

to obtain the final result. We adopted this method because we could use a conventional refinement program. If a program handling two or more sets of intensity data had been available, we could have simultaneously refined the Co/Zn and Ni/Zn ratios.

Even where the atomic numbers of the cations are considerably different, the two-wavelength anomalous-dispersion method would be useful for determining ternary-system cation distributions. One set of intensity data measured at a certain wavelength may determine a ternary-system cation distribution to some extent, but the errors would be large. To reduce the errors, two sets of intensity data measured at two different wavelengths using the anomalous-dispersion effect need to be collected.

Our two-wavelength method may be extended to other combinations such as neutron and X-ray diffraction. This combination is effective for determining a ternary-system cation distribution because the atomic scattering factors for neutron diffraction are different from those for X-ray diffraction. Mössbauer spectroscopy in combination with X-ray diffraction could also be used to determine a ternary-system cation distribution if the system includes iron. These two independent methods are effective for a ternary system.

The atoms (Co, Ni and Zn) in the *M*1 or *M*2 sites should have different positions from each other, because these sites are general positions. If we have four sets of intensity data (e.g. Co, Ni and Zn absorption edges, and Mo *K* α data), we can refine the positional parameters of each atom. Sasaki & Tsukimura (1987) reported such a procedure to determine the positional parameters of each atom in (Co,Ni,Zn)SiO₃ pyroxene.

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Structure of Pb₅Cr₃F₁₉ at 295 K, Polarization Reversal and the 555 K Phase Transition

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Abstract

Lead chromium fluoride, Pb₅Cr₃F₁₉, with $M_r = 1552.9$ is a new material with ferroelectric attributes that crystallizes in the tetragonal system. At $T = 295$ K, the space group is *I4cm* with $a = 14.384$ (5) and $c = 7.408$ (2) Å, $V = 1532.8$ (7) Å³, $Z = 4$, $D_m = 6.67$ (5), $D_x = 6.729$ g cm⁻³. For $\lambda(\text{Mo } K\alpha) =$

0.71073 Å, $\mu = 57.33$ mm⁻¹. $F(000) = 2612$. The material undergoes a first-order phase transition at 555 K. The structure was determined from 7599 (1410 independent) $F_m^2 \geq 4\sigma(F_m^2)$ with $(\sin\theta)/\lambda \leq 1.029$ Å⁻¹; least-squares refinement on wF_m^2 led to $R(F_m) = 0.044$ with $R_{\text{ini}}(F_m) = 0.040$. No atom is more than 0.72 Å from the hypothetical paraelectric state, hence the crystal is structurally ferroelectric.

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The mean atomic displacement by Cr from the zero spontaneous-polarization location corresponds to a predicted phase-transition temperature of 635 (30) K, in satisfactory agreement with the experimental temperature $T_c = 555$ K. The Cr atoms form two symmetry-independent distorted octahedra, with average Cr—F distances of 1.92 (3) and 1.85 (1) Å respectively. One Pb atom is nine-coordinated, occupying a distorted tricapped trigonal prism with average Pb—F = 2.69 (20) Å. The other Pb atom is ten-coordinated with a coordination polyhedron based on a bisdisphenoid; six F atoms are at an average distance of 2.42 (8) Å, with four additional F atoms at 3.024 (1) Å.

Introduction

Ferroelectric attributes have recently been recognized in three related families, for which the archetypes are SrAlF₅ (von der Mühl, Andersson & Galy, 1971; Ravez, von der Mühl & Hagenmuller, 1975; Abrahams, Ravez, Simon & Chaminade, 1981), Sr₃(FeF₆)₂ (von der Mühl, 1974; Abrahams, Ravez, Canouet, Grannec & Loiacono, 1984) and Pb₅W₃O₉F₁₀ (Ravez, Abrahams, Marsh, Arquis & Chaminade, 1985; Arquis-Canouet, Ravez, Chaminade, Hagenmuller, Abrahams & Marsh, 1986; Abrahams, Marsh & Ravez, 1987). These attributes include a higher than room-temperature phase transition, a nonlinear dielectric susceptibility, a dielectric permittivity maximum and a dielectric loss minimum at the phase transition in addition to an atomic arrangement capable of undergoing displacements that give rise to a reversible spontaneous polarization. All three families are tetragonal, with the following relationships among their unit cells:

$$a(\text{SrAlF}_5) \approx a[\text{Sr}_3(\text{FeF}_6)_2]/2^{1/2} \approx a(\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10})$$

$$c(\text{SrAlF}_5) \approx c[\text{Sr}_3(\text{FeF}_6)_2] \approx 2c(\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}).$$

The nonlinear optical material Pb₅Cr₃F₁₉, initially prepared as a possible isomorph of Pb₅W₃O₉F₁₀, has been reported by Arquis-Canouet, Ravez & Abrahams (1986) to undergo a first-order phase transition at 555 K. The *a* axis expands and the *c* axis contracts abruptly at the Curie temperature, both by about 0.6%. The uniaxial indicatrix sharply reverses sign from negative to positive on heating through the phase transition, with pronounced hysteresis on cooling. Phase transitions have also been reported in ten other members of the Pb₅Cr₃F₁₉ family (Ravez, Arquis, Grannec, Simon & Abrahams, 1987). Despite their similarity in lattice constants, Pb₅Cr₃F₁₉ and Pb₅W₃O₉F₁₀ crystallize in different space groups, with atomic arrangements that also are different. The structure of Pb₅Cr₃F₁₉ has now been determined at room temperature and shown to meet the structural

criteria for ferroelectricity (Abrahams, 1988). The results are presented below and compared with those reported for Pb₅W₃O₉F₁₀, Sr₃(FeF₆)₂ and SrAlF₅.

Experimental

The preparation and crystal growth of Pb₅Cr₃F₁₉ have been reported previously by Arquis-Canouet, Ravez & Abrahams (1986) together with the density and lattice constants, the latter over the temperature interval 295–610 K. A transparent, regular prismatic crystal with a brilliant, deep-green color and dimensions 0.084 × 0.112 × 0.252 mm (linear e.s.d. about 1%) was mounted on a Pyrex capillary. All integrated intensities, within the volume of reciprocal space bounded by $h - 13 \rightarrow 29$, $k - 29 \rightarrow 29$, $l - 15 \rightarrow 15$ and $(\sin\theta)/\lambda \leq 1.029 \text{ \AA}^{-1}$, were measured using an Enraf-Nonius CAD-4 diffractometer. Mo *K* α radiation, diffracted by a graphite monochromator, was used with $\omega - 2\theta$ scans over an angular range $0.85^\circ + 0.35^\circ \tan\theta$. The maximum time spent on a scan was 240 s for a counting-statistics standard deviation objective of $\sigma_c(I)/I \leq 0.01$. Six standard reflections were measured at 6 h intervals during a total exposure time of 1176 h. A linear intensity decline with time *t* (h) was observed and corrected using the fitted equation $I_t = I_o (1 - 6.24 \times 10^{-5}t)$.

A total of 16828 integrated intensities, including standards, were measured at 295 K and further corrected for Lorentz, polarization and absorption effects, the latter by numerical integration. Transmission factors varied from 0.0057 to 0.0955. The 7599 intensities that were measured more than once and that exceeded $4\sigma_c(I)$ were averaged in point group *4mm*, with separated Friedel pairs, to give 3575 structure amplitudes $\langle F_m^2 \rangle$ of which 1410 had $\langle F_m^2 \rangle \geq 4\sigma_c(F_m^2)$. The variances $\sigma^2\langle F_m^2 \rangle$ were estimated, by a variation of Abrahams, Bernstein & Keve's (1971) method, as the larger of V_1 or V_2 where V_1 is the sum of the variances derived from counting statistics (σ_c), the absorption correction, and the variations among the standard reflections; V_2 is the estimated variance of the weighted-mean amplitude $\langle F_m^2 \rangle$ of a form. The internal agreement factors are $R_{\text{int}}(F_m) = 0.040$ and $wR_{\text{int}}(F_m) = 0.037$. All agreement factors are defined as in *Notes for Authors* (1983).

The diffraction symmetry of Pb₅Cr₃F₁₉ is *4/mmm*, with systematic absences *hkl* for $h + k + l$ odd and *0kl* for *l*, (*k*) odd. Possible point groups are limited to *4mm* (space group *I4cm*) and $\bar{4}m2$ (space group $\bar{I}4c2$) by the observation of second-harmonic generation (Abrahams *et al.*, 1984) in the material which at that time was taken as having the composition Pb₃(CrF₆)₂. Point group $\bar{4}m2$ is nonpolar and may thus be eliminated if the material is ferroelectric. The structure solution described below establishes *I4cm* as the most likely space group.

Table 1. $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ atomic coordinates and equivalent isotropic temperature factors (\AA^2) with *e.s.d.*'s

Coordinates without parentheses were not varied. The z coordinate for Pb(1) defines the origin. For atoms Cr(1) and F(4)–F(6) the position $\frac{1}{2} - x, x, z$ is given. $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
Pb(1)	0.4264 (2)	0.2727 (2)	0	0.017 (1)
Pb(2)	0	0.5	0.1508 (8)	0.045 (2)
Cr(1)	0.1632	0.3368 (4)	-0.0107 (12)	0.011 (2)
Cr(2)	0	0	0.1799 (6)	0.011 (4)
F(1)	0.1085 (11)	0.2488 (11)	-0.1726 (31)	0.045 (9)
F(2)	0.1984 (8)	0.4309 (8)	0.1655 (16)	0.022 (4)
F(3)	-0.0569 (10)	0.1153 (10)	0.6875 (37)	0.070 (16)
F(4)	0.2523	0.2477 (8)	0.0571 (27)	0.022 (6)
F(5)	0.3856	0.1144 (6)	0.0195 (37)	0.021 (5)
F(6)	0.0720	0.4280 (10)	-0.0828 (44)	0.066 (16)
F(7)	0	0	0.4323 (71)	0.51 (1)

Solution and refinement of the structure

The location of two symmetry-independent Pb and two symmetry-independent Cr atoms was deduced from a three-dimensional Patterson map. Subsequent difference electron density maps gave the location of seven symmetry-independent F atoms, see Table 1. The multiplicity and Wyckoff letter for each atom is given in Table 2. Not all coordinates correspond to the first set given in *International Tables for Crystallography* (1987) but are convenient in representing the coordination polyhedra.

The structure model was refined by minimizing the function $\sum w(\langle F_m^2 \rangle - F_m^2)^2$ with weights $w = 1/\sigma^2(F_m^2)$ (see above for the estimation method). The 1410 $\langle F_m^2 \rangle \geq 4\sigma(F_m^2)$ amplitudes were used in the refinements but all values of the indicators given below are based on $\langle F_m \rangle$. A model in which the Pb and Cr atoms were allowed to vibrate harmonically with anisotropic displacement parameters while F atoms were treated isotropically converged to $R = 0.072$, $wR = 0.066$ and $S = 1.655$. All independent atoms refined rapidly to their final positions with the exception of F(7); this atom consistently appeared to have an unusually high displacement factor, possibly indicating an unresolved disorder about the c axis.

The possibility of anharmonic thermal vibrations by the Pb and Cr atoms in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ was investigated in a model that finally included all tensors to fifth order for Pb(1) and Cr(2) and fourth order for Pb(2) and Cr(1), with probability density functions given by a Gram–Charlier expansion in a locally modified version of the *ORFLS* least-squares program of Busing, Martin & Levy (1973). All F atoms except F(7) were modelled with anisotropic displacement parameters. Anharmonic tensors to fourth order were included for F(7) in addition to the anisotropic displacement parameters. The final model converged to $R = 0.044$, $wR = 0.042$ and $S = 1.140$. All atomic positional and displacement parameters had ratios $\Delta/\sigma < 0.19$. The resulting

Table 2. Polar coordinates and atomic displacements necessary for $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ to become paraelectric

$\Delta z = (z' - z'')c$, where $z' = z + 0.0405$ and z'' is the coordinate value in the hypothetical paraelectric state. The xyz coordinates are given in Table 1.

	Wyckoff position	z'	z''	Δz (\AA)
Pb(1)	16(<i>d</i>)	0.0405	0	0.300
Pb(2)	4(<i>b</i>)	0.1915	0.25	-0.433
Cr(1)	8(<i>c</i>)	0.0295	0	0.219
Cr(2)	4(<i>a</i>)	0.2205	0.25	-0.219
F(1)	16(<i>d</i>)	-0.1325	-0.1695	0.274
F(2)	16(<i>d</i>)	0.2065	0.1695	0.274
F(3)	16(<i>d</i>)	0.7285	0.75	-0.159
F(4)	8(<i>c</i>)	0.0975	0	0.722
F(5)	8(<i>c</i>)	0.0595	0	0.441
F(6)	8(<i>c</i>)	-0.0425	0	-0.315
F(7)	4(<i>a</i>)	0.4725	0.5	-0.204

atomic parameters are listed in Table 1.* Reversal of the polarization direction led to a significant increase in the value of wR . Atomic scattering factors for Pb^{2+} , Cr^{3+} and F^- , including anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974).

Atomic reversal of the spontaneous polarization

A shift of origin along the polar c axis by -0.0405 has the effect of placing Cr(1) and Cr(2) symmetrically between the planes $z = 0$ and $z = \frac{1}{4}$, resulting in the location of Cr(1) at 0.219 \AA above $z = 0$ and Cr(2) at the same distance below $z = \frac{1}{4}$. A transformation of the xyz coordinates in Table 1 to this origin is convenient when discussing the atomic model that underlies the reversal of spontaneous polarization sense in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. Any other origin increases $\text{Cr}(\Delta z)_{\text{max}}$ and hence the predicted value of T_c , see below. Table 2 contains the corresponding z' coordinates for all atoms, where $z' = z + 0.0405$. Table 2 also lists the z'' values of the xyz'' coordinates for each atom in the hypothetical paraelectric phase: this phase corresponds to space group *I4/mcm* for all atoms except F(1) and F(4), which have z'' coordinates of equal magnitude but opposite sign. The multiplicity and location of each atom at xyz'' correspond to zero polarization. A structural determination of this phase is in progress and will be reported later.

The magnitudes (\AA) of the displacements Δz between z' and z'' are also given in Table 2. All are less than 0.72 \AA , well within the range expected for ferroelectric crystals (Abrahams, 1988). A change in

* Lists of structure factors and anisotropic harmonic (all atoms) displacement and anharmonic [Pb, Cr and F(7) atoms] tensor coefficients have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52906 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the sign of all Δz gives an equivalent atomic arrangement but with a spontaneous polarization opposite in sense to that implied by the xyz' coordinates, as required for a demonstration of structural ferroelectricity.

The temperature at which the ferroelectric phase transforms to the paraelectric phase may be estimated from the magnitude of the Cr-atom Δz displacements, using the relationship in (1) (Abrahams, Kurtz & Jamieson, 1968), since Cr forms the shortest and least ionic bonds with F in this structure:

$$T_c = (\varkappa/2k)(\Delta z)^2 K, \quad (1)$$

where \varkappa is a force constant and k is Boltzmann's constant. $\varkappa/2k \approx 2 \times 10^4 \text{ K } \text{\AA}^{-2}$. The uncorrected value of Δz for Cr as given in Table 2 corresponds to $T_c = 950 \text{ K}$. The atomic displacements of Cr, however, should be considered in relation to the displacements of the F atoms that form distorted octahedra around them. The Cr atoms are significantly displaced along the polar direction from the centers of the Cr(1)F₆ and Cr(2)F₆ octahedra. The displacements are respectively 0.030 (1) and 0.043 (1) Å. Correction of Δz by these values gives $\Delta z = 0.189$ (9) Å for Cr(1) and 0.176 (4) Å for Cr(2), for a weighted-mean displacement of 0.178 (4) Å since these two values do not differ significantly. The corresponding Curie temperature predicted from (1) is hence 635 (30) K, in satisfactory agreement with the experimental $T_c = 555 \text{ K}$ (Arquis-Canouet, Ravez & Abrahams, 1986).

It may be noted from Table 2 that the polar displacement of Cr(1) is opposite in sense to that of Cr(2), hence it is likely that the spontaneous polarization P_s will be considerably less than that estimated from the mean corrected value of Δz using the relation

$$P_s = (258 \pm 9) \times 10^{-2} \Delta z \text{ C m}^{-2} \quad (2)$$

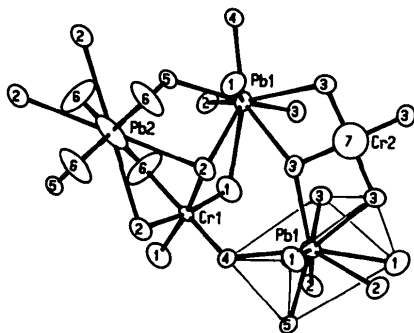


Fig. 1. The four independent metal atom-fluorine polyhedra in Pb₅Cr₃F₁₉ and their interconnections as viewed down the polar axis. Atom Cr(2) is located on the fourfold axis and Pb(2) at the mirror-plane intersection. The thermal ellipsoids for all atoms except F(7) are outlined with 50% probability. The a axis is horizontal, the b axis vertical.

Table 3. Coordination distances (Å) in Pb₅Cr₃F₁₉

The superscripts (i)–(x) denote the following equivalent coordinations with x, y, z taken from Table 1: (i) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - y, x, z$; (iii) $y, x, z - \frac{1}{2}$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - 1$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $\frac{1}{2} - y, \frac{1}{2} + x, z - \frac{1}{2}$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (viii) $-x, y, \frac{1}{2} + z$; (ix) $-y, x, z$; and (x) $x, y, z - \frac{1}{2}$.

Pb(1)—F(5)	2.357 (9)	Pb(2)—F(6)	2.267 (26) × 2
—F(1) ⁱ	2.496 (22)	—F(6) ⁱⁱⁱ	2.458 (28) × 2
—F(4)	2.565 (5)	—F(5) ^x	2.521 (12) × 2
—F(2) ⁱⁱ	2.619 (12)	—F(2)	3.025 (10)* × 4
—F(2) ⁱⁱⁱ	2.700 (12)		
—F(3) ^{iv}	2.830 (24)		
—F(3) ^v	2.837 (18)		
—F(3) ^{vi}	2.879 (19)		
—F(1) ^{vii}	2.932 (18)*		
Cr(1)—F(4)	1.881 (10)	Cr(2)—F(7) ^x	1.834 (56)
—F(1)	1.912 (20) × 2	—F(3) ^v	1.851 (14) × 4
—F(6)	1.932 (14)	—F(7)	1.870 (56)
—F(2)	1.947 (13) × 2		

*Next largest Pb(1)—F distance is 3.302 (17) Å, next largest Pb(2)—F distance is 3.588 (21) Å.

Table 4. Average values of Cr—F distances (Å) in Cr³⁺ compounds determined after 1970

Compound	Average distance*	Reference†
NH ₄ CrF ₆	1.886 (21)	ZNBAD 34 934
NaBaCr ₂ F ₉	1.892 (43), 1.897 (45)	JSSCB 56 288
KPbCr ₂ F ₉	1.898 (22), 1.900 (25)	JSSCB 41 272
Cs ₂ NaCrF ₆	1.899 [5], 1.906 [6]	JSSCB 18 39
	1.906 [5], 1.913 [6]	ZENBA 30 462
Rb ₂ CrF ₅	1.901 (67)	ACBCA 30 2688
BaCrF ₅	1.902 (33)	ZNBAD 37 54
CaCrF ₅	1.902 (43), 1.908 (71)	MRBUA 6 561
		MRBUA 8 593
BaLiCrF ₆	1.903 (22)	ZAACA 406 23
(N ₂ H ₅) ₂ CrF ₆	1.905 (26)	ACBCA 28 2028
CsCrF ₄	1.907 (43)	ZAACA 442 151
NaCrF ₄	1.908 (37)	JRPSD 1979 213
Rb ₂ NaCrF ₆	1.936 [20]	ZAACA 391 117
Cs ₂ KCrF ₆	1.936 [10]	ZAACA 391 117
Rb ₂ KCrF ₆	1.940 [10]	ZAACA 391 117

* See footnote at the bottom of this page for e.s.d.'s of average distance as given in parentheses; square brackets denote the author's own e.s.d. for uniquely determined distances.

† See *Notes for Authors* (1983) for a description of journal codens.

(Abrahams *et al.*, 1968), which results in $P_s \approx 0.46 \text{ C m}^{-2}$.

Description of the structure of Pb₅Cr₃F₁₉

The structure of Pb₅Cr₃F₁₉ consists of connected PbF₉, PbF₁₀ and CrF₆ polyhedra that share corners, edges and faces. The four independent polyhedral types and their interconnections are illustrated in Fig. 1. The resulting grouping may be considered as the building block of the structure below 555 K. Cr(1) and Cr(2) form distorted octahedra with average Cr—F distances of 1.922 (25) and 1.851 (9) Å, respectively, see Table 3* and next section. As

* The standard deviations of these and other average $\langle x \rangle = (1/n)\sum x$, distances are estimated as $\{[1/(n-1)]\sum(x - \langle x \rangle)^2\}^{1/2}$.

expected from a consideration of the larger e.s.d. for Cr(1)—F, that octahedron is more irregular, with a maximum angular distortion of 9.3° from regularity as compared with 3.5° for the Cr(2) octahedron. The Cr³⁺—F distance given by Shannon's (1976) ionic radii for coordination numbers 6 (Cr) and 3 (F) is 1.915 Å. A survey of recent reports of this distance based on determinations made later than 1970 on a variety of mixed 3*d*-metal fluoride structures, as contained in the Inorganic Crystal Structure Database (*Crystallographic Databases*, 1987), is summarized in Table 4. The average Cr(1)—F distance is normal with respect to Table 4, that of Cr(2)—F is somewhat shorter.

Nine-coordinated Pb(1), see Table 3, forms a distorted polyhedron that may be described as a tricapped trigonal prism with F(1)F(4)F(5) and F(1)F(3)F(3) forming the triangular prism faces, as outlined in Fig. 1. The average Pb(1)—F distance is 2.69 (20) Å. Pb(2) is coordinated by four F(6) and two F(5) atoms, with an average Pb—F distance of 2.42 (8) Å and with four additional F(2) atoms at

Table 5. *Unit-cell data for Pb₅Cr₃F₁₉, Pb₅W₃O₉F₁₀, Sr₃(FeF₆)₂ and SrAlF₅*

	Pb ₅ Cr ₃ F ₁₉	Pb ₅ W ₃ O ₉ F ₁₀	Sr ₃ (FeF ₆) ₂	SrAlF ₅ *
<i>a</i> (Å)	14.384 (5)	14.583 (3)	20.338 (2)	14.09 (2)
<i>c</i> (Å)	7.408 (2)	7.365 (1)	14.668 (2)	14.33 (2)
Space group	<i>I</i> 4 <i>cm</i>	<i>I</i> 4	<i>I</i> 4 ₁	<i>P</i> 4
<i>Z</i>	4	4	24	32
Unit-cell content†	Pb ₂₀ Cr ₁₂ F ₇₆	Pb ₂₀ W ₁₂ O ₃₆ F ₄₀	Sr ₁₈ Fe ₁₂ F ₇₂	Sr ₁₆ Al ₁₆ F ₈₀
Reference	Arquis-Canouet, Ravez & Abrahams (1986)	Abrahams <i>et al.</i> (1987)	von der Mühl (1974)	von der Mühl <i>et al.</i> (1971)

* Structure determination was reported in subcell with $c' = c/2$ and space group *I*4.

† Calculated for a unit-cell volume equivalent to that of the Pb₅Cr₃F₁₉ cell.

3.024 (1) Å. Taking the coordination number as ten, the resulting polyhedron may be described as bis-disphenoidal, with the four F(6) atoms forming an elongated disphenoid (tetrahedron) and the two F(5) and two pairs of F(2) atoms occupying the place of the flattened disphenoid. The distance between Pb(2) and the midpoint of the F(2) pair is 2.72 (2) Å. Shinn

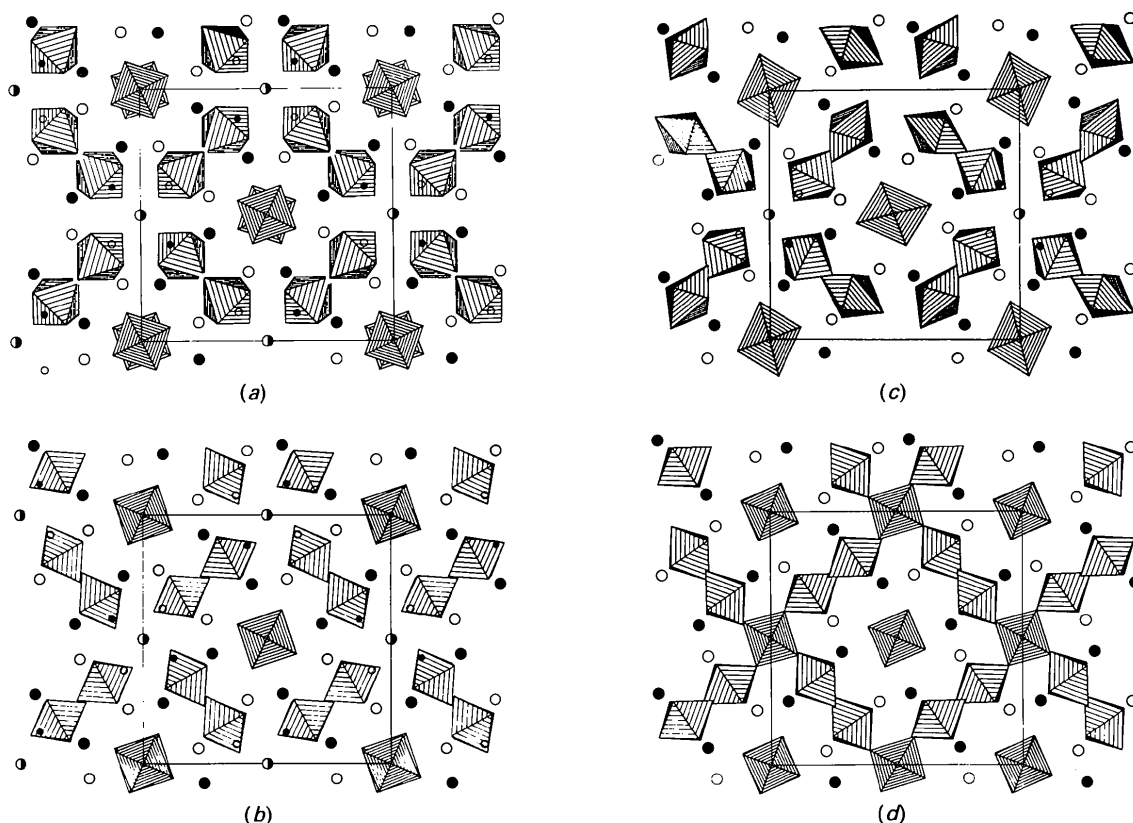


Fig. 2. Projections on the *ab* plane of the structures of (a) Pb₅Cr₃F₁₉, (b) Pb₅W₃O₉F₁₀, (c) Sr₃(FeF₆)₂ and (d) SrAlF₅. Views of Sr₃(FeF₆)₂ and SrAlF₅ are drawn slightly idealized in space groups *I*4₁ and *I*4, respectively, with the Pb₅Cr₃F₁₉-equivalent unit cells outlined. The octahedra about Cr, W, Fe or Al are shown shaded. The larger circles ○ and ● denote Pb or Sr at $z = 0$ and $\frac{1}{2}$, respectively, while ● denotes Pb at $z = 0.15$ and 0.65 in (a), Pb at $z = 0.25$ and 0.75 in (b) and Sr at 0.23 and 0.73 in (c). The smaller circles ○ and ● represent F(5) in (a), F(2) in (b) and F(11) in (c), see references in Table 5.

& Eick (1968) found a similar coordination polyhedron in La₂(CO₃)₃·8H₂O. The Pb²⁺—F distances as given by Shannon (1976) are 2.70 Å for ten-coordination, 2.65 Å for nine-coordination, and 2.49 Å for six-coordination. A wide range of Pb²⁺—F distances has been reported in the literature and the values determined for Pb₅Cr₃F₁₉ lie well within the average distribution.

Structural relationships among the SrAlF₅-like ferroelectrics

The four structural families with formulas *ABF*₅ (*A* = Sr, *B* = Al, Cr, Ga; *A* = Ba, *B* = Ti, V, Fe; *A* = Pb, *B* = Al, Ga; and *A* = Eu, *B* = Al), *A*₃(*BF*₆)₂ (*A* = Sr, *B* = Fe; and *A* = Pb, *B* = Ti, V, Cr, Fe, Ga), *A*₅*B*₃O₉F₁₀ (*A* = Pb, *B* = Mo, W) and *A*₅*B*₃F₁₉ (*A* = Pb, *B* = Cr, Al; and *A* = Sr, Ba, *B* = Ti, V, Cr, Fe, Ga) are closely interrelated (Abrahams *et al.*, 1987). The simple relationships among the unit-cell dimensions for the archetypes of each are noted in the *Introduction*; numerical values are given in Table 5.

Each family crystallizes with tetragonal symmetry but in a different space group. The equivalent formulas for each archetype, normalized to a unit cell with volume comparable to that of Pb₅Cr₃F₁₉ as listed in Table 5, show significant differences and similarities. Thus, the total number of *A* + *B* atoms in the Pb₅Cr₃F₁₉ family (32) is identical to that in the Pb₅W₃O₉F₁₀ and SrAlF₅ families but with a different *A*,*B* distribution in the latter, whereas the total number of *A* + *B* atoms in the Sr₃(FeF₆)₂ family is fewer by two. Moreover, Pb₅Cr₃F₁₉ has four fewer F atoms than SrAlF₅ and four more than Sr₃(FeF₆)₂ in the equivalent unit cell. It may also be noted that, while the role of oxygen in the Pb₅W₃O₉F₁₀ family is similar to that of fluorine in Pb₅Cr₃F₁₉ with an identical total number of O and F atoms in the equivalent unit cell, the presence of O atoms results in a space-group change.

Fig. 2 shows the structures of (a) Pb₅Cr₃F₁₉, (b) Pb₅W₃O₉F₁₀, (c) Sr₃(FeF₆)₂ and (d) SrAlF₅ projected along each *c* axis. The octahedra about Cr, W, Fe and Al, respectively, are shown together with the positions of the Pb or Sr atoms. Figs. 2(a), 2(b) and 2(c) show, in addition, the positions of F atoms not coordinated to Cr, W or Fe. The four structures are very similar although Pb₅Cr₃F₁₉, which crystallizes in space group *I4cm*, is noticeably more symmetrical than the others. The major difference between structures is that SrAlF₅ has two kinds of corner-sharing chains of *BF*₆ octahedra whereas the three other

families have only one. The *BF*₆ chains along *x* = $\frac{1}{2}$, *y* = 0 and *x* = 0, *y* = $\frac{1}{2}$ in SrAlF₅ are replaced by chains of eight- and ten-coordinated Pb in Pb₅W₃O₉F₁₀ and Pb₅Cr₃F₁₉, respectively, and by chains of eight-coordinated Sr along *x* = $\frac{1}{2}$, *y* = 0 in Sr₃(FeF₆)₂ (transformed to the same unit cell as Pb₅Cr₃F₁₉). A corresponding chain along *x* = 0, *y* = $\frac{1}{2}$ is missing in the latter compound.

Following completion of this work, we learned (LeBail, 1989) that Pb₅Fe₃F₁₉ is isostructural with Pb₅Cr₃F₁₉ but that, owing to the high displacement anisotropy of Pb²⁺, the structure determination of the former has not been published.

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