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Prediction of Ferroelectricity in Recent Inorganic Crystal Structure Database Entries under Space Group *Pba*2

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Dedicated to Professor Dr Wolfram Prandl on the occasion of his 60th birthday

Abstract

Three new entries in space group *Pba*2 in the 1995 edition of the Inorganic Crystal Structure Database have been examined in the light of previously developed criteria for the prediction of ferroelectricity. The structural prediction [Abrahams (1989). *Acta Cryst.* B**45**, 228–232] that seven of the 21 entries presented under this space group in the 1988 edition most likely corresponded to previously unrecognized ferroelectric materials is thereby updated. The atomic coordinates of $[(NH_2)_2C(NHNH_3)]ZrF_6$, among the new entries, are shown to satisfy the structural criteria; the maximum displacement along the polar axis required of any atom to undergo spontaneous polarization reversal is no larger than ~ 0.9 Å for a C or N atom and ~ 1.4 Å for a H atom, within the aminoguanidinium(2+) cation. By contrast, all atoms in the two independent ZrF_6 anions are within 0.1 Å of an arrangement with zero spontaneous polarization. The characteristic force constant of the organic group is presently unknown, hence the Curie temperature for the crystal cannot be estimated. In the second new entry, the only atoms in the structure of the superconductor $Ba_{0.6}K_{0.4}BiO_{23}$ at 403 K which depart significantly from a centrosymmetric arrangement are three of the four independent oxygens, one of which is at a site only 6% occupied. If these displacements are not artefacts, then this material is ferroelectric with an estimated Curie temperature in the range 410–740 K; a subsequent study, however, reported the structure in space group *Pbam*. The atomic coordinates of the final 1995 entry, $(Cl_3PNPCl_3)(MoOCl_4)$, do not differ significantly from centrosymmetry, in which case the material is not ferroelectic, apart from unequal occupancy of the Mo-atom sites. If the disorder model is correct and the two Mo sites are unequally occupied, then these sites cannot become equivalent and $(Cl_3PNPCl_3)(MoOCl_4)$ must remain polar without the possibility of becoming ferroelectric.

1. Introduction

The atomic coordinates for the 21 structural entries in space group *Pba*2 contained in the 1988 edition of the Inorganic Crystal Structure Data (ICSD) numerical database (see Bergerhoff & Brown, 1987) were used as a testbed for demonstrating the effectiveness of three structural criteria in predicting ferroelectricity (Abrahams, 1989). In 1988 the ICSD contained three entries in space group *Pba*2 without atomic coordinates, four that corresponded to the known ferroelectric materials $Gd_2(MoO_4)_3$and $Tb_2(MoO_4)_3$, and one for the known antiferroelectric $PbZrO_3$. Four additional entries did not satisfy the structural criteria and three referred to separate refinements of $Mo_{17}O_{47}$. The atomic coordinates for the latter entry together with those of six other materials satisfied the criteria and hence all seven were predicted to be ferroelectric. Single crystals of $Na_{13}Nb_{35}O_{94}$ and $K_3Fe_5F_{15}$ were prepared as representative of these newly predicted ferroelectrics and were subjected to dielectric and calorimetric measurement. The presence of ferroelectricity in the two materials was confirmed by the observation of anomalies in both the permittivity and the heat capacity at temperatures that closely coincided in each. In addition, the magnitude of their predicted Curie (ferroelectric to paraelectric phase transition) temperatures T_c (Abrahams, Brandle, Berkstresser, O'Bryan, Bair, Gallagher & Drotning, 1989; Ravez, Abrahams & de Pape, 1989) agreed well with experiment.

The 1995 release of the ICSD contains three additional entries for space group *Pba*2. These entries are examined below.

2. Ferroelectric aminoguanidinium(2+) hexafluorozirconate

The atomic coordinates of $[(NH_2)_2C(NHNH_3)]ZrF_6$ presented by Bukvetskii, Gerasimenko & Davidovich (1990) are contained in Table 1. They report that reaction of equimolar quantities of CN_4H_7Cl and $(H_3O)_2ZrF_6$ in aqueous solution, followed by dissolution of the reactant in H_2O and slow evaporation at room temperature, leads to the growth of small single

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crystals. They measured and corrected for absorption a total of 1215 independent reflections with $I > 3\sigma(I)$ within the range $(\sin\theta)/\lambda \leq 1.0$ Å^{-1} using monochromatized Mo $K\alpha$ radiation. Least-squares refinement, assuming anisotropic atomic displacements for the heavier atoms and isotropic displacements for the H atoms, resulted in $R = 0.035$. The z coordinates of Bukvetskii *et al.* (1990) in Table 1 have been replaced by $z^* = z + 0.00043$, thereby locating the two independent Zr atoms equidistant from and on either side of the plane at $z = 0$, which is postulated to become a mirror symmetry plane at higher temperatures. Two additional columns giving the hypothetical paraelectric z' coordinates together with the atomic displacements $\Delta z = z^* - z'$ in Å are also included in Table 1.

If a mirror plane develops at $z = 0$, then another is expected to develop at $z = \frac{1}{2}$ as the space group transforms from *Pba*2 to *Pbam*. Examination of Table 1 shows that F1 and F2 are close to $z = \frac{1}{2}$ and F3 and F4 to $z = 0$. The remaining pairs of F atoms, F5 and F10, F6 and F9, F7 and F11, F8 and F12, are close to being equidistant from, but on opposite sides of, the plane at $z = 0$. It may be noted that $x_1 \simeq x_2$ and $y_1 \simeq y_2$ for each pair of atoms at $x_1y_1z_1$ and $x_2y_2z_2$ with $z_1 \simeq -z_2$, as required by the developing mirror plane. All remaining atoms are close either to the plane at $z = 0$ or to that at $z = \frac{1}{2}$. The final Δz column in Table 1 gives the distance that each atom must be displaced at room temperature in order for these planes to become symmetry mirrors.

It is notable that all displacements along the polar axis by the independent Zr and F atoms required to satisfy a phase transition from *Pba*2 to *Pbam* are less than 0.07 Å. By contrast, many of the independent N, C and H atoms are located at distances that are further, at a high significance level, from the developing mirror planes than their expected r.m.s. thermal and/or static displacements of ~0.2 Å; the least-squares refined values of U^{ij} (or equivalent parameter) are not given by Bukvetskii *et al.* (1990). The largest polar displacement by a N atom is 0.43 Å (for N1), that by a C atom is 0.18 Å (for C2) and that by a H atom is 0.7 Å (for H2 and H5) with a displacement by five other H atoms greater than 0.5 Å. Each atomic displacement undergone in polarization reversal is necessarily double that given in Table 1 from the zero spontaneous polarization location.

The Curie temperature T_c of many inorganic ferroelectrics with known crystal structure may be predicted with confidence on the basis of Abrahams, Kurtz & Jamieson's (1968) relationship $T_c = (\mathcal{K}/2k)(\Delta z)^2$ K, where $\mathcal{K}$ is a force constant, k is Boltzmann's constant and Δz is the largest displacement along the polar axis required to achieve zero spontaneous polarization by the atom forming the shortest and least ionic bonds in the crystal. For structures in which the latter occupies an octahedron of O and/or F atoms, $\mathcal{K}/2k = 2.00(9) \times 10^4$ K Å^{-2}.

Table 1. *Atomic coordinates for $[C(NH_2)_2(N_2H_4)]ZrF_6$ at ~ 300 K, hypothetical paraelectric z' coordinates and polar displacements*

$a = 10.089(2)$, $b = 18.349(3)$, $c = 7.560(1)$ Å

	x	y	z†	z'	Δz (Å)
Zr1*	0.2724 (1)	0.3697 (1)	−0.2496	−0.2496	0.000
Zr2*	0.2709 (1)	0.3686 (1)	0.2496 (2)	0.2496	0.000
F1	0.2186 (6)	0.3102 (3)	0.5060 (23)	1/2	0.045
F2	0.3185 (6)	0.4259 (3)	0.4906 (18)	1/2	−0.071
F3	0.3791 (5)	0.3404 (3)	0.0005 (21)	0	0.004
F4	0.1695 (5)	0.3996 (3)	0.0047 (24)	0	0.035
F5	0.1815 (7)	0.2749 (3)	0.1827 (4)	0.1882	−0.042
F10	0.1932 (9)	0.2743 (5)	−0.1937 (14)	−0.1882	−0.042
F6	0.3565 (9)	0.4673 (5)	0.1871 (11)	0.1860	0.008
F9	0.3627 (8)	0.4625 (4)	−0.1848 (11)	−0.1860	0.009
F7	0.4459 (9)	0.3263 (7)	0.3123 (13)	0.3128	−0.004
F11	0.4455 (5)	0.3184 (3)	−0.3132 (9)	−0.3128	−0.004
F8	0.0892 (7)	0.4069 (4)	0.3119 (11)	0.3129	−0.008
F12	0.0964 (6)	0.4157 (4)	−0.3138 (9)	−0.3129	−0.007
N1	0.1230 (11)	0.5616 (6)	0.9432 (16)	0	−0.429
N2	0.4163 (10)	0.1815 (5)	0.0166 (26)	0	0.125
N3	0.2069 (9)	0.1357 (6)	0.0447 (16)	0	0.338
N4	0.3893 (10)	0.5860 (6)	0.0154 (24)	0	0.116
N5	0.6425 (12)	0.4122 (6)	0.5403 (21)	1/2	0.305
N6	0.1454 (10)	0.5538 (6)	0.5397 (20)	1/2	0.300
N7	0.1904 (10)	0.6730 (5)	0.5281 (24)	1/2	0.212
N8	0.567 (9)	0.6943 (5)	0.4897 (30)	1/2	−0.078
C1	0.3345 (9)	0.1267 (9)	0.0109 (27)	0	0.082
C2	0.2282 (11)	0.6062 (7)	0.5232 (13)	1/2	0.175
H1	0.351 (4)	0.039 (4)	0.013 (4)	0	0.098
H2	0.462 (4)	0.053 (4)	−0.093 (4)	0	−0.703
H3	0.496 (4)	0.175 (4)	0.006 (4)	0	0.045
H4	0.401 (4)	0.220 (4)	0.003 (4)	0	0.023
H5	0.166 (4)	0.181 (4)	0.094 (4)	0	0.711
H6	0.124 (4)	0.046 (4)	0.072 (4)	0	0.544
H7	0.046 (4)	0.050 (4)	−0.074 (4)	0	−0.559
H8	0.049 (4)	0.122 (4)	−0.005 (4)	0	−0.038
H9	0.089 (4)	0.130 (4)	0.584 (4)	1/2	0.635
H10	0.118 (4)	0.049 (4)	0.504 (4)	1/2	0.030
H11	0.444 (4)	0.071 (4)	0.583 (4)	1/2	0.627
H12	0.342 (4)	0.004 (4)	0.585 (4)	1/2	0.643
H13	0.203 (4)	0.206 (4)	0.510 (4)	1/2	0.076
H14	0.446 (4)	0.242 (4)	0.501 (4)	1/2	0.008
H15	0.481 (4)	0.154 (4)	0.512 (4)	1/2	0.091
H16	0.554 (4)	0.211 (4)	0.489 (4)	1/2	−0.083

* The coordinates of both Zr atoms have been rounded from five to four significant figures. † All z coordinates have been shifted by 0.00043, relative to the values of Bukvetskii *et al.* (1990), placing the two independent Zr atoms at an equal distance from the mirror plane that forms at T_c.

Assuming the atomic coordinates in Table 1 to be reliable, the Δz displacements for the organic cation may be seen to satisfy fully the structural criteria for ferroelectricity (Abrahams, 1989). The N,N—C—N framework of the two symmetry-independent aminoguanidinium(2+) cations is close to planar, but the remaining nonplanar $N4H_3$ and $N8H_3$ groups and all the H atoms are free in principle to rotate about their respective N—N or N—C bonds. It may be noted that the cation in the related disassociation product aminoguanidinium(1+) pentafluorozirconate is completely planar except for two H atoms (Pugmire, Ross, Nielson & Abrahams, 1995).

Unlike inorganic ferroelectrics in which the critical atoms are displaced within the interior of coordinating polyhedra, neither of the two independent aminoguanidinium(2+) cations is capable of simple displacement. Both cations form redistributable multiple hydrogen bonds to F atoms in the edge-sharing columns of ZrF_8 dodecahedra parallel to the polar axis. It is apparent from Table 1 that full compliance by the relatively bulky cations with the expected *Pbam* symmetry at T_c is readily achievable. A structural prediction of T_c is not feasible at present, since $\mathcal{K}$ from the aminoguanidinium(2+) cation is unknown, but experimental investigation (Pugmire, Christen, Mirsky, Nielson & Abrahams, 1995) reveals both calorimetric and dielectric phase transitions at ~ 420 K followed by loss of HF.

3. Ferroelectric/centrosymmetric $Ba_{0.6}K_{0.4}BiO_{2.3}$

The atomic coordinates determined by Rietveld analysis of the time-of-flight neutron diffraction powder pattern measured at the fixed scattering angle $2\theta = 90°$ from a sample of $Ba_{0.6}K_{0.4}BiO_{2.3}$ at $T = 403$ K (Hinks, Jorgensen, Richards, Pei, Zheng, Dabrowski & Mitchell, 1991) are contained in Table 2. The structure is derived from that of perovskite and has been found to be stable below ~ 830 K. The space group is reported as *Pba*2 and was hence included in the ICSD under this space group, but neither supporting evidence for this assignment nor the standard agreement indicators between measurement and model were presented by Hinks *et al.* (1991). The given z coordinates are replaced in Table 2 by $z^* = z + 0.056$, thereby placing the origin at the jointly occupied Ba, K site. The O2 and O3 sites are reported to be fully occupied (O3 is given at 104%), the O1 site as 68% and the O4 site as only 6% occupied. Mirror plane formation at $z' = 0$ and $\frac{1}{2}$ is expected if the given structure transforms to space group *Pbam* at a temperature above 403 K, see column 6 of Table 2. The final column gives $\Delta z = z^* - z'$ in Å.

Table 2. *Atomic coordinates of* $Ba_{0.6}K_{0.4}BiO_{2.3}$ *at 403 K,* z' *coordinates in centrosymmetric space group, and* Δz *polar displacements*

$a = 6.127$, $b = 12.016$, $c = 4.378$ Å

	Wyckoff position	x	y	z^*	z'	Δz (Å)
Ba, K	4(c)	0.806 (1)	0.138 (1)	−0.011 (8)	0	−0.050
Bi	4(c)	0.283 (1)	0.114 (1)	0.511 (7)	1/2	0.050
O1	4(c)	0.299 (2)	0.116 (1)	0.004 (9)	0	0.018
O2	4(c)	0.710 (1)	0.246 (1)	0.553 (9)	1/2	0.234
O3	2(a)	0	0	0.544	1/2	0.193
O4	2(b)	0	1/2	0.544	1/2	0.193

* All z coordinates have been shifted by 0.044, relative to the value of Hinks *et al.* (1991), to equalize the Δz displacements of the Ba, K and the Bi atoms.

The z^* coordinates for atoms Ba, K, Bi and O1 do not differ significantly from their corresponding z' values, *i.e.* these atoms are close to a centrosymmetric arrangement. The z coordinates of atoms O3 and O4 were not varied in the Rietveld profile fit, hence are given by Hinks *et al.* (1991) without experimental uncertainty. Assuming their uncertainty is comparable to that of O1 and O2, these two atoms and O2 are significantly displaced from the mirror at $z' = \frac{1}{2}$. If this assumption is correct, then O2, O3 and O4 fulfill the criteria for ferroelectricity. Neglecting the Δz displacement of O1, which is within a standard uncertainty (s.u.) of its mirror plane, the displacement Δz(Bi) with respect to O2, O3 and O4 needed to achieve zero spontaneous polarization is $0.214 - 0.050 = 0.164$ Å, based on the average O-atom displacement. The predicted T_c for this value of Δz(Bi), using the relationship of Abrahams *et al.* (1968), is 540 K. The thermal uncertainty, based on the atomic coordinate s.u.'s for O1 and O2, may be estimated at ~ 200 K. Since the uncertainty range in the predicted T_c magnitude includes the measurement temperature T and since, if $Ba_{0.6}K_{0.4}BiO_{2.3}$ is indeed ferroelectric it must have $T_c > T$, then T_c is likely to range from above 403 K to ~ 740 K.

A private communication (Jorgensen, 1994) pointed out a subsequent paper on $Ba_{0.6}K_{0.4}BiO_{2.3}$ (Pei, Jorgensen, Hinks, Zheng, Richards, Dabrowski & Mitchell, 1991) in which the structure had been refined in space group *Pbam* to give $R_{wp} = 0.121$, $R_{exp} = 0.071$; these authors noted that further refinement in *Pba*2 did not improve the fit significantly, although agreement indicator values were not given for the polar space group. This structure illustrates the advisability of databases providing cross-references in each entry to any other structural paper on the same material measured under comparable conditions, but entered under a different space group. The centrosymmetric choice of space group is generally more likely to be correct for a comparable fit to the data, but only a definitive experiment in such cases can lead to an unambiguous assignment.

4. Nonferroelectric polar/centrosymmetric $(Cl_3PNPCl_3)(MoOCl_4)$

Determination of the disordered crystal structure of bis(trichlorophosphane)iminium oxotetrachloromolybdate(V) by Müller, Conradi, Patt-Siebel, Kersting, Schmidt, Khabou & Dehnicke (1988), on the assumption that the space group is *Pba*2, led to the atomic coordinates presented in Table 3. Müller *et al.* (1988) report the observation of planes of diffuse scattering normal to c^* in addition to the 675 sharp independent reflections used in refinement; the latter gave an averaged structure with split atom positions from which the coordinates in Table 3 were derived, with a final value of $R = 0.067$. The Mo1 site was reported as 74% and Mo2 as 26% occupied; the two Cl-atom sites

Table 3. *Atomic coordinates of $(Cl_3PNPCl_3)(MoOCl_4)$ at 297K, the hypothetical centrosymmetric z' coordinates, and the $\Delta z = z^* - z'$ displacements (Å)*

$a = 15.984(2)$, $b = 11.412(2)$, $c = 4.151(1)$ Å

	x	y	z^*	z'	Δz
Mo1	0	0	0.101	0.101_5	−0.002
Mo2	0	0	−0.102 (3)	-0.101_5	−0.002
O	0	0	0.502 (7)	1/2	0.008
Cl1	0.1289 (2)	0.0902 (3)	0.002 (2)	0	0.008
Cl2	−0.0646 (2)	0.1821 (2)	0.002 (2)	0	0.008
P1	0.1572 (3)	0.4300 (4)	0.353 (3)	0.354	−0.004
P2	0.1572 (3)	0.4300 (4)	−0.356 (5)	−0.354	−0.008
N	0.1580 (40)	0.4270 (60)	0.012 (10)	0	0.050
Cl3	0.1547 (3)	0.5882 (4)	0.558 (6)	0.565	−0.029
Cl6	0.1547 (3)	0.5882 (4)	−0.572 (5)	−0.565	−0.029
Cl4	0.2622 (3)	0.3667 (4)	0.566 (4)	0.576	−0.040
Cl7	0.2622 (3)	0.3667 (4)	−0.587 (6)	−0.576	−0.046
Cl5	0.0687 (3)	0.3440 (4)	0.557 (5)	0.555	0.008
Cl8	0.0687 (3)	0.3440 (4)	−0.554 (6)	−0.555	0.004

* All z coordinates have been shifted by 0.002, relative to the values of Müller *et al.* (1988).

as fully occupied and all other atom sites as 50% occupied. The origin shift used for z^* in Table 3 relates the two Mo atoms by a mirror with respect to the plane at $z' = 0$.

Examination of Table 3 shows that the mirror relationship holds for all other atoms, with a maximum violation of mirror symmetry no greater than 0.05 Å. Atoms Cl4 and Cl5 have been rearranged in Table 3 to give sequential pairs of mirror-plane related atoms Mo1 and Mo2, P1 and P2, Cl3 and Cl6, Cl4 and Cl7, and Cl5 and Cl8. Atoms Cl1, Cl2 and N are located close to one of the mirror planes, O to the other. Apart from the unequal occupancies of the Mo-atom sites, the structure as presented does not differ significantly from that in space group *Pbam*, in which case the material is not ferroelectric. If the interpretation of disorder is correct, and the two Mo sites are unequally occupied, then these sites cannot become equivalent and $(Cl_3PNPCl_3)(MoOCl_4)$ must remain polar, but without the possibility of becoming ferroelectric. The structure should be investigated further, making full allowance for anomalous dispersion.

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