3$, respectively, with many closely comparable atomic coordinates among models. Lekston et al. (1999) theoretically derived and experimentally confirmed the space group of isostructural Ni$_{48}$(V$_{12}$)$_{50}$(Co$_{1.3}$)$_2$ at ambient to be $P31m$, but did not determine the atomic coordinates. Examination of Gong et al.’s (2006) coordinates shows two Ni atoms $\sim 0.44$ Å and two Ti atoms $\sim 0.25$ Å from $P31m$ symmetry, see Table S20; both required displacements are large enough that the likelihood of a ferroelectric phase transition in NiTi approaches zero. The resistivity of NiTi has been reported by Kovalev et al. (1975) as 0.715 $\mu$Ω m.

3.13. V[C(NH$_2$)$_2$I]$_2$(SO$_4$)$_2$(H$_2$O)$_6$ [170206]

Refinement of 2444 vanadium guanidinium hexaaquidisulfate $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, measured diffractometrically by Tragenna-Piggott et al. (2004) using Mo $K\alpha$, resulted in $R = 0.0215$. Coordinate analysis shows no atom to be further than $\sim 0.4$ Å, with most within $\sim 0.2$ Å, of corresponding locations that satisfy supergroup $P31m$ symmetry, see Table S21. Although the atomic displacement criteria for ferroelectricity are almost satisfied, the large $\Delta z(V1) \simeq 0.36$ Å displacement, together with the major reorientations required by the guanidinium, hydroxyl and sulfate ions, preclude any prediction of ferroelectricity with moderate confidence: dielectric study at ambient, however, would be appropriate for this possibly improper ferroelectric, cf. §2.8.

4. Structures likely to remain polar at higher temperatures

4.1. Mn$_{13}$SbSi$_{12}$O$_{34}$, långbanite [69610]

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

4.2. Ba$_{21}$Al$_{40}$ [170238]

Ba$_{21}$Al$_{40}$, one of eight binary and ternary intermetallics studied by Ameriou et al. (2004), was refined with 1184 $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ measured diffractometrically with Mo $K\alpha$ to yield $R = 0.024$. The resulting atomic positions do not approach the symmetry of any relevant supergroup closely; six of the nine independent Ba atoms present have 2.0 $\geq \Delta \xi \geq 2.5$ Å with six of the 13 independent Al atoms having 1.6 $\geq \Delta \xi \geq 3.3$ Å with respect to $P31m$ symmetry, see Table S23. Inversion centers are hence unlikely to develop in Ba$_{21}$Al$_{40}$ at elevated temperatures.

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

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

4.4. Pb(ReO$_4$)$_2$ [201430]

The 3402 Pb(ReO$_4$)$_2$ reflections measured diffractometrically by Picard et al. (1984) using Mo $K\alpha$ yielded a total of 567 independent $I_{\text{obs}} > 0$. Structure solution and refinement gave the atomic coordinates in Table S25, with $R = 0.066$. The largest departure from supergroup $P6_2m$ symmetry by Re or Pb is 0.34 Å for the former, 0.42 Å for the latter; none of the six O atoms depart more than $\sim 1.2$ Å. The displacement sense for all four metal atoms is opposite that of all six O atoms, hence is unlikely; an independent structural determination, preferably by neutron diffraction, is advisable before any property prediction for Pb(ReO$_4$)$_2$ is made.

Indebtedness to an anonymous referee for this suggestion is gratefully acknowledged.
5. Structures misassigned to space group $P31m$

5.1. 2PbCO$_3$Pb(OH)$_2$, hydrocerussite [16630]

The unit cell of basic lead carbonate, reported by Cowley (1956) in an electron diffraction study as exhibiting $P31m$ symmetry, was subsequently shown by Martinetto et al. (2002) to be related to another cell larger by the factor $\sim 3^{1/2}$, with rhombohedral symmetry and space group $R3m$. The centro-symmetric structure of hydrocerussite thus eliminates its further consideration within the present context.

5.2. Ag$_3$Pb$_2$O$_6$ [24038, 172975]

An approximate structure for Ag$_3$Pb$_2$O$_6$ with $R \approx 0.48$ was presented by Byström & Evers (1950) on the basis of 52 visually estimated $F_{\text{obs}} > F_{\text{max}}$, see Table S26(a). Coordinate analysis shows that none of the six independent atoms departs more than $\sim 0.09 \text{ Å}$ from $P31m$ symmetry, hence is indicative of a misassigned space group. Independent confirmation of centrosymmetry has been provided by several authors, with Yoshii et al. (2007) most recently reporting a neutron diffraction determination in space group $P31m$ with final $R = 0.0248$, see Table S26(b), i.e. Ag$_3$Pb$_2$O$_6$ is indeed nonpolar.

5.3. Cd$_{0.61}$Pt$_{0.59}$Zn$_{4.27}$ [654683]

Khan & Schubert (1970) reported the structure of three CdPtZn compositions of different symmetry, one of which assumed the space group to be $P31m$ on the basis of 28 $I_{\text{obs}}$ derived from a Cu $K\alpha$ Guinier X-ray diffraction powder pattern. The analysis in Table S27 shows that the structural coordinates exhibit supergroup $P62m$ symmetry, hence the space-group designation currently listed by ICSD requires correction.

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

References
