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addenda and errata

Systematic prediction of new ferroelectrics in space groups $P3_1$ and $P3_2$. Erratum

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The alignment in Tables 1–4 of the paper by Abrahams (2003) was incorrect. The corrected tables are reproduced herein.

Table 1
Atomic positions for Cu_2BaGeS_4 at room temperature (Teske, 1979), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u^{33} displacements in Å.

$a = 6.215$ and $c = 15.534$ Å. Uncertainties not reported. $z^* = z - 0.0907$, $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u^{33}
Cu1	3(*a*)	0.2587 (6)	0.2487 (6)	0.2487 (2)	0.2960	0.3099	0.2565	−0.232	−0.380	−0.121	0.09
	6(*c*)†										
Cu2	3(*a*)	−1/3	0.0750 (3)	0.0690 (2)	−0.2960	0.0139	0.0768	−0.232	0.380	−0.121	0.15
Ge	3(*a*), 3(*a*)	1/3	0.3807 (3)	−0.0083 (2)	0.3570	0.3570	0	−0.147	0.147	−0.129	0.14
Ba	3(*a*), 3(*b*)	−0.1029 (2)	2/3	0.1593	0	~0.6667	0.1667	−0.639	~0	−0.115	0.08
S1	3(*a*)	0.3703 (9)	0.1870 (9)	0.1076 (3)	0.2586	0.2971	0.0863	0.694	−0.684	0.331	0.07
	6(*c*)										
S2	3(*a*)	−0.1468 (9)	0.1486 (9)	0.2683 (3)	−0.2586	0.0385	0.2470	0.695	0.684	0.331	0.10
S3	3(*a*)	0.0035 (9)	0.4292 (9)	−0.0023 (3)	−0.1183	0.5466	0.0034	0.758	−0.730	−0.089	0.10
	6(*c*)										
S4	3(*a*)	0.6639 (9)	0.7598 (9)	−0.0091 (3)	0.5466	0.8817	−0.0034	0.729	−0.758	−0.089	0.10

† See footnote **1** for equivalent positions.

Table 2
Atomic positions for $K_2HCr_2AsO_{10}$ at room temperature (Averbuch-Pouchot *et al.* 1978), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u_{eq} displacements in Å.

$a = 7.712$ (3) and $c = 14.644$ (8) Å. $z^* = z - 0.0046$, $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u_{eq}
Cr1	3(*a*)	0.4278 (3)	0.4243 (3)	0.2403	0.4242	0.4217	0.2460	0.028	0.020	−0.083	0.14
	6(*c*)†										
Cr2	3(*a*)	0.4191 (3)	0.4205 (4)	0.7484 (2)	0.4217	0.4242	0.7540	−0.020	−0.028	−0.082	0.14
As	3(*a*), 3(*a*)	0.1281 (2)	0.0199 (2)	0.3447 (2)	0.1281	0	0.3333	0	0.153	0.167	0.14
K1	3(*a*), 3(*b*)	0.5520 (5)	−0.0182 (5)	0.8343 (3)	0.5520	0	0.8333	0	−0.140	0.015	0.17
K2	3(*a*), 3(*a*)	0.6083 (5)	0.0061 (5)	0.3277 (3)	0.6083	0	0.3333	0	0.047	−0.082	0.17
O1	3(*a*)	0.356 (2)	0.186 (2)	0.2975 (8)	0.3465	0.188	0.3077	0.073	−0.015	−0.149	0.17
	6(*c*)										
O5	3(*a*)	0.190 (2)	0.337 (2)	0.6821 (8)	0.188	0.3465	0.6923	0.015	−0.073	−0.149	0.17
O2	3(*a*)	0.625 (2)	0.480 (2)	0.1805 (11)	0.6148	0.4615	0.1794	0.078	0.143	0.016	0.21
	6(*c*)										
O7	3(*a*)	0.143 (2)	0.557 (2)	0.4885 (9)	0.1533	0.5385	0.4874	−0.079	0.143	0.016	0.19
O3	3(*a*)	0.469 (3)	0.594 (2)	0.3163 (9)	0.487	0.584	0.3198	−0.139	0.077	−0.051	0.22
	6(*c*)										
O8	3(*a*)	0.495 (2)	0.087 (2)	0.0101 (9)	0.513	0.097	0.0136	−0.139	−0.077	−0.051	0.20
O4	3(*a*)	0.245 (2)	0.390 (2)	0.1713 (10)	0.237	0.398	0.1835	0.066	−0.062	−0.179	0.20
	6(*c*)										
O6	3(*a*)	0.772 (2)	0.170 (2)	0.1376 (12)	0.763	0.162	0.1498	0.066	0.062	−0.179	0.22
O9	3(*a*)	0.087 (2)	0.097 (2)	0.4436 (8)	0.023	0.057	0.4170	0.497	0.312	0.390	0.19
	6(*c*)										
O10	3(*a*)	0.016 (2)	−0.042 (2)	0.6096 (9)	0.057	0.023	0.5830	−0.312	−0.497	0.390	0.19

† See footnote **1** for equivalent positions.

Table 3
(*a*) Atomic positions for $RbNO_3$ in phase IV (Shamsuzzoha & Lucas, 1982) at room temperature, with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u_{eq} displacements in Å.

$a = 10.55\ (2)$ and $c = 7.47\ (2)$ Å; $z^* = z - 0.0949$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u_{eq}
Rb1	3(*a*), 3(*b*)	0.4566 (3)	0.5691 (3)	0.5287 (5)	0.5129	0.5129	0.5	−0.59	0.59	0.21	0.19
Rb2	3(*a*)	0.1184 (3)	0.2192 (3)	−0.0949	0.1706	0.3056	−0.1524	−0.55	−0.91	0.43	0.22
	6(*c*)†										
Rb3	3(*a*)	−0.2228 (4)	0.2214 (3)	0.5432 (6)	−0.1706	0.1350	0.4857	−0.55	0.91	0.43	0.24
N1	3(*a*), 3(*a*)	0.4388 (4)	0.5668 (4)	0.0104 (6)	0.5028	0.5028	0	−0.68	0.68	0.08	0.22
N2	3(*a*)	0.0962 (3)	0.2042 (3)	0.4369 (6)	0.1771	0.2935	0.3742	−0.85	−0.94	0.47	0.20
	6(*c*)										
N3	3(*a*)	−0.2580 (3)	0.2057 (3)	0.0219 (7)	−0.1771	0.1164	−0.0408	−0.85	0.94	0.47	0.20
O1	3(*a*)	0.3371 (6)	0.5582 (5)	−0.0855 (8)	0.2773	0.6062	−0.0023	0.63	−0.51	−0.62	0.25
	6(*c*)										
O9	3(*a*)	0.6541 (5)	0.2174 (5)	−0.0809 (7)	0.6062	0.2773	0.0023	0.51	−0.63	−0.62	0.25
O2	3(*a*)	0.3964 (5)	0.4704 (5)	0.1331 (8)	0.3521	0.4717	0.1555	0.47	−0.01	−0.17	0.25
	6(*c*)										
O7	3(*a*)	0.6922 (5)	0.1208 (5)	0.1554 (7)	0.6479	0.1196	0.1778	0.47	0.01	−0.17	0.25
O3	3(*a*), 3(*a*)	0.5646 (5)	0.6512 (5)	−0.0285 (9)	0.6079	0.6079	0	−0.46	0.46	−0.21	0.26
O4	3(*a*), 3(*b*)	−0.0011 (4)	0.1089 (4)	0.5296 (7)	0.0550	0.0550	0.5	−0.58	0.58	0.22	0.21
O5	3(*a*), 3(*b*)	0.2309 (5)	0.2495 (5)	0.4688 (8)	0.2402	0.2402	0.5	−0.10	0.10	−0.23	0.25
O6	3(*a*)	0.0581 (5)	0.2465 (5)	0.3000 (8)	0.0930	0.3085	0.3191	−0.37	−0.65	−0.14	0.25
	6(*c*)										
O8	3(*a*)	−0.1279 (6)	0.2774 (6)	−0.0052 (8)	−0.0930	0.2155	0.0140	−0.37	0.65	−0.14	0.26

(*b*) As in Table 3(*a*) but based on the atomic coordinates of Pohl *et al.* (1992), with atom O1 in an equivalent position.† $a = 10.474\ (1)$ and $c = 7.443\ (1)$ Å; $z^* = z - 0.1049$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u_{eq}
Rb1	3(*a*), 3(*b*)	0.4474 (2)	0.5575 (2)	0.5434 (4)	0.5024	0.5024	0.5	−0.58	0.58	0.32	0.18
Rb2	3(*a*)	0.1231 (1)	0.2201 (1)	−0.1049	0.1696	0.3098	−0.1455	−0.49	−0.94	0.30	0.18
	6(*c*)										
Rb3	3(*a*)	−0.2161 (1)	0.2299 (1)	0.5193 (1)	−0.1696	0.1402	0.4788	−0.49	0.94	0.30	0.17
N1	3(*a*), 3(*a*)	0.4612 (7)	0.5915 (7)	0.0579 (15)	0.5264	0.5264	0	−0.68	0.68	0.43	0.17
N2	3(*a*)	0.1009 (8)	0.2047 (8)	0.4167 (15)	0.1673	0.2990	0.3795	−0.85	−0.99	0.28	0.17
	6(*c*)										
N3	3(*a*)	−0.2337 (9)	0.2260 (6)	−0.0090 (14)	−0.1673	0.1317	−0.0462	−0.85	0.99	0.28	0.15
O1	3(*a*)	0.2283 (7)	0.5505 (7)	−0.1669 (8)	0.2799	0.6630	−0.1969	−0.54	1.18	−0.22	0.22
	6(*c*)										
O9	3(*a*)	0.6685 (6)	0.2246 (7)	−0.1064 (8)	0.6169	0.3370	−0.1364	0.54	−1.18	0.22	0.21
O2	3(*a*)	0.3927 (8)	0.4597 (7)	0.0886 (10)	0.3328	0.4692	0.1499	0.63	−0.10	−0.45	0.25
	6(*c*)										
O7	3(*a*)	0.7271 (9)	0.1458 (8)	0.1220 (9)	0.6672	0.1552	0.1834	0.63	−0.10	−0.46	0.24
O3	3(*a*), 3(*a*)	0.5465 (7)	0.6419 (8)	−0.0660 (9)	0.5942	0.5942	0	−0.50	0.50	−0.49	0.23
O4	3(*a*), 3(*b*)	0.0022 (6)	0.1101 (6)	0.5152 (9)	0.0562	0.0562	0.5	−0.58	0.58	0.11	0.21
O5	3(*a*), 3(*b*)	0.2310 (6)	0.2476 (7)	0.4519 (10)	0.2393	0.2393	0.5	−0.07	0.06	−0.36	0.23
O6	3(*a*)	0.0637 (7)	0.2519 (7)	0.2870 (8)	0.0836	0.3223	0.3350	−0.21	−0.74	−0.36	0.22
	6(*c*)										
O8	3(*a*)	−0.1034 (6)	0.3091 (7)	−0.0496 (11)	−0.0836	0.2387	−0.0017	−0.21	0.74	−0.36	0.24

† See footnote **1** for equivalent positions.

Table 4
Atomic positions for KYF_4 at room temperature (Le Fur *et al.*, 1992), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u^{33} displacements in Å.

$a = 14.060\ (10)$ and $c = 10.103\ (10)$ Å; $z^* = z - 0.3195$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z)c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u^{33}
K1	3(*a*), 3(*a*)	0.7818 (2)	0.7190 (2)	−0.0282 (2)	0.7504	0.7504	0	0.442	−0.442	−0.285	0.12
K2	3(*a*), 3(*a*)	0.2677 (2)	0.2208 (3)	0.0057 (3)	0.2443	0.2443	0	0.329	−0.330	0.046	0.16
K3	3(*a*)	0.1050 (2)	0.3945 (3)	−0.0331 (4)	0.0851	0.4247	−0.0034	0.280	−0.425	−0.300	0.17
	6(*c*)†										
K6	3(*a*)	0.4549 (3)	0.0652 (3)	−0.0264 (4)	0.4247	0.0851	0.0034	0.425	−0.280	−0.301	0.15
K4	3(*a*)	0.6111 (2)	0.8778 (2)	0.0028 (3)	0.5851	0.9122	0.0021	0.366	−0.484	0.005	0.13
	6(*c*)										
K5	3(*a*)	0.9466 (3)	0.5591 (2)	−0.0018 (3)	0.9122	0.5851	−0.0021	0.484	−0.366	0.005	0.16
Y1	3(*a*)	0.12871 (6)	0.88764 (6)	−0.0135	0.09321	0.91451	0.0018	0.499	−0.378	−0.155	0.09
	6(*c*)										
Y4	3(*a*)	0.94137 (7)	0.05770 (7)	−0.0171 (2)	0.91451	0.09321	−0.0018	0.378	−0.499	−0.155	0.12

Table 4 (continued)

	Wyckoff position $P3_1$, $P3_121$	x	y	z*	x'	y'	z'	Δx	Δy	Δz	u^{33}
Y2	3(*a*) 6(*c*)	0.28157 (7)	0.73104 (7)	−0.0238 (8)	0.24375	0.75554	−0.0082	0.531	−0.344	−0.158	0.09
Y3	3(*a*)	0.78003 (7)	0.20592 (6)	−0.0074 (1)	0.75554	0.24375	0.0082	0.344	−0.532	−0.158	0.08
Y5	3(*a*) 6(*c*)	0.45256 (7)	0.54579 (7)	−0.0215 (1)	0.41959	0.57477	−0.0096	0.464	−0.407	−0.120	0.11
Y6	3(*a*)	0.60374 (7)	0.38662 (6)	−0.0024 (7)	0.57477	0.41959	0.0096	0.407	−0.464	−0.121	0.07
F1	3(*a*) 6(*c*)	0.1304 (7)	0.9342 (7)	−0.2280 (9)	0.095	0.967	−0.270	0.50	−0.46	0.42	0.16
F7	3(*a*)	0.000 (1)	0.059 (1)	0.312 (2)	0.967	0.095	0.270	0.46	−0.51	0.42	0.25
F2	3(*a*) 6(*c*)	0.0692 (8)	0.8779 (8)	0.199 (1)	0.096	0.963	0.197	−0.38	−1.20	0.02	0.17
F8	3(*a*)	0.0489 (8)	0.1223 (8)	−0.195 (2)	0.963	0.096	−0.197	1.20	0.37	0.02	0.24
F3	3(*a*) 6(*c*)	0.2105 (8)	0.5934 (8)	0.125 (1)	0.2366	0.5162	0.123	−0.37	1.09	0.02	0.18
F5	3(*a*)	0.7372 (5)	0.2023 (5)	0.2133 (8)	0.7634	0.2796	0.211	−0.37	−1.09	0.02	0.11
F4	3(*a*) 6(*c*)	0.334 (1)	0.7286 (7)	0.309 (1)	0.301	0.7594	0.263	0.46	−0.43	0.46	0.21
F6	3(*a*)	0.7901 (6)	0.2684 (6)	−0.2163 (9)	0.7594	0.301	−0.263	0.43	−0.46	0.47	0.13
F9	3(*a*) 6(*c*)	0.3954 (6)	0.5413 (6)	0.1908 (8)	0.4257	0.6267	0.1695	−0.43	−1.20	0.22	0.13
F11	3(*a*)	0.5440 (6)	0.2863 (6)	0.1852 (8)	0.5743	0.2010	0.1639	−0.43	1.20	0.22	0.13
F10	3(*a*) 6(*c*)	0.4618 (7)	0.5950 (6)	0.7645 (8)	0.4281	0.6799	0.7172	0.47	−1.19	0.48	0.14
F12	3(*a*)	0.6057 (7)	0.3368 (7)	0.6637 (1)	0.5720	0.2519	0.6161	0.47	1.19	0.48	0.16
F13	3(*a*) 6(*c*)	0.7727 (6)	0.7346 (6)	−0.283 (1)	0.7495	0.7740	−0.256	0.33	−0.55	−0.27	0.14
F14	3(*a*)	0.8133 (9)	0.7262 (6)	0.229 (1)	0.7740	0.7495	0.256	0.55	−0.33	−0.27	0.16
F15	3(*a*) 6(*c*)	0.2533 (6)	0.2289 (6)	0.2593 (1)	0.2242	0.2625	0.253	0.41	−0.47	0.06	0.15
F16	3(*a*)	0.8050 (6)	0.0719 (6)	0.0864 (8)	0.7758	0.0383	0.080	0.41	0.47	0.06	0.14
F17	3(*a*) 6(*c*)	0.1339 (6)	0.3916 (6)	0.2234 (8)	0.1094	0.4193	0.2565	0.34	−0.39	−0.33	0.12
F24	3(*a*)	0.4469 (7)	0.0849 (6)	−0.2896 (9)	0.4193	0.1094	−0.2565	0.39	−0.34	−0.33	0.15
F18	3(*a*) 6(*c*)	0.0941 (7)	0.4031 (8)	−0.284 (1)	0.0817	0.4431	−0.254	0.17	−0.56	−0.30	0.16
F23	3(*a*)	0.4830 (7)	0.0692 (7)	0.2240 (9)	0.4431	0.0817	0.254	0.56	−0.18	−0.30	0.14
F19	3(*a*) 6(*c*)	0.1535 (6)	0.7561 (7)	0.0808 (9)	0.1073	0.7188	0.0790	0.65	0.53	0.02	0.14
F21	3(*a*)	0.9390 (6)	0.5741 (7)	0.2561 (9)	0.8927	0.6115	0.2543	0.65	−0.53	0.02	0.14
F20	3(*a*) 6(*c*)	0.5874 (6)	0.8816 (7)	0.2576 (9)	0.5595	0.9127	0.2555	0.39	−0.44	0.02	0.13
F22	3(*a*)	0.9438 (6)	0.5316 (6)	−0.2534 (8)	0.9127	0.5595	−0.2555	0.44	−0.39	0.02	0.12

† See footnote **1** for equivalent positions.

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Systematic prediction of new ferroelectrics in space groups $P3_1$ and $P3_2$

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Release 2002/2 of the Inorganic Crystal Structure Database (FIZ Karlsruhe, Germany, and Institute Laue–Langevin, Grenoble, France) contains 62 entries in space group $P3_1$ and ten entries in space group $P3_2$ for 49 different materials including eight families with two or more isostructural members. The structural criteria for ferroelectricity are satisfied for 16 new structure types at a confidence level that depends on the reliability of each determination. $LaBGeO_5$, a mineral with stillwellite structure, was previously reported as ferroelectric and forms an additional family with seven other members or related structures that satisfy the criteria. Ten structures reported in space group $P3_1$ or $P3_2$ are dubious or incorrect, with atomic coordinates that satisfy supergroup symmetry. One material is probably pyroelectric but is unlikely to become ferroelectric, and three others are either incompletely solved or incompletely refined. Among the predicted new ferroelectrics are Cu_2BaGeS_4, $Fe_3(Fe,Si)O_4(OH)_5$, Se_4S_5, $K_2HCr_2AsO_{10}$, IV-$RbNO_3$, $Rb_2Sc(NO_3)_5$, Na_3ReO_5, $Nd_{14}(GeO_4)_2(BO_3)_6O_8$, $CsHgCl_3$, $Ba_2Cu_2AlF_{11}$, KYF_4, $SrS_2O_6{\cdot}4H_2O$, $Cu_3PbTeO_6(OH)_2$, $ReH(CO)_4$, $Ni_2(NH_3)_9Mo(CN)_8{\cdot}2H_2O$ and the 6T polytype of $Ca_{1.89}Ta_{1.80}Sm_{0.16}Ti_{0.10}O_7$, in addition to β-$LaBSiO_5$, $PbBAsO_5$ and $BaBAsO_5$ in the stillwellite family.

1. Introduction

1.1. Previous results reported in point group 3

Analysis of all contemporaneous entries under point groups 6*mm*, 6, 4*mm* and 4 in the Inorganic Crystal Structure Database (ICSD; FIZ Karlsruhe/ILL, 2002) has led to the identification of over 170 materials that satisfy the structural criteria for ferroelectricity (Abrahams, 1988, 1990, 1996, 1999). However, presentation of the analysis of all entries in point group 3, with 57 in space group $P3$, 62 in $P3_1$, ten in $P3_2$ and 124 in $R3$, would have been unwieldy. Analysis of the 21 candidates for ferroelectricity in space group $P3$ was hence presented separately (Abrahams, 2000), with each entry under space groups $P3_1$ and $P3_2$ considered here, and those in space group $R3$ considered later. The introduction to the analysis of all entries in space group $P3$ presented by Abrahams (2000) can also be considered as the introduction to the present set of results. The order in which materials are presented follows the ICSD Collection Code sequence in these two space groups, with the exception that subsequent entries for the same substance or family are grouped with the first entry, as are isostructural and enantiomorphic materials, unless noted otherwise.

1.2. Structural criteria for the prediction of ferroelectricity

The criteria that are used to determine whether a structure reported in a polar space group is likely to be ferroelectric have been presented previously (*e.g.* Abrahams, 2000). These criteria are briefly (*a*) that the *i*th atom forming the shortest and least-ionic bonds in the unit cell undergoes no polar displacement, Δz_i, greater than ~1 Å between the location reported at $x_i y_i z_i$ and that at which the resulting spontaneous polarization, P_s, vanishes and (*b*) that the largest displacement, $\Delta\xi_i$, exceeds ~0.1 Å or the r.m.s. thermal or static displacement, u_i, of that atom.

A recent study of the atomic displacements undergone at the four separate phase transitions in ferroic $Pb_5Al_3F_{19}$ (Abrahams *et al.*, 2003) over the temperature range 120–670 K has revealed individual $\Delta\xi$ magnitudes as large as ~1.2 Å. The upper limit for $\Delta\xi$ at ferroelectric phase transitions, which was taken to be ~1.0 Å for many years, may hence be revised upward.

The predicted Curie temperature, T_c, in structures for which the *i*th atom occupies an octahedron of O or F atoms is related (Abrahams *et al.*, 1968) to Δz_i by

$$T_c = (\kappa/2k)(\Delta z_i)^2\,\mathrm{K}, \qquad (1)$$

where the force constant κ is ~5.52 kPa, k is Boltzmann's constant, Δz_i is the largest displacement of the *i*th atom along the polar *c* axis as defined in criterion (*a*) and $\kappa/2k = 2.00\,(9) \times 10^4\ \mathrm{K}\ \mathrm{\AA}^{-2}$.

1.3. Dielectric properties at the subgroup–supergroup transition

The minimal non-isomorphic supergroups of $P3_1$ in the trigonal system are $P3_112$, $P3_121$ and $R3$; those of $P3_2$ are $P3_212$, $P3_221$ and $R3$. The phase transition at T_c reduces the active piezoelectric moduli, d_{15}, d_{16}, d_{21}, d_{22}, d_{24}, d_{31}, d_{32} and d_{33}, of the subgroup to zero in the supergroup, the related $d_{26} = 2d_{12} = -2d_{11}$ and $d_{14} = -d_{25}$ moduli remaining active. The permittivity coefficients are active above and below the phase transition, but the single pyroelectric coefficient, p_3, is reduced to zero in the supergroups, together with the possibility of ferroelectricity. By contrast, all piezoelectric and pyroelectric moduli become zero at the ferroelectric phase transitions in the four point groups previously considered, as a result of the generation of inversion centers (see Abrahams, 1994).

1.3.1. Validation of predicted state. Confirmation of ferroelectricity in structures satisfying the criteria in §1.2 is most direct if dielectric hysteresis is observed at room temperature and is supported by the dielectric permittivity thermal dependence. Characterization of the phase transition through the Curie temperature is most readily determined calorimetrically. Structural reinvestigation is generally advisable.

1.4. Subgroup–supergroup atomic distributions and equivalent positions

Pyroelectricity in a crystal is a necessary condition for the development of ferroelectricity and becomes sufficient if, in addition, the atomic distribution approaches supergroup symmetry (see §§1.2 and 1.3). The number of structures reported in nonpyroelectric supergroups generally exceeds that in related pyroelectric subgroups; thus, the 2002/2 release of the ICSD lists 366 entries in nonpyroelectric $P3_112$, $P3_121$, $P3_212$ and $P3_221$ but only 72 entries in the pyroelectric space groups $P3_1$ and $P3_2$. It may hence be an indication of difficulties associated with structural determination in space groups $P3_1$ and $P3_2$ that the symmetry of at least one-third of the structure types reported therein can be regarded as dubious. Remarkably, the atomic distribution in only one of the remaining reports departs substantially from supergroup symmetry.

Atomic locations in structures that can undergo a phase transition from ferroelectric to nonferroelectric are related to equivalent positions in the resulting supergroup. Hypothetical supergroup coordinates, which are indicated by primes (′) in the tables that follow, are obtained by averaging the experimental values in the subgroup. The component axial displacements, $\Delta\xi$, of each atom at the structure determination temperature (T) to a hypothetical nonpyroelectric phase, with spontaneous polarization $P_s = 0$, may thereby be determined. P_s reversal at T requires the z coordinate of each atom to undergo a total displacement of $2\Delta z$ that also reverses the sense of *c*; nonzero x and y coordinates are without symmetry restriction and may relax to the original values. All $|\Delta\xi|$ values are probably temperature dependent. The equivalent positions in space groups $P3_1$ and $P3_2$ and in their supergroups are given in the footnote below as an aid in clarifying these tables.[1] Consideration of the atomic paths followed under ferroelectric switching or in the approach to the supergroup at the phase transition would be of most interest once the predicted ferroelectric property has been confirmed.

2. New inorganic ferroelectrics predicted in space groups $P3_1$ and $P3_2$

2.1. Cu_2SrSnS_4 family

The Cu_2ABS_4 family (A = Sr or Ba, and B = Ge or Sn) includes Cu_2SrSnS_4, Cu_2BaGeS_4, Cu_2SrGeS_4 and $Cu_2BaGeSe_4$.

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[1] Each subgroup atom occupies the general 3(*a*) Wyckoff position with coordinates $x, y, z; \bar{y}, x - y, z + \frac{1}{3}; \bar{x} + y, \bar{x}, z + \frac{2}{3}$ in space group $P3_1$, and $x, y, z; \bar{y}, x - y, z + \frac{2}{3}; \bar{x} + y, \bar{x}, z + \frac{1}{3}$ in space group $P3_2$. In supergroup $P3_112$, the special 3(*a*) positions are $x, \bar{x}, \frac{1}{3}; x, 2x, \frac{2}{3}; 2\bar{x}, \bar{x}, 0$, and the 3(*b*) positions are $x, \bar{x}, \frac{5}{6}; x, 2x, \frac{1}{6}; 2\bar{x}, \bar{x}, \frac{1}{2}$, with the 6(*c*) positions as in $P3_1 + (x, x - y, \bar{z}; \bar{x} + y, y, \bar{z} + \frac{1}{3}; \bar{y}, \bar{x}, \bar{z} + \frac{2}{3})$. In $P3_121$, the special 3(*a*) positions are $x, 0, \frac{1}{3}; 0, x, \frac{2}{3}; \bar{x}, \bar{x}, 0$, and the 3(*b*) positions are $x, 0, \frac{5}{6}; 0, x, \frac{1}{6}; \bar{x}, \bar{x}, \frac{1}{2}$, with the 6(*c*) positions as in $P3_1 + (y, x, \bar{z}; \bar{x}, \bar{x} + y, \bar{z} + \frac{1}{3}; x - y, \bar{y}, \bar{z} + \frac{2}{3})$. In $P3_212$, the special 3(*a*) positions are $x, \bar{x}, \frac{2}{3}; x, 2x, \frac{1}{3}; 2\bar{x}, \bar{x}, 0$, and the 3(*b*) positions are $x, \bar{x}, \frac{1}{6}; x, 2x, \frac{5}{6}; 2\bar{x}, \bar{x}, \frac{1}{2}$, with the 6(*c*) positions as in $P3_2 + (x, x - y, \bar{z}; \bar{y}, \bar{x}, \bar{z} + \frac{1}{3}; \bar{x} + y, y, \bar{z} + \frac{2}{3})$. In $P3_221$, the special 3(*a*) positions are $x, 0, \frac{2}{3}; 0, x, \frac{1}{3}; \bar{x}, \bar{x}, 0$, and the 3(*b*) positions are $x, 0, \frac{1}{6}; 0, x, \frac{5}{6}; \bar{x}, \bar{x}, \frac{1}{2}$, with the 6(*c*) positions as in $P3_2 + (y, x, \bar{z}; x - y, \bar{y}, \bar{z} + \frac{1}{3}; \bar{x}, \bar{x} + y, \bar{z} + \frac{2}{3})$.

Table 1
Atomic positions for Cu_2BaGeS_4 at room temperature (Teske, 1979), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u^{33} displacements in Å.

$a = 6.215$ and $c = 15.534$ Å. Uncertainties not reported. $z^* = z - 0.0907$, $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u^{33}
Cu1	3(*a*), 6(*c*)†	0.2587 (6)	0.2487 (6)	0.2487 (2)	0.2960	0.3099	0.2565	−0.232	−0.380	−0.121	0.09
Cu2	3(*a*)	−1/3	0.0750 (3)	0.0690 (2)	−0.2960	0.0139	0.0768	−0.232	0.380	−0.121	0.15
Ge	3(*a*), 3(*a*)	1/3	0.3807 (3)	−0.0083 (2)	0.3570	0.3570	0	−0.147	0.147	−0.129	0.14
Ba	3(*a*), 3(*b*)	−0.1029 (2)	2/3	0.1593	0	~0.6667	0.1667	−0.639	~0	−0.115	0.08
S1	3(*a*), 6(*c*)	0.3703 (9)	0.1870 (9)	0.1076 (3)	0.2586	0.2971	0.0863	0.694	−0.684	0.331	0.07
S2	3(*a*)	−0.1468 (9)	0.1486 (9)	0.2683 (3)	−0.2586	0.0385	0.2470	0.695	0.684	0.331	0.10
S3	3(*a*), 6(*c*)	0.0035 (9)	0.4292 (9)	−0.0023 (3)	−0.1183	0.5466	0.0034	0.758	−0.730	−0.089	0.10
S4	3(*a*)	0.6639 (9)	0.7598 (9)	−0.0091 (3)	0.5466	0.8817	−0.0034	0.729	−0.758	−0.089	0.10

† See footnote **1** for equivalent positions.

2.1.1. Cu_2SrSnS_4. Structural determination by Teske (1976), on the basis of 1552 independent reflections, resulted in a best fit with $R = 0.06$ for the Sn atom fixed at $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ and all remaining position coordinates and anisotropic u^{ij} parameters were allowed to vary; neither $u_{\rm iso}$ nor u^{ij} values were reported.[2] The final atomic coordinates, following an origin displacement of −0.0814 that minimizes $\Sigma\Delta z_i$ for all i atoms, where Δz_i is the difference between adjusted experimental and hypothetical z_i coordinates, are given in Table S1(*a*).[3] No atom is further than ~1.1 Å from the corresponding Wyckoff position in supergroup $P3_121$, and hence the revised criteria for structural ferroelectricity given in §1.2 are clearly satisfied. The polarization, P_s, in Cu_2SrSnS_4, however, is expected to be small, since $\Delta z \leq 0.030$ Å for all i atoms; $u^{33}_{\rm max}$ displacements are unstated for Cu_2SrSnS_4 but are likely to be in the range given for Cu_2BaGeS_4 (see Table 1). Individual Δx or Δy displacement components in Cu_2SrSnS_4 between subgroup atom positions and the corresponding locations in the nonpyroelectric supergroup are as large as 0.73 Å for the S1/S2 pair, 0.72 Å for the S3/S4 pair and 0.64 Å for Δx(Sr). Average bond distances in the structure are normal, with $\langle d_{\rm Cu-S}\rangle = 2.337$ Å, $\langle d_{\rm Sr-S}\rangle = 3.199$ Å and $\langle d_{\rm Sn-S}\rangle = 2.389$ Å.

The potential barrier in Cu_2SrSnS_4 to polar displacement may be low enough to allow reversal of the sense of P_s under the application of small electric fields at room temperature, as x, y, z atomic coordinates change to y, x, $\bar{z}$ *etc.*; dielectric measurement is necessary in order to determine if the x and y coordinates can undergo the displacements necessary for polarization switching. If the field required for domain-wall motion is small then this material may have useful applications.

2.1.2. Cu_2BaGeS_4. Refinement in space group $P3_1$, on the basis of 1210 independent reflections with $F_{\rm obs} > 6\sigma(F_{\rm obs})$, led to $R = 0.067$ (Teske, 1979). The atomic coordinates (after an origin shift of −0.0907 to minimize $\Sigma\Delta z_i$) are given in Table 1, together with the u^{33} parameters. Note that all Δz_i magnitudes in Cu_2BaGeS_4 are significantly larger than those in Cu_2SrSnS_4, with Δz(S1) and Δz(S2) equal to 0.33 Å and no other Δz magnitude being less than ~0.09 Å; the maximum Δx and Δy displacements (~0.75 Å), however, are comparable to those in Cu_2SrSnS_4.

2.1.3. Cu_2SrGeS_4. Teske (1979) reported the structure in the enantiomorphic space group $P3_2$, based on 1030 independent reflections with $F_{\rm obs} > 6\sigma(F_{\rm obs})$. The atomic coordinates in Table S1(*b*) (an origin shift of 0.0839 minimizes $\Sigma\Delta z_i$) correspond to a final R value of 0.056. All atoms are close to the Wyckoff position 6(*c*), 3(*a*) or 3(*b*), as is the case for both Cu_2SrSnS_4 and Cu_2BaGeS_4, but are in the nonpyroelectric space group $P3_221$ rather than $P3_121$. The largest $\Delta\xi$ displacements between sub- and supergroups in Cu_2SrGeS_4 are Δx(S3,S4) and Δy(S3,S4) at 0.72 Å and Δx(S1,S2) at 0.70 Å.

2.1.4. $Cu_2BaGeSe_4$. The atomic coordinates, given in Table S1(*c*), were recently determined by Tampier & Johrendt (2001) in space group $P3_1$ and refined with 982 independent reflections with $I_{\rm obs} > 2\sigma(I_{\rm obs})$ to $R = 0.024$ and $wR = 0.048$; $Cu_2BaGeSe_4$ is a new member of the Cu_2SrSnS_4 family. With the largest Δx(Se3,Se4) and Δy(Se3,Se4) values being ~0.76 Å, the ferroelectricity criteria in §1.2 are satisfied. All four quaternary thio- or selenostannate or germanate members of the Cu_2SrSnS_4 family are hence ferroelectric candidates (but see §1.3.1).

2.2. Cronstedtite-3T

The first structural determination and refinement of the cronstedtite-3T polytype, with idealized composition $Fe_3(Fe,Si)O_4(OH)_5$ (ACCRA 16 1),[4] was noted as incomplete by Smrčok *et al.* (1994), who measured a carefully selected crystal of the formula $Fe_{2.96}Al_{0.02}Mg_{0.02}[(Si_{1.26}Fe_{0.74})O_5](OH)_4$ by the use of Ag $K\alpha$ radiation. Refinement of 1336 indepen-

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[2] All tables contain the displacement u^{33}, $u_{\rm eq}$ or $u_{\rm iso}$ for each atom, if reported, for comparison with the corresponding Δx, Δy, Δz magnitudes. Following the recommendations of Trueblood *et al.* (1996), the atomic displacement parameters are assigned the dimension of length, whereas the mean-square displacements U^{33} *etc.* have the dimension length squared.

[3] Tables S1–S31 have been deposited. Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0135). Services for accessing these data are described at the back of the journal.

[4] Coden-type references are given throughout this paper for most structure determinations for which atomic coordinates are not reproduced (see Notes for Authors, 1985). The ICSD omits the final check letter of the journal abbreviation, providing only five letters in each coden. The year of publication is given implicitly in the coden by the volume number following the journal's modified acronym; the final entry in the coden is the number of the first page.

Table 2
Atomic positions for $K_2HCr_2AsO_{10}$ at room temperature (Averbuch-Pouchot *et al.* 1978), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and $u_{\rm eq}$ displacements in Å.

$a = 7.712$ (3) and $c = 14.644$ (8) Å. $z^* = z - 0.0046$, $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	$u_{\rm eq}$
Cr1	3(*a*), 6(*c*)†	0.4278 (3)	0.4243 (3)	0.2403	0.4242	0.4217	0.2460	0.028	0.020	−0.083	0.14
Cr2	3(*a*)	0.4191 (3)	0.4205 (4)	0.7484 (2)	0.4217	0.4242	0.7540	−0.020	−0.028	−0.082	0.14
As	3(*a*), 3(*a*)	0.1281 (2)	0.0199 (2)	0.3447 (2)	0.1281	0	0.3333	0	0.153	0.167	0.14
K1	3(*a*), 3(*b*)	0.5520 (5)	−0.0182 (5)	0.8343 (3)	0.5520	0	0.8333	0	−0.140	0.015	0.17
K2	3(*a*), 3(*a*)	0.6083 (5)	0.0061 (5)	0.3277 (3)	0.6083	0	0.3333	0	0.047	−0.082	0.17
O1	3(*a*), 6(*c*)	0.356 (2)	0.186 (2)	0.2975 (8)	0.3465	0.188	0.3077	0.073	−0.015	−0.149	0.17
O5	3(*a*)	0.190 (2)	0.337 (2)	0.6821 (8)	0.188	0.3465	0.6923	0.015	−0.073	−0.149	0.17
O2	3(*a*), 6(*c*)	0.625 (2)	0.480 (2)	0.1805 (11)	0.6148	0.4615	0.1794	0.078	0.143	0.016	0.21
O7	3(*a*)	0.143 (2)	0.557 (2)	0.4885 (9)	0.1533	0.5385	0.4874	−0.079	0.143	0.016	0.19
O3	3(*a*), 6(*c*)	0.469 (3)	0.594 (2)	0.3163 (9)	0.487	0.584	0.3198	−0.139	0.077	−0.051	0.22
O8	3(*a*)	0.495 (2)	0.087 (2)	0.0101 (9)	0.513	0.097	0.0136	−0.139	−0.077	−0.051	0.20
O4	3(*a*), 6(*c*)	0.245 (2)	0.390 (2)	0.1713 (10)	0.237	0.398	0.1835	0.066	−0.062	−0.179	0.20
O6	3(*a*)	0.772 (2)	0.170 (2)	0.1376 (12)	0.763	0.162	0.1498	0.066	0.062	−0.179	0.22
O9	3(*a*), 6(*c*)	0.087 (2)	0.097 (2)	0.4436 (8)	0.023	0.057	0.4170	0.497	0.312	0.390	0.19
O10	3(*a*)	0.016 (2)	−0.042 (2)	0.6096 (9)	0.057	0.023	0.5830	−0.312	−0.497	0.390	0.19

† See footnote **1** for equivalent positions.

dent $F_{\rm meas}$, with $I_{\rm meas} > 3\sigma(I_{\rm meas})$, to which analytical absorption corrections were applied, led to final values of $R = 0.050$ and $wR = 0.031$ for the atomic coordinates in Table S2 (an origin shift of 0.02011 has been applied in order to minimize $\Sigma\Delta z$ for all atoms). The table shows the largest $|\Delta x|$ and $|\Delta y|$ values to be ~0.9 Å; 16 of the remaining independent $|\Delta x|$ and $|\Delta y|$ values are less than ~0.02 Å and all other values are between 0.2 and 0.6 Å. The largest $|\Delta z|$ value is ~1.1 Å, and the other z components range from 0.3 to 0.8 Å, where $\Delta\xi$ ($\xi = x, y$ or z) is the axial component of the difference between a location in space group $P3_1$ and that in the corresponding Wyckoff position of space group $P3_212$. The diffraction pattern produced by this polytype reveals appreciable diffuse scattering indicative of disorder; the octahedral Fe sites with the largest $|\Delta z|$ values are occupied by ~23% Si atoms and ~2% each of Al and Mg atoms. Nevertheless, the cronstedtite-3T polytype structure fulfills the criteria for ferroelectricity given in §1.2. A transition involving a change from a 3_1 to a 3_2 screw axis may imply an integral change in the length of the polar axis, for which evidence is presently lacking. Further structural investigation would be of interest (see also §1.3.1).

2.3. S_5Se_4

The structure of the pressure-induced phase S_5Se_4 was reported by Geller & Lind (1970) in space group $P3_1$ or $P3_2$. The final disordered model was deduced from packing considerations to have three atoms per helix segment. Despite difficulties that included parameter correlation, rotational twinning and positional disorder, the authors claimed that this model fitted the data better than any other model examined. Refinement on the basis of 131 visually estimated reflections gave $R = 0.11$, with the atomic coordinates modified by an origin shift of 0.3788 along the polar axis (see Table S3). The six independent sites in Table S3 are related to four sites with Wyckoff positions 3(*a*), 6(*c*) and 3(*b*) in the space group $P3_112$ by Δx and Δy components of less than ~0.41 Å and Δz of less than ~0.21 Å for $u_{\rm iso}$(S/Se) = 0.27 Å. Each site is reported as partially occupied by S/Se atoms at room temperature. Assuming that the original structure determination is correct, the S/Se displacements satisfy the structural criteria for ferroelectricity given in §1.2; since all $\Delta\xi$ values are less than ~$2u_{\rm iso}$, however, the possibility also exists that the space group at room temperature is the piezoelectric but nonpyroelectric space group $P3_112$. Further investigation is indicated (see §1.3.1).

2.4. $K_2HCr2AsO_{10}$

Averbuch-Pouchot *et al.* (1978) determined the structure of $K_2HCr_2AsO_{10}$ in space group $P3_1$ on the basis of 1170 reflections with $F_{\rm obs} > n\sigma(F_{\rm obs})$, derived from 2201 independent reflections (n not stated). An initial model that could not be reduced below $R = 0.08$ was modified by placing all atoms close to locations in the Wyckoff position 6(*c*) of the space group $P3_121$. Consequently, many correlation coefficients in the least-squares refinement became large, but holding some parameters constant in intermediate cycles led to refinement with a final value of $R = 0.054$. The resulting atomic coordinates are given in Table 2, where the origin along the polar axis is shifted by −0.0046 to minimize $\Sigma\Delta z_i$. Polar displacements from equivalent positions in the supergroup are $\Delta z \lesssim u_{\rm eq}$ for all atoms except O9 and O10; the latter have $\Delta z \simeq 2u_{\rm eq}$. The criteria for ferroelectricity given in §1.2 are hence satisfied. All thermal/static atomic displacements, $u_{\rm eq}$, fall in the range 0.14–0.22 Å.

The As, Cr1 and Cr2 atoms occupy distorted tetrahedra, that of As being the least distorted; the three tetrahedra share corner O atoms to form a $Cr_2AsO_{10}^{3-}$ anion. Atoms Cr1 and Cr2 are within 0.03 Å of their tetrahedral charge centers along the polar axis and hence have polarizations that nearly cancel. The As atom is within 0.05 Å of its tetrahedral center and is displaced 0.167 Å from $c/3$. Both K atoms are coordinated by seven O atoms, with $d_{\mathrm{K-O}} \leq 3.10$ Å. The force constant in tetrahedral geometry is presently unknown; if this constant is comparable to that in octahedral geometry then T_c is ~560 K, assuming that the pyroelectric space group can be confirmed. Preliminary calorimetric measurements (Ylvisaker *et al.*, 2001) reveal a reversible thermally hysteretic phase transition at ~540 K on heating, with $\Delta S \lesssim 1.9$ J mol^{-1} K^{-1}.

2.5. $RbNO_3$ phase IV family

2.5.1. $RbNO_3$ phase IV. The $RbNO_3$ phase IV family includes $CsNO_3$ phase II and $TlNO_3$ phase II. Three separate phase transitions at 437, 492 and 564 K have been reported for $RbNO_3$ between phase IV at room temperature and melting by phase I at ~587 K (DANKA 108 645); Pohl *et al.* (1992) report a new phase, V, that remains stable or metastable over the range 296–437 K and forms above a sluggish and irreversible first-order phase transition at 346 K. Room-temperature phase IV was reported by Brown & McLaren (1962) in space group $P3_112$ or $P3_121$, but the observation by Bury & McLaren (1969) of pyroelectric charge generation demonstrated that the space group was polar. Shamsuzzoha & Lucas (1982) reported the systematic absence of $I(00l)$ for $l \neq 3n$ using neutron diffraction, with $I(hkl) \neq I(khl)$, thereby eliminating all possible space-group choices but $P3_1$ (or enantiomorphic $P3_2$) for phase IV; these authors refined an earlier but unpublished structural model, determined by X-ray diffraction and referenced in their paper, in space group $P3_1$ using 371 independent neutron diffraction measurements with $I > 1\sigma(I)$. With 141 variable parameters including the anisotropic extinction coefficients, the final R value was 0.068 for the atomic coordinates in Table 3(*a*), where an origin displacement of −0.0949 has been applied along the polar axis to minimize $\Sigma\Delta z_i$. Pohl *et al.* (1992) refined the structure of phase IV with 754 independent measurements, $I > 3\sigma(I)$, at 296 K to give the atomic coordinates in Table 3(*b*), after an origin displacement of −0.1049, which corresponds to a final R value of 0.0254.

The structural criteria for ferroelectricity (§1.2) are clearly satisfied by all atomic positions in the $RbNO_3$ phase IV studies in Tables 3(*a*) and 3(*b*). The force constant in (1), and hence the possibility of predicting the value of T_c, is inapplicable to planar NO_3^- ions and irregular RbO_{12} decahedra. Note that P_s necessarily reduces to zero in cubic phase III at $T_{\mathrm{IV,III}} = 437$ K.

Examination of corresponding pairs of Δx, Δy and Δz displacements in Tables 3(*a*) and 3(*b*), *e.g.* Δx(O1) and Δx(O9), and Δz(N2) and Δz(N3), reveals magnitudes that differ with high significance. The u_{eq} displacements are also large, namely $0.26 > u_{\mathrm{eq}} > 0.19$ Å in Table 3(*a*) and $0.25 > u_{\mathrm{eq}} > 0.15$ Å in Table 3(*b*).

Differences between atomic coordinates resulting from comparable studies are readily analyzed by means of normal probability Q_{exp}–Q_{norm} plots (Abrahams & Keve, 1971) (see Fig. 1). Comparisons are made by calculating $Q_{\mathrm{exp}(i)} = |\xi_i(1) - \xi_i(2)|/[\sigma^2\xi_i(1) + \sigma^2\xi_i(2)]^{1/2}$, where $\xi_i(1)$ and $\xi_i(2)$ are the *i*th atomic coordinate magnitudes reported in the first and second studies, respectively. The ranked $Q_{\mathrm{exp}(i)}$ are plotted against the expected value of $Q_{\mathrm{norm}(i)}$ for each *i*th normal deviate modulus. The latter can be found in the *International Tables for X-ray Crystallography* (1974). If the resulting plot is linear, with unit slope and zero intercept, then the experimental deviates can be taken to be free from systematic error, with standard uncertainties well estimated.

In the present sample of 44 deviates [z(Rb3) was taken to be the origin in both studies, without standard uncertainty], the results in Fig. 1 reveal two major outliers with $Q_{\mathrm{exp}(i)}$ greater than ~72 normal deviates for $i = x$(O1) and z(O1). The systematic departure of the remaining 42 terms from linearity, although smaller, indicates the presense of systematic error. The slope of the array shows that the combined uncertainties in atomic/nuclear positions, excluding the O1-atom coordinates, are underestimated by a factor of 19.2 (9). The O1 coordinates, however, differ by as much as 118σ or 6.1 joint standard uncertainties after compensating for the underestimation. Such large differences suggest a systematic error beyond normal instrumental error, possibly due to the existence of more than one set of metastable equilibrium positions in phase IV at room temperature under different preparation conditions. Pohl *et al.* (1992) report a sluggish transition to a new phase at ~346 K, in which the orientation of one of the three independent NO_3^- ions changes as the space group changes to $P3_2$. Q_{exp}–Q_{norm} differences larger than normal are consistent with metastable specimens.

Brown & McLaren (1962) propose a transformation at $T_{\mathrm{IV,III}} = 437$ K on heating, in which the c axis in phase IV becomes the [111] cube-diagonal in phase III, the trigonal [101] forming the cubic [100]; an increase of ~10^3 Ω^{-1} in conductance was also noted on heating through $T_{\mathrm{IV,III}}$, with a symmetry change at 492 K as the conductance decreases by ~1.5×10^3 Ω^{-1} between cubic phase III and tetragonal phase II. A neutron diffraction study on a single crystal of phase III at 461 K by Shamsuzzoha & Lucas (1987) was unable to distinguish definitively between models with disordered NO_3^-

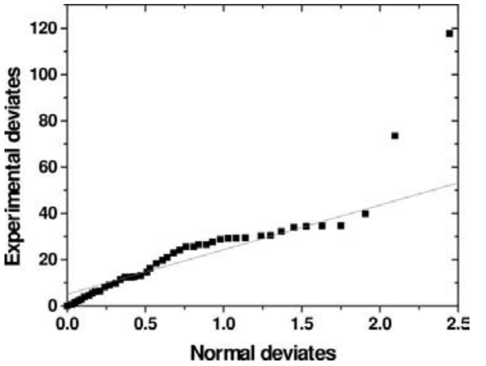

Figure 1
Normal probability plot of the atomic coordinates independently determined for $RbNO_3$ phase IV by Shamsuzzoha & Lucas (1982) and by Pohl *et al.* (1992). The dotted line obtained by linear regression has a slope of 22.6 (5) at a confidence level of 99.2%.

Table 3

(*a*) Atomic positions for $RbNO_3$ in phase IV (Shamsuzzoha & Lucas, 1982) at room temperature, with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u_{eq} displacements in Å.

$a = 10.55\ (2)$ and $c = 7.47\ (2)$ Å; $z^* = z - 0.0949$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u_{eq}
Rb1	3(*a*), 3(*b*)	0.4566 (3)	0.5691 (3)	0.5287 (5)	0.5129	0.5129	0.5	−0.59	0.59	0.21	0.19
Rb2	3(*a*), 6(*c*)†	0.1184 (3)	0.2192 (3)	−0.0949	0.1706	0.3056	−0.1524	−0.55	−0.91	0.43	0.22
Rb3	3(*a*)	−0.2228 (4)	0.2214 (3)	0.5432 (6)	−0.1706	0.1350	0.4857	−0.55	0.91	0.43	0.24
N1	3(*a*), 3(*a*)	0.4388 (4)	0.5668 (4)	0.0104 (6)	0.5028	0.5028	0	−0.68	0.68	0.08	0.22
N2	3(*a*), 6(*c*)	0.0962 (3)	0.2042 (3)	0.4369 (6)	0.1771	0.2935	0.3742	−0.85	−0.94	0.47	0.20
N3	3(*a*)	−0.2580 (3)	0.2057 (3)	0.0219 (7)	−0.1771	0.1164	−0.0408	−0.85	0.94	0.47	0.20
O1	3(*a*), 6(*c*)	0.3371 (6)	0.5582 (5)	−0.0855 (8)	0.2773	0.6062	−0.0023	0.63	−0.51	−0.62	0.25
O9	3(*a*)	0.6541 (5)	0.2174 (5)	−0.0809 (7)	0.6062	0.2773	0.0023	0.51	−0.63	−0.62	0.25
O2	3(*a*), 6(*c*)	0.3964 (5)	0.4704 (5)	0.1331 (8)	0.3521	0.4717	0.1555	0.47	−0.01	−0.17	0.25
O7	3(*a*)	0.6922 (5)	0.1208 (5)	0.1554 (7)	0.6479	0.1196	0.1778	0.47	0.01	−0.17	0.25
O3	3(*a*), 3(*a*)	0.5646 (5)	0.6512 (5)	−0.0285 (9)	0.6079	0.6079	0	−0.46	0.46	−0.21	0.26
O4	3(*a*), 3(*b*)	−0.0011 (4)	0.1089 (4)	0.5296 (7)	0.0550	0.0550	0.5	−0.58	0.58	0.22	0.21
O5	3(*a*), 3(*b*)	0.2309 (5)	0.2495 (5)	0.4688 (8)	0.2402	0.2402	0.5	−0.10	0.10	−0.23	0.25
O6	3(*a*), 6(*c*)	0.0581 (5)	0.2465 (5)	0.3000 (8)	0.0930	0.3085	0.3191	−0.37	−0.65	−0.14	0.25
O8	3(*a*)	−0.1279 (6)	0.2774 (6)	−0.0052 (8)	−0.0930	0.2155	0.0140	−0.37	0.65	−0.14	0.26

(*b*) As in Table 3(*a*) but based on the atomic coordinates of Pohl *et al.* (1992), with atom O1 in an equivalent position.† $a = 10.474\ (1)$ and $c = 7.443\ (1)$ Å; $z^* = z - 0.1049$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z')c$.

	Wyckoff position $P3_1$, $P3_121$	x	y	z^*	x'	y'	z'	Δx	Δy	Δz	u_{eq}
Rb1	3(*a*), 3(*b*)	0.4474 (2)	0.5575 (2)	0.5434 (4)	0.5024	0.5024	0.5	−0.58	0.58	0.32	0.18
Rb2	3(*a*), 6(*c*)	0.1231 (1)	0.2201 (1)	−0.1049	0.1696	0.3098	−0.1455	−0.49	−0.94	0.30	0.18
Rb3	3(*a*)	−0.2161 (1)	0.2299 (1)	0.5193 (1)	−0.1696	0.1402	0.4788	−0.49	0.94	0.30	0.17
N1	3(*a*), 3(*a*)	0.4612 (7)	0.5915 (7)	0.0579 (15)	0.5264	0.5264	0	−0.68	0.68	0.43	0.17
N2	3(*a*), 6(*c*)	0.1009 (8)	0.2047 (8)	0.4167 (15)	0.1673	0.2990	0.3795	−0.85	−0.99	0.28	0.17
N3	3(*a*)	−0.2337 (9)	0.2260 (6)	−0.0090 (14)	−0.1673	0.1317	−0.0462	−0.85	0.99	0.28	0.15
O1	3(*a*), 6(*c*)	0.2283 (7)	0.5505 (7)	−0.1669 (8)	0.2799	0.6630	−0.1969	−0.54	1.18	−0.22	0.22
O9	3(*a*)	0.6685 (6)	0.2246 (7)	−0.1064 (8)	0.6169	0.3370	−0.1364	0.54	−1.18	0.22	0.21
O2	3(*a*), 6(*c*)	0.3927 (8)	0.4597 (7)	0.0886 (10)	0.3328	0.4692	0.1499	0.63	−0.10	−0.45	0.25
O7	3(*a*)	0.7271 (9)	0.1458 (8)	0.1220 (9)	0.6672	0.1552	0.1834	0.63	−0.10	−0.46	0.24
O3	3(*a*), 3(*a*)	0.5465 (7)	0.6419 (8)	−0.0660 (9)	0.5942	0.5942	0	−0.50	0.50	−0.49	0.23
O4	3(*a*), 3(*b*)	0.0022 (6)	0.1101 (6)	0.5152 (9)	0.0562	0.0562	0.5	−0.58	0.58	0.11	0.21
O5	3(*a*), 3(*b*)	0.2310 (6)	0.2476 (7)	0.4519 (10)	0.2393	0.2393	0.5	−0.07	0.06	−0.36	0.23
O6	3(*a*), 6(*c*)	0.0637 (7)	0.2519 (7)	0.2870 (8)	0.0836	0.3223	0.3350	−0.21	−0.74	−0.36	0.22
O8	3(*a*)	−0.1034 (6)	0.3091 (7)	−0.0496 (11)	−0.0836	0.2387	−0.0017	−0.21	0.74	−0.36	0.24

† See footnote **1** for equivalent positions.

ions in space groups $P\overline{4}3m$, $P432$ or $Pm3m$, although the data favored the latter. Pohl *et al.* (1992) report that phase III is cubic, with CsCl structure, $Z = 1$, in space group $Pm3m$. It is noted that, if phase IV transforms to space group $P3_112$ at $T < T_{IV,III}$, the only cubic supergroups of subgroups 3 and 32 are $m3m$ and 432. This apparently simple phase system, including the possible existence of space group $P3_121$ over a narrow thermal range, remains to be investigated further.

2.5.2. $CsNO_3$ phase II. Five entries for $CsNO_3$ phase II, based on separate structural investigations, are included in ICSD release 2002/2. PHSSA 16 K175 gives $T_{II,I} = 427$ K and ACSCE 40 1512 gives 434 K. The most recent structural study of $CsNO_3$ phase II (Pohl & Gross, 1993), using 1036 independent F_{obs} and a model based on these authors' $RbNO_3$ phase IV results, led to $R = 0.0187$ for the coordinates presented in Table S4 (adjusted by an origin shift of −0.1523 to minimize $\Sigma\Delta z_i$). Comparison with Tables 3(*a*) and 3(*b*) confirms that $RbNO_3$ phase IV and $CsNO_3$ phase II are isostructural; the closest similarity is found between the results of Pohl & Gross (1993) and Pohl *et al.* (1992), although several atoms are related differently by the supergroup in $CsNO_3$ and in $RbNO_3$. $CsNO_3$ phase II satisfies the criteria in §1.2.

2.5.3. $TlNO_3$ phase II. The atomic coordinates of $TlNO_3$ phase II, which is stable between 352 and 417 K, were determined by Sastry & Sequeira (1997). With $a = 10.435$ Å and $c = 7.451$ Å at 388 K in space group $P3_1$, the coordinates are comparable to those in Tables 3(*a*) and 3(*b*), although the paper does not refer to the work of Pohl & Gross (1993). Measurements such as those outlined in §1.3.1 should be made for all family members.

2.6. $(NH_4)_2Tm(NO_3)_5$ and family

The double nitrate $(NH_4)_2Tm(NO_3)_5$ and its family members, including $Rb_2Sc(NO_3)_5$ and $Rb_2Y(NO_3)_5$, are considered out of database sequence in view of the similarity to the $RbNO_3$ phase IV family (see §2.5).

2.6.1. $(NH_4)_2Tm(NO_3)_5$. The structure was solved by Manek & Meyer (1993*a*) on the basis of 3209 independent $F_{\rm obs} \gtrsim 2\sigma(F_{\rm obs})$ and refined to $R = 0.062$ and $wR = 0.034$ for the atomic coordinates in Table S5(*a*)[1] after an origin shift of 0.1914 to minimize $\Sigma\Delta z_i$. The largest displacement component of any atom from a corresponding Wyckoff position in space group $P3_121$ is found for the O10/O15 pair; each atom has $\Delta y = 1.25$ Å. In addition, 20 components have $\Delta\xi \gtrsim 0.5$ Å with $0.33 \gtrsim u_{\rm eq} \gtrsim 0.11$ Å. Both independent NH_4^+ ions, in general 3(*a*) positions, undergo maximum $\Delta\xi$ component displacements of 0.68 Å in satisfying the 6(*c*) Wyckoff position of space group $P3_121$. All subgroup–supergroup displacements in $(NH_4)_2Tm(NO_3)_5$ hence satisfy the ferroelectricity criteria given in §1.2.

2.6.2. $Rb_2Y(NO_3)_5$. Crystals were grown from component nitrates heated to ~600 K, and the structure was refined by Manek & Meyer (1993*b*) using 2849 independent reflections with $F_{\rm obs} \gtrsim 2\sigma(F_{\rm obs})$ to give $R = 0.121$ and $wR = 0.072$. The resulting atomic coordinates, after an origin shift of −0.0350 to minimize $\Sigma\Delta z_i$, are presented in Table S5(*b*). The choice of *a* and *b* axes is enantiomorphically related to that in Table S5(*a*). Unlike in $(NH_4)_2Tm(NO_3)_5$, which contains supergroup-related NH_4^+ ions, the Rb2 and Y atoms in $Rb_2Y(NO_3)_5$ (atomic numbers 37 and 39) appear to be related by the 6(*c*) Wyckoff position, which suggests chemical identity. The large *R* value and coordination number reported, with Y = 10, Rb1 = 8, Rb2 = 6, and $0.2 \lesssim u_{\rm all\ atoms} \lesssim 0.4$ Å, may be consistent with misassignment. All but eight atoms have displacement components with $\Delta\xi < 1$ Å (see Table S5*b*); of these eight atoms, the displacements Δx(O8), Δx(O11) $\simeq$ 1.7 Å and Δy(O8), Δy(O11) $\simeq$ 1.8 Å are the largest, with six other $\Delta\xi$ values being ~1.2 Å. If reinvestigation confirms the structure and $Rb_2Y(NO_3)_5$ is shown to exhibit ferroelectricity then an upper limit of ~1.2 Å, or even ~1.5 Å, for maximum atomic displacements at phase transitions may be too small. However, comparable $\Delta\xi$ magnitudes are smaller in the other family members.

2.6.3. $Rb_2Sc(NO_3)_5$. The structure was refined by Meyer & Stockhause (1994) to $R = 0.065$ using 2292 independent reflections with $F_{\rm obs} > 2\sigma(F_{\rm obs})$ to give the atomic coordinates shown in Table S5(*c*); an origin shift of −0.0098 has been applied to minimize $\Sigma\Delta z_i$. The $\Delta\xi$ displacements in Table S5(*c*), as in Tables S5(*a*) and S5(*b*), are generally consistent with the criteria for ferroelectricity given in §1.2. Like the Rb2 and Y atoms in $Rb_2Y(NO_3)_5$ (§2.6.2), the Rb2 and Sc atoms in $Rb_2Sc(NO_3)_5$ are related by a 6(*c*) Wyckoff position in the supergroup. It is noted that the largest Δz value is ~0.85 Å for atoms O11, O14 and O15. The thermal/static displacement range $0.32 \gtrsim u^{33} \gtrsim 0.16$ Å along the polar direction is such that T_c may prove lower than the $\Delta\xi$ displacements imply, although the atomic arrangement does not allow T_c to be estimated by (1).

Tables S5(*a*), S5(*b*) and S5(*c*) show that the unit cell, chemical formula and structure of all three double nitrates are comparable and likely to be ferroelectric, although metastable equilibrium positions may exist in one or more, such as in $RbNO_3$ phase IV (see §2.5). Structural confirmation would suggest that other members of the $Rb_2Ln(NO_3)_5$ family (Ln = Eu–Lu) can be identified as potential ferroelectrics (see also §1.3.1).

2.7. Na_3ReO_5

A total of 1091 independent reflections with $F^2_{\rm obs} > 2\sigma(F^2_{\rm obs})$ were measured and corrected for absorption by Vielhaber & Hoppe (1992). Solution followed by refinement led to $R = 0.0614$ and $wR = 0.0608$. The structure contains distorted triangular bipyramidal ReO_5^{3-} ions, in which z(O3,O4,O5) $\simeq$ z(Re) with z(O1), z(O2) $\simeq$ z(Re) ± 1.4 Å, hence z(O-atom charge center) $\simeq$ z(Re) ± 0.03 Å. The resulting ReO_5^{3-} ionic contribution to P_s is thus small, as is the contribution of the Na^+ ions (see Table S6, in which the origin has been displaced −0.0042 along the *c* axis to minimize $\Sigma\Delta z_i$). Three atoms occupy special 3(*a*) or 3(*b*) positions in space group $P3_121$[1] under displacements Δy(Rb) = 0.23 Å, Δy(Na1) = 0.33 Å, Δx(O2) = 0.95 Å and Δz(O2) = 1.45 Å from the positions in $P3_1$. The remaining atoms then form pairs related by the 6(*c*) position in space group $P3_121$ for displacements no larger than 0.59 Å. All atoms in the structure as refined hence satisfy the criteria for ferroelectric behavior given in §1.2. Confirmation of the structural details is desirable, as is application of the methods noted in §1.3.1.

2.8. $Nd_{14}(GeO_4)_2(BO_3)_6O_8$ and family

Ilyukhin & Dzhurinskii (1994) reported the structures of the rare-earth borogermanates $Nd_{14}(GeO_4)_2(BO_3)_6O_8$ and $Sm_{14}(GeO_4)_2(BO_3)_6O_8$ in space group $P3_1$. The Nd compound was measured at 295 K and refined to $R = 0.079$ on the basis of 3902 independent reflections; the Sm compound at 170 K was refined to $R = 0.042$ using 2219 reflections, with $I_{\rm obs} > 2\sigma(I_{\rm obs})$ for both.

2.8.1. $Nd_{14}(GeO_4)_2(BO_3)_6O_8$. The final atomic coordinates of the Nd compound (as given in Table S7, in which an origin shift of −0.0122 has been applied along the polar axis to minimize $\Sigma\Delta z_i$) show that all 14 independent Nd atoms (atom Nd14 was reported to be split between two partially occupied sites 0.51 Å apart, 63% in the Nd14 site and 37% in the Nd14′ site) form related pairs with $0.7 \gtrsim \Delta\xi \gtrsim 0.4$ Å of a general Wyckoff 6(*c*) position in space group $P3_121$. In addition, 32 of the 34 O atoms and four of the six B atoms form similarly related pairs with $1.4 \gtrsim \Delta\xi \gtrsim 0.3$ Å from 6(*c*) positions and x, y(Ge1) $\simeq$ y, x(Ge2). Atoms O24, O25 and O26 are reported to be split between pairs of sites $\lesssim 1.4$ Å apart, each with 50% occupancy; split pairs are related to single O atoms by Wyckoff 6(*c*) positions with $2.0 \gtrsim \Delta\xi \gtrsim 0.3$ Å. Assuming that the approach to space group $P3_121$ by 50 of the 56 independent atoms (including three B and two O atoms) is indicative of a possible transition to higher symmetry, then added translations of $a_1/2$, $a_2/2$ or $c/2$ produce paired 6(*c*) relationships in *all* remaining atomic cooordinates, with maximum displacements of ~1.5 Å. Thus, z(Ge2) can be replaced by $\frac{1}{2} + z$, z(O27) by $\frac{1}{2} + z$, x(O30) by $\frac{1}{2} + x$, y(O30) by $\frac{1}{2} + y$, z(B1) by $\frac{1}{2}+z$, z(B3) by $\frac{1}{2}+z$ and z(B4) by $\frac{1}{2}+z$ (as in Table S7). Comparable results follow if the x, y or z coordinate of the other member of each pair of related atoms is replaced by $\frac{1}{2}+x$, $\frac{1}{2}+y$ or $\frac{1}{2}+z$. Structural reinvestigation is necessary to confirm the possibility of such replacement.

The resulting Δx, Δy and Δz displacements of all atoms in Table S7 fully satisfy the structural criteria for ferroelectricity given in §1.2. The Nd atoms occupy a variety of O polyhedra, ranging from distorted octahedral for Nd13 through 7- (×3), 8- (×5), 9- (×4) and 11-coordination (the number of each kind of polyhedron is given in parentheses). The Ge atoms form distorted tetrahedra, with $d_{\rm Ge-O}$ ranging from 1.753 to 2.013 Å and angles of 105.6–114.3°. The B atoms lie near the centers of the O triangles, with $d_{\rm B-O}$ ranging from 1.338 to 1.374 Å (except for atom B6, which has six $d_{\rm B-O}$, three from 100% and three from 50% occupied O sites, ranging from 1.340 to 1.427 Å) and angles ranging from 114.1 to 129.5° (22–158° for B6). The force constant in (1) is unknown for tetrahedral and triangular sites, and hence T_c cannot be estimated for this structure.

X-ray scattering by 14 Nd atoms (atomic number 60) dominates that by Ge, B and O atoms, opening the possibility that some lighter-atom coordinates may be misassigned by $a/2$ or $c/2$, as noted above. Half-cell shifts in seven coordinates for six lighter atoms of the 170 coordinates varied are likely to have little effect on the final value of R, although the coordinates reported give normal $\langle d_{\rm Nd-O}\rangle$, $\langle d_{\rm Ge-O}\rangle$ and $\langle d_{\rm B-O}\rangle$ distances of 2.454, 1.775 and 1.352 Å, respectively.

2.8.2. $Sm_{14}(GeO_4)_2(BO_3)_6O_8$. The atomic coordinates at 170 K presented by Ilyukhin & Dzhurinskii (1994) are nearly identical to those in Table S7 and hence are also consistent with ferroelectricity. Further structural study of this family is expected to be revealing, particularly with regard to the possibility of phase transitions with integral change in cell volume, as in the case of $YMnO_3$ (Abrahams, 2001; see also §1.3.1).

2.9. $CsHgCl_3$ family

2.9.1. $CsHgCl_3$. Structural refinement reported by Albarski *et al.* (2000), without reference to the previous study of $Cs_{0.7}(NH_4)_{0.3}HgCl_3$ by Kabadou *et al.* (1998) (see §2.9.2), was based on 1724 independent reflections with $I > 2\sigma(I)$ and led to $R = 0.0228$ and $wR = 0.0501$. The resulting atomic coordinates are transformed in space group $P3_2$ and reordered in Table S8(a) for direct comparison with those of Kabadou *et al.* (1998) in Table S8(b) (an origin displacement of 0.18701 has been applied in order to minimize $\Sigma\Delta z$ for all atoms). Table S8(a) shows that the three independent Cs and three Hg atoms meet the symmetry of space group $P3_212$ for $0.18 \gtrsim \Delta\xi \gtrsim 0.04$ Å with $u_{\rm eq}({\rm Cs,Hg}) \leq 0.24$ Å, while the largest displacement among the nine independent Cl atoms is 0.59 Å for atom Cl3 with $u_{\rm eq}({\rm Cl3}) = 0.23$ Å. The structural criteria for ferroelectricity given in §1.2 are hence satisfied.

2.9.2. $Cs_{0.7}(NH_4)_{0.3}HgCl_3$. The structure of this substituted family member was solved in space group $P3_2$ by Kabadou *et al.* (1998) and refined by the use of 700 independent reflections with $I_{\rm obs} > 2\sigma(I_{\rm obs})$. The final R value was 0.057 for the atomic coordinates in Table S8(b) (the origin has been displaced by 0.0012 to minimize $\Sigma\Delta z$ for all atoms). The largest displacement among the three independent Cs and Hg atoms for a transition to space group $P3_212$ is $\Delta z({\rm Cs1}) = 0.17$ Å, whereas $u_{\rm eq}({\rm Cs1}) = 0.21$ Å (*cf.* §2.9.1). However, the 12 Cl atomic displacement components with $0.54 \geq \Delta\xi \geq 0.17$ Å, together with 27 geometrically located H atoms that have $1.07 \geq \Delta\xi \geq 0.24$ Å, satisfy the structural ferroelectricity criteria of §1.2. All Cs sites are reported to be 70% occupied by Cs^+ and 30% occupied by NH_4^+. The atomic coordinates of the Cs, Hg and Cl atoms in both family members are very similar (see Tables S8a and S8b). The successful partial substitution of NH_4^+ (octahedral radius $\simeq$ 1.61 Å) for Cs^+ (~1.67 Å) suggests the possible substitution of Rb^+ (~1.52 Å) and Tl^+ (~1.50 Å) as extensions of the $CsHgCl_3$ family.

All three Hg atoms in both structures occupy distorted octahedra formed by six Cl atoms, with axes inclined to the polar direction; each Hg atom is located within 0.03 Å of a special plane at $z = \frac{1}{6}, \frac{1}{2}$ or $\frac{5}{6}$. The net displacement of atom Hg1 from its octahedral charge center is 0.25 Å, that of atom Hg2 is 0.23 Å and that of atom Hg3 is 0.07 Å based on Table S8(b). Corresponding displacements based on Table S8(a) are 0.10, 0.16 and 0.10 Å respectively. Assuming that both reports are equally reliable, with no significant change caused by NH_4^+-ion substitution, then the largest atomic displacement is that of the $Hg2/Cl_6$ octahedron, with $\Delta z_{\rm max} = 0.195$ Å. Assuming that (1) is directly applicable to Cl octahedra results in a value of $T_c = 760$ K, with an uncertainty of comparable magnitude. It is notable that Kabadou *et al.* (1998) report an anomalous peak at 449 K in the dielectric permittivity of $Cs_{0.7}(NH_4)_{0.3}HgCl_3$, over the frequency range 10^3–10^6 Hz, with maximum strength at ~5 kHz. Measurements as outlined in §1.3.1 may show that the dielectric anomaly occurs at T_c.

2.10. $Ba_2Cu_2AlF_{11}$

The structure was solved in space group $P3_2$ and refined by Dupont *et al.* (1998) using 2476 reflections with $F_{\rm obs} > 4\sigma(F_{\rm obs})$. The final R value is 0.062 for the atomic coordinates in Table S9 (an origin shift of 0.2151 has been applied in order to minimize $\Sigma\Delta z$ for all 16 atoms). The Cu atoms form distorted edge-sharing octahedra that give Cu_2F_9 entities linked to regular AlF_6 octahedra, which results in twisted chains along the polar direction. Examination of Table S9 shows that the location of each atom is related to a corresponding Wyckoff position in space group $P3_212$. The maximum atomic displacement components between such positions are $\Delta x({\rm F8,F9}) \simeq 0.6$, $\Delta y({\rm F1,F2}) \simeq 0.6$ and $\Delta z({\rm F3,F6}) \simeq 0.9$ Å, with $\Delta z({\rm Al}) \simeq 1.2$ Å (between the Al-atom location in space group $P3_2$ and Wyckoff position $x, 2x, \frac{1}{3}$ in the supergroup). All $\Delta\xi$ are less than required in §1.2, and hence $Ba_2Cu_2AlF_{11}$ meets the structural criteria for ferroelectricity. Although the large magnitude of Δz(Al) is indicative of a high T_c, z(Al) differs by only 0.225 Å from the charge center of its F octahedron, which corresponds to $T_c \simeq 1015$ K in (1). The large Δz(Al) and the normal displacement of Al from its octahedral center suggest the possibility of an integral change in lattice parameter at T_c, such as the factor of 3 in unit-cell volume at the phase transition of $YMnO_3$ (from space group $P6_3cm$ to $P6_3/mmc$ at its Curie point; Łukaszewicz & Karat-Kalicińska, 1974). High-temperature X-ray diffraction measurements together with those outlined in §1.3.1 may be revealing.

2.11. KYF_4 family

2.11.1. KYF_4. A selected subset of 1286 absorption-corrected reflections with $I_{obs} > 3.3\sigma(I_{obs})$, from a total of 3045 measured at room temperature, were used by Le Fur *et al.* (1992*a*) in solving the structure. The full data set led to a final R_F value of 0.038 for the atomic coordinates in Table 4 (an origin shift of −0.3195 minimizes $\Sigma\Delta z_i$). Table 4 shows that the largest Δz displacement between an atom in space group $P3_1$ and its corresponding position in supergroup $P3_121$ is 0.48 Å, for atoms F4, F6, F10 and F12. Corresponding values of Δz for the metal atoms range from ~0.01 to 0.30 Å for K atoms and from 0.12 to 0.16 Å for Y atoms. The largest Δx or Δy displacements range from 1.0 to 1.2 Å for atoms F2, F8, F3, F5, F9, F11, F10 and F12. The criteria for ferroelectricity given in §1.2 are clearly satisfied, and hence the methods in §1.3.1 are applicable.

Three Y atoms form monocapped YF_7 trigonal prisms with $\langle d_{Y-F}\rangle = 2.225$ Å, three pentagonal YF_7 bipyramids have $\langle d_{Y-F}\rangle = 2.227$ Å, and six independent K atoms occupy distorted KF_8 cubes with $\langle d_{K-F}\rangle = 2.759$ Å. The Y-atom contribution to the force constant, κ in (1), with less ionic bonds, is expected to exceed the K-atom contribution. The maximum displacement by a Y atom from the charge center of its YF_7 pentagonal bipyramidal is 0.176 Å (Y1). Assuming that κ is identical to that in (1) gives $T_c \simeq 610$ K, with a nominal uncertainty of ~50 K that is increased by an unknown factor as a result of the eight Δx(F), Δy(F) displacements greater than 1 Å (see Table 4).

2.11.2. $KY_{0.95}Er_{0.05}F_4$. Le Fur *et al.* (1992*b*) reported this structure, refined using 2667 reflections with $I_{obs} > 3.5\sigma(I_{obs})$ to final values of $R = 0.032$ and $wR = 0.035$. Half of the LnF_7 bipyramids were found to contain an unsubstituted Y atom; the other half contain 90% Y and 10% Er. Comparison of corresponding atomic coordinates following an origin shift of −0.3435 (the atomic numbering and order differ in the two studies, with F12 in the $\bar{y}, x-y, \frac{1}{3}-z$ location relative to x, y, z in Table 4) reveals no differences greater than 0.08 Å in x, 0.07 Å in y and 0.08 Å in z. The properties of $KY_{0.95}Er_{0.05}F_4$ are hence expected to resemble closely those of KYF_4.

2.12. $SrS_2O_6\cdot 4H_2O$

Fábry (1995) reported the $SrS_2O_6\cdot 4H_2O$ structure in a unit cell with doubled a_1 and a_2 axes and space group $P3_2$, based on the presence of numerous weak reflections, in contrast to earlier determinations (ZEKGA 135 399; ASBSD B47 12) in the smaller cell with space group $P6_2$ or $P6_422$, respectively. A total of 10 330 independent I_{all}, 5789 with $I_{obs} > 3\sigma(I)$, were used in the refinement, for which the Sr- and O*W*-atom positions, where O*W* denotes an O atom belonging to a water of hydration, were taken directly from the smaller cell. The dithionate ions appeared disordered in the smaller cell but are compatible with eight different ordered arrangements in the larger cell, one being favored by the intensity data. Refinement then led to $R_{all} = 0.111$ and $R_{obs} = 0.044$ for the atomic coordinates in Table S10. Refinement in the alternative space groups $P3_1$, $P6_2$, $P6_4$, $P6_222$ and $P6_422$ gave larger indicator values; results in space group $P3_121$ were not reported.

Table S10 (in which the reported origin is displaced by 0.33011 to minimize $\Sigma\Delta z$) contains no Δz values greater than u_{eq}. All $\Delta\xi$ magnitudes required to satisfy space-group $P3_121$ symmetry are less than the corresponding u_{eq} in half of the 52 independent atoms, including the four Sr atoms. The remaining 26 atoms, however, have $1.63 \geq \Delta x, \Delta y \geq 0.17$ Å. If the structure determination is reliable, then the atomic positions generally satisfy the criteria of §1.2. Since $\Delta z_{max} = 0.14$ Å, T_c is not likely to be high if the potential barrier associated with the larger Δx and Δy displacements is readily overcome, in which case, ferroelectric hysteresis may be readily observable at room temperature (see §1.3.1).

2.13. $Cu_3PbTeO_6(OH)_2$

The structure of the mineral parakhinite, $Cu_3PbTeO_6(OH)_2$, was determined (Burns *et al.*, 1995) by the use of 744 symmetry-independent reflections with $I_{obs} \geq 2.5\sigma(I_{obs})$, corrected by an empirical absorption factor and modeling the crystal as a plate. An additional 380 reflections with a plate-glancing angle of less than 11° were discarded. All crystals examined were twinned, thus preventing the observation of uniaxial interference figures. An earlier report (AMMIA 63 1016) gave the space group as $P6_222$ or $P6_422$, but a structure solution could be found in neither. Burns *et al.* (1995) suggest that the twinning may originate in a possible transition from a higher-temperature phase with $P6_2$ symmetry. Structural refinement in $P3_2$ gave final values of $R = 0.081$ and $wR = 0.087$ for the coordinates in Table S11 (with an origin shift of 0.3103 to minimize $\Sigma\Delta z$). The locations of all 13 independent atoms, except the H atoms, which were not determined, are related to corresponding positions in space group $P3_212$, with $\Delta x_{max} = 1.41$ Å for atoms Cu2 and Cu3, $\Delta y_{max} = 0.95$ Å for Te, and $\Delta z_{max} = 0.71$ Å for Te. The 1.41 Å displacement exceeds the range noted in §1.2, and hence spontaneous polarization reversal at room temperature may not be possible but will become more likely at higher temperatures if $|\Delta\xi|$ decreases appreciably on heating.

Burns *et al.* (1995) inferred that H atoms were bonded to OH1 and OH2; it can be seen from Table S11 that, if the structure and space-group–supergroup relationship are confirmed, with hypothetical coordinates $x, 2x, \frac{1}{3}$ for each ($x \simeq 0.474$ for H1 and 0.211 for H2), H1 forms a symmetrical bond between O3 and OH1, and H2 forms a symmetrical bond between O1 and OH2, unless either or both H atoms are disordered.

The asymmetric unit contains an irregular TeO_6 octahedron, three independently distorted CuO_6 octahedra and one irre-

Table 4
Atomic positions for KYF_4 at room temperature (Le Fur *et al.*, 1992*a*), with hypothetical x', y' and z' coordinates and Δx, Δy, Δz and u^{33} displacements in Å.

$a = 14.060$ (10) and $c = 10.103$ (10) Å; $z^* = z - 0.3195$, with $\Delta x = (x - x')a$, $\Delta y = (y - y')a$ and $\Delta z = (z^* - z)c$.

	Wyckoff position $P3_1$, $P3_1211$	x	y	z^*	x'	y'	z'	Δx	Δy	$\Delta z^{\simeq}$	u^{33}
K1	3(*a*), 3(*a*)	0.7818 (2)	0.7190 (2)	−0.0282 (2)	0.7504	0.7504	0	0.442	−0.442	−0.285	0.12
K2	3(*a*), 3(*a*)	0.2677 (2)	0.2208 (3)	0.0057 (3)	0.2443	0.2443	0	0.329	−0.330	0.046	0.16
K3	3(*a*), 6(*c*)†	0.1050 (2)	0.3945 (3)	−0.0331 (4)	0.0851	0.4247	−0.0034	0.280	−0.425	−0.300	0.17
K6	3(*a*), 6(*c*)	0.4549 (3)	0.0652 (3)	−0.0264 (4)	0.4247	0.0851	0.0034	0.425	−0.280	−0.301	0.15
K4	3(*a*), 6(*c*)	0.6111 (2)	0.8778 (2)	0.0028 (3)	0.5851	0.9122	0.0021	0.366	−0.484	0.005	0.13
K5	3(*a*)	0.9466 (3)	0.5591 (2)	−0.0018 (3)	0.9122	0.5851	−0.0021	0.484	−0.366	0.005	0.16
Y1	3(*a*), 6(*c*)	0.12871 (6)	0.88764 (6)	−0.0135	0.09321	0.91451	0.0018	0.499	−0.378	−0.155	0.09
Y4	3(*a*)	0.94137 (7)	0.05770 (7)	−0.0171 (2)	0.91451	0.09321	−0.0018	0.378	−0.499	−0.155	0.12
Y2	3(*a*), 6(*c*)	0.28157 (7)	0.73104 (7)	−0.0238 (8)	0.24375	0.75554	−0.0082	0.531	−0.344	−0.158	0.09
Y3	3(*a*)	0.78003 (7)	0.20592 (6)	−0.0074 (1)	0.75554	0.24375	0.0082	0.344	−0.532	−0.158	0.08
Y5	3(*a*), 6(*c*)	0.45256 (7)	0.54579 (7)	−0.0215 (1)	0.41959	0.57477	−0.0096	0.464	−0.407	−0.120	0.11
Y6	3(*a*)	0.60374 (7)	0.38662 (6)	−0.0024 (7)	0.57477	0.41959	0.0096	0.407	−0.464	−0.121	0.07
F1	3(*a*), 6(*c*)	0.1304 (7)	0.9342 (7)	−0.2280 (9)	0.095	0.967	−0.270	0.50	−0.46	0.42	0.16
F7	3(*a*)	0.000 (1)	0.059 (1)	0.312 (2)	0.967	0.095	0.270	0.46	−0.51	0.42	0.25
F2	3(*a*), 6(*c*)	0.0692 (8)	0.8779 (8)	0.199 (1)	0.096	0.963	0.197	−0.38	−1.20	0.02	0.17
F8	3(*a*)	0.0489 (8)	0.1223 (8)	−0.195 (2)	0.963	0.096	−0.197	1.20	0.37	0.02	0.24
F3	3(*a*), 6(*c*)	0.2105 (8)	0.5934 (8)	0.125 (1)	0.2366	0.5162	0.123	−0.37	1.09	0.02	0.18
F5	3(*a*), 6(*c*)	0.7372 (5)	0.2023 (5)	0.2133 (8)	0.7634	0.2796	0.211	−0.37	−1.09	0.02	0.11
F4	3(*a*), 6(*c*)	0.334 (1)	0.7286 (7)	0.309 (1)	0.301	0.7594	0.263	0.46	−0.43	0.46	0.21
F6	3(*a*)	0.7901 (6)	0.2684 (6)	−0.2163 (9)	0.7594	0.301	−0.263	0.43	−0.46	0.47	0.13
F9	3(*a*), 6(*c*)	0.3954 (6)	0.5413 (6)	0.1908 (8)	0.4257	0.6267	0.1695	−0.43	−1.20	0.22	0.13
F11	3(*a*)	0.5440 (6)	0.2863 (6)	0.1852 (8)	0.5743	0.2010	0.1639	−0.43	1.20	0.22	0.13
F10	3(*a*), 6(*c*)	0.4618 (7)	0.5950 (6)	0.7645 (8)	0.4281	0.6799	0.7172	0.47	−1.19	0.48	0.14
F12	3(*a*)	0.6057 (7)	0.3368 (7)	0.6637 (1)	0.5720	0.2519	0.6161	0.47	1.19	0.48	0.16
F13	3(*a*), 6(*c*)	0.7727 (6)	0.7346 (6)	−0.283 (1)	0.7495	0.7740	−0.256	0.33	−0.55	−0.27	0.14
F14	3(*a*), 6(*c*)	0.8133 (9)	0.7262 (6)	0.229 (1)	0.7740	0.7495	0.256	0.55	−0.33	−0.27	0.16
F15	3(*a*), 6(*c*)	0.2533 (6)	0.2289 (6)	0.2593 (1)	0.2242	0.2625	0.253	0.41	−0.47	0.06	0.15
F16	3(*a*), 6(*c*)	0.8050 (6)	0.0719 (6)	0.0864 (8)	0.7758	0.0383	0.080	0.41	0.47	0.06	0.14
F17	3(*a*), 6(*c*)	0.1339 (6)	0.3916 (6)	0.2234 (8)	0.1094	0.4193	0.2565	0.34	−0.39	−0.33	0.12
F24	3(*a*), 6(*c*)	0.4469 (7)	0.0849 (6)	−0.2896 (9)	0.4193	0.1094	−0.2565	0.39	−0.34	−0.33	0.15
F18	3(*a*), 6(*c*)	0.0941 (7)	0.4031 (8)	−0.284 (1)	0.0817	0.4431	−0.254	0.17	−0.56	−0.30	0.16
F23	3(*a*)	0.4830 (7)	0.0692 (7)	0.2240 (9)	0.4431	0.0817	0.254	0.56	−0.18	−0.30	0.14
F19	3(*a*), 6(*c*)	0.1535 (6)	0.7561 (7)	0.0808 (9)	0.1073	0.7188	0.0790	0.65	0.53	0.02	0.14
F21	3(*a*), 6(*c*)	0.9390 (6)	0.5741 (7)	0.2561 (9)	0.8927	0.6115	0.2543	0.65	−0.53	0.02	0.14
F20	3(*a*), 6(*c*)	0.5874 (6)	0.8816 (7)	0.2576 (9)	0.5595	0.9127	0.2555	0.39	−0.44	0.02	0.13
F22	3(*a*), 6(*c*)	0.9438 (6)	0.5316 (6)	−0.2534 (8)	0.9127	0.5595	−0.2555	0.44	−0.39	0.02	0.12

† See footnote **1** for equivalent positions.

gular $PbO_6(OH)_2$ polyhedron; all have small effective polarizations because of the near-coincidence of z(Te), z(Cu) and z(Te) with their polyhedral O-atom charge centers, despite the fact that $\Delta z(\mathrm{Te}) = 0.71$ Å and $\Delta z(\mathrm{Cu1}) = 0.67$ Å. $Cu_3PbTeO_6(OH)$ is hence a candidate for testing, as noted in §1.3.1.

2.14. $HRe(CO)_4$

Ab initio solution of the X-ray powder diffraction pattern of α-poly[$\{ReH(CO)_4\}_n$] followed by Rietveld refinement (Masciocchi *et al.*, 2000) gave $R_p = 0.055$, $wR_p = 0.071$ and $R_F = 0.054$. The resulting atomic coordinates are given in Table S12, with an origin shift of −0.0084 that minimizes $\Sigma\Delta z$ for the three independent Re atoms. Recognition of a 3_1 or 3_2 axis in the Patterson function led to analysis in space group $P3_1$, which revealed three independent Re atoms. Use of either of the supergroups $P3_121$ or $P3_112$ 'dramatically worsened pattern matching' in subsequent refinement.

Examination of Table S12 reveals a range of displacement components between the refined atomic coordinates in space group $P3_1$ and those anticipated in space group $P3_121$ with $1.10 \geq \Delta x, \Delta y \geq 0.02$ and $0.25 \geq \Delta z \geq 0.01$ Å. The structure hence satisfies the criteria for ferroelectricity given in §1.2, although 26 Δx and Δy components exceed 0.63 Å. Accepting the u_{iso} values in Table S12 (Re was assigned as 0.19 Å, the remainder 0.25 Å), the $\Delta\xi$ displacements satisfy the criteria in §1.2 and a phase transition at moderate temperatures appears likely. Further investigation by the methods of §1.3.1 is necessary for confirmation.

2.15. $Ni_2(NH_3)_9Mo(CN)_8{\cdot}2H_2O$

The structure at 153 (2) K was determined by Meske & Babel (1999) and refined on the coordinates presented in Table S13, with an origin displacement of −0.12993 to minimize $\Sigma\Delta z_{\mathrm{i}}$. The compound decomposes easily, with positional disorder exhibited by the N1/N18, O1/O2 and O3/O4 pairs. Table S13 shows that all atoms have displacement components from corresponding locations in space group $P3_121$ of less than $\Delta x \simeq 1.7$ Å, $\Delta y \simeq 1.9$ Å and $\Delta z \simeq 1.4$ Å, with 45 having

$0.6 \gtrsim \Delta\xi \gtrsim 0.3$ Å and 42 having $\Delta\xi \lesssim 0.3$ Å. The exception is Δx(NH13) = Δy(NH13) = 2.57 Å taking the coordinates as reported; both values reduce to ~0.4 Å if a negative sign has been omitted in the report. Many $\Delta\xi$ displacement magnitudes along each axis are larger than usual, resulting in increased uncertainty. A new diffraction study of a fully ordered crystal is necessary for property prediction at a higher confidence level, but the methods of §1.3.1 would be definitive.

2.16. $Ca_{1.89}Ta_{1.80}Sm_{0.16}Ti_{0.10}O_7$ (6T polytype)

The structure of 6T-$Ca_2Ta_2O_7$, a polytype doped with ~6 mol% $Sm_2Ti_2O_7$, has recently been reported by Grey & Roth (2000). Initial determination of the Ca/Ta ordering based on Rietveld methods and an experimental powder pattern led to a model with only metal atoms that refined in space group $P3_121$ to $R = 0.13$ for 2660 reflections with $F > 4\sigma(F)$. O atoms located from difference maps completed the model, which refined to $R = 0.07$. Unusually large displacement factors ($0.17 \leq u_{\rm iso} \leq 0.22$ Å) for several O atoms led to refinement in space group $P3_1$, with final R values of 0.038 (0.051 for all reflections) after a change in origin (see below). Unlike the 5M polytype (formed by $Ca_2Ta_2O_7$ doped with ~10 mol% $Sm_2Ti_2O_7$), significant ordering of Sm and Ti atoms into specific Ca and Ta sites was not reported. The final coordinates in Table S14(a) show that, of a total of 132 independent atomic coordinates, 53 are displaced from related locations in space group $P3_121$ by $0.56 \geq \Delta\xi \geq 0.11$ Å, with 52 of the remaining $\Delta\xi$ being ≤ 0.05 Å. All displacements satisfy the structural criteria for ferroelectricity given in §1.2, although Table S14(a) shows that a phase transition from $P3_1$ to $P3_121$ would equate Ca and Ta atoms in two pairs of atomic positions.

Resolution of this difficulty (Grey, 2002) is achieved by an origin change of $+(\frac{1}{3}, \frac{2}{3}, \frac{1}{6})$ (see Table S14b). A total of 123 atomic coordinates following refinement in space group $P3_1$ differ from those in $P3_121$ by $\Delta\xi \leq 0.03$ Å, with $\Delta\xi$ generally less than $u_{\rm iso}$. The largest $\Delta\xi$ is ~0.12 Å for Δx(Ta3), Δy(Ta3), Δz(Ca1) and Δz(Ca12). Refinement of the $P3_1$ model gave a significantly better fit than the best R value (0.05) in space group $P3_121$, with its high thermal parameters, and hence the criteria of §1.2 are satisfied. The diffraction evidence thus favors ferroelectricity in this polytype, but investigation as outlined in §1.3.1 is necessary for confirmation.

3. Known ferroelectrics and related predictions in space group $P3_1$

3.1. Stillwellite family

The ICSD release 2002/2 reports 16 determinations of materials structurally related to the mineral stillwellite, space group $P3_1$, $a \simeq c \simeq 7$ Å, and formula X[BO(MO$_4$)], where X = La and other rare-earth metals with M = Ge or Si, or X = Ba or Pb with M = As. Composition of the mineral generally includes a range of elements, the study by Callegari *et al.* (1992) reporting X = 0.56 Ce, 0.34 La, 0.04 Th and 0.02 Ca (see Table S15a). Burns *et al.* (1993) report 0.50 Ce, 0.32 La, 0.08 Nd, 0.05 Th, 0.03 Pr, 0.01 Ca and 0.01 Sm (see Table S15b).

After the stillwellite structure was found to satisfy the criteria in §1.2, and hence could be predicted to be ferroelectric, a literature search revealed that $LaBGeO_5$ had been reported to undergo a ferroelectric phase transition at 790–800 K (Stefanovich *et al.*, 1992; Onodera *et al.*, 1993), with $P_s = 2.7 \times 10^{-2}$ C m^{-2}.[5] Strukov *et al.* (1997, 1998) subsequently reported $T_c = 802$ K with $\Delta S = 0.95$ (3) J mol^{-1} K^{-1} and $P_s = 2.4$ (8) $\times 10^{-2}$ C m^{-2}, magnitudes consistent with the displacements in Table S15(c).

3.1.1. (Ce,La)BSiO$_5$. The atomic coordinates in Table S15(a), with an origin shift of 0.0096 along the polar c axis to minimize $\Sigma\Delta z_i$, are based on 1070 unique $I_{\rm exp}$, of which 1043 have $I_{\rm exp} \geq 5\sigma(I_{\rm exp})$. The final R value is 0.015 for all $I_{\rm exp}$ and 0.014 for the observed set. There are 11 displacements with $\Delta\xi \geq u_{\rm iso}$, the largest being for atom O5 ($\Delta x = 0.40$ Å and $\Delta z = 0.29$ Å) and the next largest being for the B atom ($\Delta y = 0.12$ Å). Callegari *et al.* (1992) note that the absolute configuration of their specimen corresponds to $P3_2$, but gave the results in $P3_1$. The refinement by Burns *et al.* (1993) used 1003 independent $F > 5\sigma(F)$ with $R = 0.027$ and $wR = 0.033$. The sense of their x and y coordinates is reversed, equivalent positions with atomic renumbering are used, and the origin is displaced by 0.8326 for direct comparison with the values in Table S15(a). All coordinates in both tables agree closely, the primary difference between the two sets being the disorder reported in Table S15(b) for the atom at the O5 site; the data are also comparable to earlier results (KRISAJ 12 258). The maximum $\Delta\xi$ displacements between positions in space group $P3_1$ and in the supergroup are again reported in atom O5 (and atom O5′), with $|\Delta z| \simeq 0.33$ Å and $|\Delta x| = |\Delta y| \simeq 0.20$ Å, which are comparable with $\Delta\xi$(O5) in Table S15(a). The structural criteria for ferroelectricity given in §1.2 are hence satisfied by both mineral stillwellite determinations.

3.1.2. LaBGeO$_5$. The structure of synthetic $LaBGeO_5$, which is isostructural with mineral stillwellite, was determined by Kaminskii *et al.* (1990) and Belokoneva *et al.* (1991, 1997). Refinement gave the atomic coordinates in Table S15(c), following an origin shift of 0.8505 along the polar axis to minimize $\Sigma\Delta z_i$, with $R = 0.030$ and $wR = 0.028$ on refinement with 1407 unique reflections. Table S15(c) shows all atoms with $0.40 \geq \Delta\xi \geq 0$ Å at the transition from space group $P3_1$ to $P3_121$. As with mineral stillwellite, $|\Delta z$(O5)$| = 0.24$ Å is the largest polar displacement, with Δx(O5) = 0.40 Å. All other Δx and Δy are less than 0.08 Å. The criteria given in §1.2 for the existence of ferroelectricity are thus again satisfied.

3.1.3. PrBGeO$_5$ phase II. Strukov *et al.* (1997) report a first-order ferroelectric–ferroelectric phase transition in $PrBGeO_5$ at ~800 K, with an integral change in cell volume, and a second-order ferroelectric–nonferroelectric phase transition at $T_c = 1016$ K. Belokoneva *et al.* (1998) also detected phase transitions at ~823 and ~1023 K and determined the structure of all three phases in the course of a neutron powder

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[5] P_s magnitudes are customarily given in units of 10^{-2} C m^{-2}, although SI nomenclature requires units such as mC m^{-2}.

diffraction study. Phase II forms above 823 K in space group $P3_1$, and phase III forms below 823 K (see §3.1.4). Rietveld fitting of the powder profile for phase II at 923 K led to the atomic coordinates presented in Table S16(*a*), after an origin shift of 0.842 to minimize $\Sigma\Delta z_i$, with $R_{\rm prof} = 0.055$ and $wR_{\rm prof} = 0.061$ for 2503 observations. The distribution of atomic displacements from phase II to the postulated structure in space group $P3_121$ is comparable to that reported in §§3.1.1 and 3.1.2, the largest magnitudes again being $\Delta x({\rm O5}) = 0.38$ and $\Delta z({\rm O5}) = 0.28$ Å. The Δz displacements are fully consistent with the experimental Curie temperature.

3.1.4. PrBGeO$_5$ phase III. The space group of phase III (see §3.1.3) is also $P3_1$ as in phase II but with $a_{\rm III} \simeq 3^{1/2}a_{\rm II}$ for a unit cell of tripled volume (Belokoneva *et al.*, 1998). The structure of phase III was determined at 293 K from single-crystal X-ray diffraction and high-resolution neutron powder diffraction data. Table S16(*b*) contains the final atomic coordinates refined using 2849 independent single-crystal reflections to $R = 0.038$ and $wR = 0.038$ and modified by an origin shift of 0.6807. The coordinates for atoms O13, O14 and O15 derived from neutron powder diffraction data are substituted in Table S16(*b*) for the single-crystal X-ray diffraction values, since the latter were reported without uncertainties. The neutron powder Rietveld refinement used 5957 profile values and gave $R_{\rm profile} = 0.072$ and $wR_{\rm profile} = 0.063$; the X-ray single-crystal data used 2827 independent $F_{\rm obs}$ and gave a final value of $R \simeq 0.04$.

It is of interest to determine whether phase III satisfies the criteria in §1.2 for a hypothetical transition to nonferroelectric supergroup phase I, in view of the intermediate formation of ferroelectric phase II. Table S16(*b*) shows that the $\Delta\xi$ values for two pairs of O atoms, namely O1/O2 and O4/O5, are unusually large for such a transition ($2.10 \geq |\Delta x,\Delta y| \geq 1.96$ Å). No other value of Δx or Δy is larger than 1.3 Å and no Δz magnitude exceeds 1.04 Å. Although the criteria are not satisfied by phase III, the implication of these large displacements is obviated by the intervention of phase II before the nonferroelectric state is reached. The first-order transition at $T_{\rm III,II} \simeq 810$ K was reported by Stefanovich *et al.* (1995) to exhibit strong thermal hysteresis, with anomalies in dielectric permittivity and loss at the phase transition. Phases II and III generate second harmonics. All atomic displacements in Tables S16(*a*) and S16(*b*) are consistent with this report.

3.1.5. LaBSiO$_5$. The remaining reports of stillwellite-type structures in space group $P3_1$ concern the compositions CeBSiO$_5$, LaBSiO$_5$, BaBAsO$_5$ and PbBAsO$_5$. The earliest study was based on two-dimensional projections of the CeBSiO$_5$ structure (KRISA 12 258). Similarities in the lattice constants and structures of synthetic LaBSiO$_5$ and LaBGeO$_5$, together with the small peak observed at ~400 K in the dielectric permittivity by Ono *et al.* (1996), suggested space groups $P3_121$ above and $P3_1$ below the transition. The structure determined at 293 K was based on 2047 independent reflections with $F_{\rm obs} > 3\sigma(F_{\rm obs})$ and refined to a final $wR(F)$ value of 0.068 for the atomic coordinates in Table S17(*a*), which are shifted 0.0008 along the polar axis; refinement at 443 K in space group $P3_121$ with 1064 independent $F_{\rm obs}$ gave a final $wR(F)$ value of 0.058. The closeness of these coordinates to the values determined in LaBGeO$_5$ at ~295 K (Table S15*c*), to those of Samygina *et al.* (1993) (also KRISAJ 38 61) in the structural determinations of synthetic LaBSiO$_5$ in Table S17(*b*) and to those of Belokoneva *et al.* (1996) in Table S17(*c*) confirms that LaBGeO$_5$ and LaBSiO$_5$ are isostructural at room temperature.

Ono *et al.* (1996) noted that no atom in LaBSiO$_5$ at 293 K is significantly displaced from the experimental locations determined at 443 K in space group $P3_121$. The atomic coordinates of LaBSiO$_5$ in Table S17(*a*) confirm this observation, with Δx, Δy, $\Delta z \leq 0.014$ Å for all atoms with respect to the hypothetical structure in space group $P3_121$. By contrast, the LaBGeO$_5$ arrangement in space group $P3_1$ clearly differs from the supergroup structure, with $\Delta z({\rm O5}) \simeq 0.24$ Å (see Table S15*c*). Furthermore, each $\Delta\xi \leq u^{ii}$ in Table S17(*a*), and in Tables S17(*b*) and S17(*c*), and no atomic coordinate differs significantly from those determined in the supergroup (see Table S17*d*).

The dielectric permittivity anomaly in LaBSiO$_5$ reported by Ono *et al.* (1996) was confirmed by Strukov *et al.* (1998), with transition temperature 412 K and entropy change $\Delta S = 1.05\ (3)$ J mol^{-1} K^{-1}, in agreement with the possibility noted earlier (CAMIA 31 147) that LaBSiO$_5$ may be ferroelectric. Stefanovich *et al.* (1998) report that LaBSiO$_5$ generates second harmonics robustly from 300 to ~415 K, at which temperature their occurence decreases sharply by a factor of ~4 and remains constant to at least 520 K. The physical evidence of a phase transition in LaBSiO$_5$ at ~410 K is hence indubitable. Ferroelectric hysteresis in the lower-temperature phase has not yet been reported; it is possible that LaBSiO$_5$ forms twins as it undergoes a transition to subgroup $C2$ below $T_c \simeq 410$ K (Belokoneva, 2002). Further investigation of LaBSiO$_5$ is expected.

3.1.6. *β*-LaBSiO$_5$. A fourth independent structural determination of LaBSiO$_5$ was reported by Chi *et al.* (1997). Their sample was prepared by heating the mixed oxides with V$_2$O$_5$ in an evacuated quartz tube. The presence of Si in the resulting purple–pink crystals was attributed to the quartz. Refinement of 1094 unique reflections with $I_{\rm obs} \geq 3\sigma(I_{\rm obs})$ gave $R = 0.017$ and $wR = 0.022$ for the atomic coordinates listed in Table S18(*a*), after an origin shift of −0.0064 to minimize $\Sigma\Delta z_i$. Inspection of the table shows that, despite maximum displacement magnitudes of 1.12 Å and 18 other displacements with $0.7 \gtrsim \Delta\xi \gtrsim 0.5$ Å, the coordinates fulfill the structural criteria for ferroelectricity given in §1.2. It is notable, however, that the coordinates of β-LaBSiO$_5$ differ widely from those in phase II of α-LaBSiO$_5$; furthermore, the supergroup in the ferroelectric phase transition is space group $P3_112$ rather than $P3_121$. The possibility of structural modification by V or traces of Si remains to be investigated, as do the dielectric properties of β-LaBSiO$_5$.

3.1.7. PbBAsO$_5$. The structure was determined by Park & Bluhm (1996*a*), who refined 951 symmetry-independent reflections with $F_{\rm obs} > 4\sigma(F_{\rm obs})$ to final values of $R = 0.060$ and $wR2 = 0.092$. The atomic coordinates after an origin translation of 0.3019 along the polar axis are given in Table S18(*b*). $PbBAsO_5$ is isostructural with β-$LaBSiO_5$ (*cf.* §3.1.6) but is fully ordered. All atomic displacements required for a transition to centrosymmetric space group $P3_112$, as with β-$LaBSiO_5$, are consistent with the structural criteria for ferroelectricity given in §1.2; $\Delta\xi_{\max} \simeq 1.2$ Å for the same atom in both structures. If both independent determinations are reliable then the displacements noted are consistent with polarization reversal, and β-$LaBSiO_5$ and $PbBAsO_5$ are new ferroelectric candidates.

3.1.8. $BaBAsO_5$. Park & Bluhm (1996*b*) determined the structure using a total of 461 independent reflections with $F_{\rm obs} > 4\sigma(F_{\rm obs})$, with final refinement to $R = 0.053$ and $wR2 = 0.096$. The chemical formula and unit-cell dimensions of $BaBAsO_5$ are similar to those of β-$LaBSiO_5$ and $PbBAsO_5$ (see §§3.1.6 and 3.1.7), and also those of stillwellite, $LaBGeO_5$ and $LaBSiO_5$ (see §§3.1.1–3.1.3 and 3.1.5). The structure of $BaBAsO_5$ exhibits both resemblances to and differences from the stillwellite family. Many of the atomic coordinates in Table S18(*c*), in which the origin is shifted ~0.0030 to minimize $\Sigma\Delta z_i$, are comparable to those in β-$LaBSiO_5$ and $PbBAsO_5$ on transformation. However, *y*(Ba) and *y*(As) in $BaBAsO_5$ differ by ~1.5 and ~1.4 Å, respectively, from *y*(Pb) and *y*(As) in $PbBAsO_5$, with *z*(O5), *z*(O2) and *z*(O4) differing by ~1.9, 2.0 and 2.6 Å. Nevertheless, the largest $\Delta\xi$ displacement magnitudes in Table S18(*c*) are comparable to those in β-$LaBSiO_5$ and $PbBAsO_5$, with all $\Delta x \lesssim 0.9$ Å, $\Delta y \lesssim 0.8$ Å and $\Delta z \lesssim 0.2$ Å. All atomic displacements in $BaBAsO_5$ required for a transition to the supergroup fully satisfy the criteria in §1.2, and hence the compound is a new candidate for ferroelectricity.

4. Incorrect or dubious structures in space groups $P3_1$ and $P3_2$

4.1. $KTlF_4$

The space group $P3_1$ for $KTlF_4$ was selected by Hebecker (1975) from six possible choices based on model building; supporting physical measurements were not reported. The final *R* value was 0.105 for all 491 independent reflections. The resulting atomic coordinates, adjusted by an origin shift of 0.139 along the polar axis to minimize $\Sigma\Delta z_i$, are presented in Table S19. All atoms in $KTlF_4$ have $\Delta\xi_{\max} \lesssim u_{\rm iso}$, except atom F8, which has Δx and Δy of ~0.6 Å, with $u_{\rm iso} \simeq 0.2$ Å. A major physical property is unlikely to depend on a single atom with displacements of low significance. Atom F8 forms part of both TlF_7 distorted pentagonal bipyramids; the Tl1—F1 and Tl1—F8 distances are 2.46 and 2.49 Å, respectively, whereas the longest Tl2—F distance is 2.32 Å. Structural redetermination at higher accuracy may eliminate the anomalous $\Delta\xi$ values.

4.2. Fe_7Se_8 family

4.2.1. Fe_7Se_8. Andresen & Leciejewicz (1964) determined the structure of Fe_7Se_8 at 493, 293 and 4.2 K in the course of an early neutron diffraction study of magnetic ordering. Attempts at accommodating the Se atoms in space groups $P6_2$ or $P6_4$, as suggested previously (JUPSA 12 929), failed, but a fit was obtained on the basis of the NiAs structure in space group $P3_1$ or $P3_2$ (see Table S20*a*). All calculated spacings match the observed lines in the published neutron powder pattern. The arrangement reported, however, corresponds *exactly* to space group $P3_121$ (see Table S20). An independent X-ray diffraction study, without reference to the neutron paper, was reported (ACBCA 35 1210) in 1979 on a twinned single crystal. Despite apparent 6/*mmm* Laue symmetry, the twin laws were recognized and the structure was determined with enantiomorphic domains in $P3_121$ and $P3_221$ to give a final *wR* value of 0.036 over all 527 independent $F_{\rm obs}$.

4.2.2. Fe_7S_8. The structure of synthetic pyrrhotite was determined by Fleet (1971) using 317 Weissenberg-derived $F_{\rm obs}$ corrected for twinning, with a final *R* value of 0.108. An initial relationship noted between the refined Fe atomic coordinates and those in Table S20(*a*) was strengthened by shifting the origin by 0.3364 and replacing Fe7(*xyz*) by Fe7($xy\bar{z}$); in addition, an origin shift of 0.1712 was applied to the S atoms (see Table S20*b*). The difference of ~*z*/6 between these two shifts leaves many structure factors unaffected and all Fe atoms coordinated to six S atoms at distances ranging from 2.15 to 2.61 Å, which are comparable to those reported. The atomic arrangement in Table S20(*b*), with $0.23 \geq \Delta\xi \geq 0.03$ Å and $u_{\rm iso} \simeq 0.10$ Å, does not differ significantly from that in supergroup $P3_121$. Alternative models are possible and the final choice requires a full structural reinvestigation. Nevertheless, all models are likely to be consistent with supergroup symmetry.

4.3. B_2O_3

Structural models proposed previously (ACBCA 24 1032; ACSAA 7 611; ACCRA 5 389) for B_2O_3 were shown by Gurr *et al.* (1970) to be incorrect. In a new structural determination that used 130 independent reflections with $F_{\rm obs} > 2\sigma(F_{\rm obs})$, $I(00l)$ was reported with $l \neq 3n$ as the only absence. Two space groups, namely $P3_1$ and $P3_2$, were considered in solving the structure, and the former was chosen. The final atomic coordinates, corresponding to $R = 0.0494$, are presented in Table S21, which includes an origin shift of 0.7972 to minimize $\Sigma\Delta z$. Table S21 reveals that all atomic coordinates are within 0.02 Å of the corresponding locations in supergroup $P3_121$. Since $0.13 > u_{\rm iso} > 0.09$ Å for all atoms, it can be concluded that the present space-group assignment is in error.

4.4. $Na_4Ca_4Si_6O_{18}$

The structure of mineral low-combeite, $Na_4Ca_4Si_6O_{18}$, was reported by Fischer & Tillmanns (1983) in space group $P3_1$; the determination was based on 2669 independent reflections with $I > 2\sigma(I)$ and a final *R* value of 0.07. The resulting atomic coordinates (Table S22) show that there are 19 displacements with $1.8 \gtrsim \Delta\xi \gtrsim 0.4$ Å, and $\Delta\xi \lesssim 3u_{\rm iso}$ for the remaining 80 displacements. It is unlikely that these $\Delta\xi$ values would stabilize the structure in subgroup $P3_1$ in view of the preponderance of otherwise minor displacements from $P3_121$.

A subsequent study of synthetic low-temperature $Na_4Ca_4Si_6O_{18}$ (ACSCEE 42 934) gave satisfactory refinement in space group $P3_121$, as later confirmed (ACSCEE 43 1852) by a revised study of the original data, in which disorder was noted at several Na and Ca sites.

4.5. $Ti_6C_{3+\delta}$

The ordered δ'-phase was first reported with an NaCl-type arrangement compressed along [111] of the basic cubic δ-phase to give a unit cell with lattice parameters $a_{\delta'} \simeq 2^{-1/2}a_\delta$ and $c_{\delta'} \simeq 2 \times 3^{1/2}a_\delta$ (KRISA 34 1513) in space group $P3_121$. The initial agreement with $R = 0.11$ for the δ'-phase model was subsequently improved by Kukol' *et al.* (1995) using 668 reflections with $I_{\rm obs} > 3\sigma(I_{\rm obs})$ to $R = 0.070$ for the $P3_1$ vacancy model in Table S23. A strong correlation, however, was noted between the Ti1 site-occupancy factor and $u_{\rm iso}$(Ti1). The unusually high magnitude of $u_{\rm iso}$(C2) may indicate additional correlation. Table S23 shows that the atomic coordinates of Ti1 and Ti2 are consistent with the 6(c) Wyckoff position in $P3_121$, as the vacancy distribution must also be if both sites are equally occupied rather than having the postulated 4σ difference. The 12σ difference reported in the site occupancy of atoms C1 and C2 is fully consistent with the unrelated Wyckoff 3(a) and 3(b) locations in space group $P3_121$. A change in Ti site occupancy to bring the structure into conformity with space group $P3_121$ would be significant only if the standard deviations were well estimated; the strong parameter correlation noted in the course of refinement, leading most likely to an underestimation of σ, suggests that the δ'-phase structure is not pyroelectric.

4.6. $IrGe_4$

A structural choice between space groups $P3_1$ and $P3_121$ was made by Panday & Schubert (1969) in favor of the former. Estimated $I(hk0)$–$I(hk5)$ values from Weissenberg photographs were used to refine the model, the final value of R being 0.147. The atomic coordinates following an origin shift of 0.0086 to minimize $\Sigma\Delta z$ are listed in Table S24; uncertainties were not reported but may be substantial. The largest displacement component between refined coordinates and the corresponding locations in space group $P3_121$ is Δz(Ir) = 0.13 Å; with $u_{\rm iso}$(Ir) $\simeq$ 0.08 Å, Δz(Ir) is most likely without significance. The editors of the ICSD also noticed that the space group was probably $P3_121$ and that several very small thermal/static atomic displacement factors [*e.g.* $u_{\rm iso}$(Ge3) $\simeq$ 0.03 Å] were implausible.

4.7. $Nb_6C_{4.73}$

A twinned crystal of nominal composition Nb_6C_5, annealed at 1375 K under He at 0.4 Mpa, was used by Christensen (1985) for the neutron diffraction measurements. Severe extinction was reported. A total of 150 reflections with $I > 10\sigma(I)$ were used in the refinement to give a final R value of 0.064. Twinning prevented thermal-parameter variation but each site occupancy refined satisfactorily. The atomic coordinates listed in Table S25 include an origin shift of 0.168 along the c axis to minimize $\Sigma\Delta z$. The uncertainties in the x, y and z coordinates are reported as ~0.03, ~0.03 and ~0.08 Å. Examination of the table shows that no displacement component between the coordinates reported and those expected in space group $P3_112$ differs significantly from zero. The data are hence consistent with space group $P3_112$.

4.8. $NaCa_3(CO_3)_2F_3 \cdot H_2O$ (sheldrickite)

Grice *et al.* (1997) reported merohedral pseudohexagonal twinning in crystals of the recently identified mineral sheldrickite and solved the structure in space group $P3_2$. A total of 867 reflections with $F > 5\sigma(F)$ gave poor agreement in space groups $P6_222$ and $P6_422$; refinement in $P3_221$ located several atoms and reduced the value of R to 0.16, but the CO_3^{2-} ions were not found, whereas refinement in $P3_2$ revealed the remaining heavier atoms and gave $R = 0.046$. All resulting atomic coordinates in $P3_2$, except those of the two independent undetermined H atoms, are presented in Table S26. Examination of the 47 $\Delta\xi$ component displacements between these coordinates and those satisfying the symmetry of supergroup $P3_121$, as given in the table, shows that all but two are less than 0.1 Å; since $0.2 \gtrsim u_{\rm iso} \gtrsim 0.1$ Å for all atoms with $\sigma(\Delta\xi)$ nominally ranging between 0.01 and 0.03 Å, these magnitudes are probably not significant. The exceptions Δz(F3) = 0.30 (2) Å and Δx(OW) = 1.37 (1) Å, if not a result of uncorrected error in the model, such as a misplaced OW atom, satisfy the criteria given in §1.2. It is unlikely, however, that a ferroelectric crystal would have so few departures from a dipole array that otherwise cancels. The space-group choice should hence be reexamined.

4.9. ZnTe, phase I

The atomic coordinates of ZnTe phase I at 11.5 GPa in Table S27 were proposed by Kusaba & Weidner (1994) on the basis of an energy-dispersive X-ray diffraction pattern taken at NSLS; the model is intermediate between the structure of zinc blende and rocksalt and estimates of uncertainty were not presented. The best agreement in space group $P3_1$ was $R \simeq 0.40$, the major discrepancy arising from a poor fit with the 101 line at 41 keV. Although four other space groups were noted as compatible with the only observed systematic absence, namely $I(00l)$ for $l \neq 3n$, models with alternative symmetry were not mentioned. With $u_{\rm iso} \simeq 0.10$ Å and $0.30 \gtrsim \Delta\xi \gtrsim 0.14$ Å in Table S27, and distorted interlocking tetrahedra of Te and Zn atoms in which $d_{\rm Zn-Te}$ ranges from 2.179 to 2.748 Å, space group $P3_121$ is more likely.

4.10. $CaCO_3 \cdot H_2O$ (monohydrocalcite)

Effenberger (1981) determined and refined the structure in a subcell with a' = 6.0931 (9), c' = 7.545 (2) Å and space group $P3_121$ to $R = 0.039$ using 408 independent reflections with $F_{\rm meas} > 3\sigma(F_{\rm meas})$. The supercell with $a = 3^{1/2}a'$ and $c = c'$ has 226 additional reflections. Refinement in the supercell with space group $P3_1$ gave $R = 0.086$ for the atomic coordinates in Table S28; the origin here is shifted by +0.3333 along the c axis to place z(Ca1) at 0. All three independent Ca atoms, the three water O atoms and six of the nine O atoms of the CO_3^{2-} ion are located within 0.12 Å of Wyckoff positions in space group $P3_112$. Since all $u_{\rm iso} \simeq 0.13$ Å, these locations do not differ significantly from the symmetry of space group $P3_112$. The remaining atoms (O7, O8, O9, C1, C2 and C3) are displaced with $\Delta\xi$ components ranging from 0.02 to 0.35 Å; the significance of these $\Delta\xi$ values is low. If these $\Delta\xi$ components were confirmed then $CaCO_3{\cdot}H_2O$ would satisfy the criteria in §1.2; however, it is more likely that the symmetry does not depart significantly from that of $P3_112$.

5. Nonferroelectric pyroelectric structure in space groups $P3_1$

5.1. $Li_7Cu_7Si_5$

The unit cell contains 21 independent Cu atoms with 12 reported as substituted by as much as 27% Si, 14 Si atoms with five substituted by up to 18% Cu, and 22 Li atoms with seven sites substituted by up to 17% Cu. The structure was solved and refined by Pavlyuk *et al.* (1995) in space group $P3_1$ to $R = 0.056$, using 1207 independent reflections with $I_{\rm obs} \geq 3\sigma(I_{\rm obs})$ (atomic coordinates are given in Table S29). The structure was not found to approach a symmetry higher than that stated and hence this compound is not a candidate for ferroelectricity.

6. Entries with incomplete coordinates in space groups $P3_1$ and $P3_2$

6.1. Lithiophorite

The structure of $(Al,Li)MnO_2(OH)_2$ as initially reported (ACBCA 5 676) in space group $C2/m$ corresponds to complete octahedral layers in which MnO_2 layers alternate with an Li-filled $(Al,Li)(OH)_2$ layer. This arrangement led Pauling & Kamb (1982) to propose a superstructure involving Mn^{2+}, Mn^{4+} ordering with formula $Li_6Al_{14}(OH)_{42}Mn_3Mn_{18}O_{42}$ in space group $P3_1$, based on Pauling's electroneutrality principle. The suggested atomic coordinates are presented in Table S30. In view of the original symmetry assignment and the lack of diffraction data supporting the proposed symmetry, property prediction on structural grounds would be inappropriate.

6.2. $K_4SiW_{12}O_{40}{\cdot}18H_2O$

Atomic coordinates for $K_4SiW_{12}O_{40}{\cdot}18H_2O$ in space group $P3_2$ were not presented in this early study (ZEKGA 94 256). No subsequent entry for the material appears in the database, and the original entry under Collection Code #38538 was later eliminated; anhydrous $K_4SiW_{12}O_{40}$ is reported to form in space group *Pnma*.

6.3. $K_5CoW_{12}O_{40}{\cdot}20H_2O$

The structure, first reported in space group $P6_222$ by Yannoni (1961), was recently redetermined at 150 K by Muncaster *et al.* (2000); this new study illustrates the major role played by tetrahedral Co^{III} ions in the catalytic behavior of CoAlPO-type agents. A total of 15 171 unique reflections were measured, and the structure was independently solved in space group $P3_1$, after the previous choice of space group failed to give a satisfactory structure; the new model refined to $R = 0.054$ for $I > 2\sigma(I)$, with $R = 0.120$ for all data. The final atomic coordinates are presented in Table S31 for an origin shift of 0.4572 to set $z({\rm Co}) = 5/6$. Examination of the displacement components between the coordinates of all atoms determined (two K, 12 W, one Co, 40 O and 12 O*W* atoms) and the corresponding locations in space group $P3_121$ shows that none are larger than 0.02 Å, except for those of atoms O*W*11 and O*W*12 ($0.08 \gtrsim \Delta\xi \gtrsim 0$ Å). It is noted that $0.24 > u_{\rm iso} > 0.16$ Å for all atoms except six O*W* atoms, for which $0.48 > u_{\rm iso} > 0.29$ Å.

Muncaster *et al.* (2000) succeeded in locating all atoms in this large structure except for three K, eight O*W* and 40 H atoms. On the basis of the unambiguous evidence in Table S31 that space group $P3_121$ fits the model equally well but with many fewer parameters than in $P3_1$, it is expected that these 'missing' atoms will appear if additional refinement in the supergroup is undertaken.

Access to the ICSD has been through CD-ROM DOS products, the WWW Windows version by Fachinformationszentrum (FIZ) Karlsruhe with the Institute Laue–Langevin, and the current Windows version issued jointly by FIZ and the National Institute of Standards and Technology in cooperation with the International Union of Crystallography. Support of this work by the National Science Foundation (grant Nos. DMR-9708246 and DMR-0137323) is gratefully acknowledged. It is a pleasure to thank Professor E. L. Belokoneva and Dr I. E. Grey for personal communications.

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