Sr1—O7	2.525 (6)	Sr3—O9	2.902 (6)
Sr2—O1	2.639 (12)	Sr3—O1^{i}	2.992 (11)
Sr2—O1^{iv}	2.639 (12)	Sr3—O6^{xi}	3.005 (10)
Sr2—O1^{vii}	2.699 (13)	Sr3—O1^{xii}	3.064 (11)
O3—Nb1—O1	88.7 (4)	O7—Nb2—O6^{iii}	88.3 (2)
O3—Nb1—O1^{i}	88.7 (4)	O8—Nb2—O8^{ii}	161.9 (4)
O3—Nb1—O2	93.0 (4)	O8—Nb2—O5^{v}	86.5 (4)
O3—Nb1—O2^{i}	93.0 (4)	O8—Nb2—O6^{iii}	77.7 (4)
O3—Nb1—O3^{ii}	180.0	O8^{ii}—Nb2—O5^{v}	84.1 (5)
O1—Nb1—O1^{i}	177.8 (5)	O8^{ii}—Nb2—O6^{iii}	85.3 (3)
O1—Nb1—O2	88.2 (2)	O5^{v}—Nb2—O6^{iii}	78.8 (2)
O1—Nb1—O2^{i}	91.9 (2)	O6^{iii}—Nb3—O5^{iii}	102.3 (2)
O1—Nb1—O3^{ii}	91.3 (4)	O6^{iii}—Nb3—O9	91.8 (4)
O1^{i}—Nb1—O2	91.9 (2)	O6^{iii}—Nb3—O9^{ii}	102.1 (4)
O1^{i}—Nb1—O2^{i}	88.2 (2)	O6^{iii}—Nb3—O2	90.6 (2)
O1^{i}—Nb1—O3^{ii}	91.3 (4)	O6^{iii}—Nb3—O1^{iv}	170.9 (5)
O2—Nb1—O2^{i}	174.0 (7)	O5^{iii}—Nb3—O9	91.8 (5)
O2—Nb1—O3^{ii}	87.0 (4)	O5^{iii}—Nb3—O9^{ii}	90.6 (5)
O2^{i}—Nb1—O3^{ii}	87.0 (4)	O5^{iii}—Nb3—O2	167.0 (2)
O4^{v}—Nb2—O7	96.6 (2)	O5^{iii}—Nb3—O1^{iv}	82.7 (2)
O4^{v}—Nb2—O8	99.7 (6)	O9—Nb3—O9^{ii}	165.0 (4)
O4^{v}—Nb2—O8^{ii}	96.7 (6)	O9—Nb3—O2	88.8 (4)
O4^{v}—Nb2—O5^{v}	96.4 (2)	O9—Nb3—O1^{iv}	80.4 (4)
O4^{v}—Nb2—O6^{iii}	174.7 (3)	O9^{ii}—Nb3—O2	85.5 (4)
O7—Nb2—O8	93.2 (5)	O9^{ii}—Nb3—O1^{iv}	85.3 (4)
O7—Nb2—O8^{ii}	92.5 (5)	O2—Nb3—O1^{iv}	84.7 (2)
O7—Nb2—O5^{v}	166.9 (2)		

Symmetry codes: (i) $1-x, 1-y, z$; (ii) $x, y, 1+z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (iv) $1-x, -y, z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (vii) $x, y, z-1$; (viii) $1-x, -y, z-1$; (ix) $x, y-1, z$; (x) $x, 1+y, z$; (xi) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (xii) $1-x, 1-y, z-1$.

Data collection, cell refinement and crystal-face indexing: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement and absorption correction: *SHELX*76 (Sheldrick, 1976). 12 reflections affected by extinction were excluded from the final cycles of least-squares refinement. Anisotropic displacement factors were refined only for Sr and Nb atoms. Molecular graphics: *SCHAKAL* (Keller, 1986). Geometry calculations: *ORFFE*3 (Busing *et al.*, 1971)

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Lists of structure factors, anisotropic displacement parameters and complete geometry, and a plot of the projection of the structure on the *ac* plane, have been deposited with the IUCr (Reference: BR1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Type of Mixed Anionic Framework in the Structure of $K_3[Al_4F_9(PO_4)_2]$

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Abstract

X-ray analysis of a hydrothermally synthesized potassium aluminium fluoride orthophosphate, $K_3[Al_4F_9(PO_4)_2]$, showed that this compound has a new type of

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crystal structure. Three kinds of *cis*-AlF_4O_2 octahedra share common vertices to form branched $[Al_4F_9O_8]_n$ chains parallel to the *a* axis of the monoclinic unit cell. In the *b* and *c* directions these chains are linked by PO_4 tetrahedra to give a three-dimensional framework of octahedra and tetrahedra. The open structure exhibits several crossed channels suggesting possible cationic transport properties. The two largest of these channels are occupied by the K^+ cations.

Comment

As part of wider attempts to synthesize and investigate pegmatite-related phosphates, we are studying the products of hydrothermal growth experiments in the system $KF–Al_2O_3–H_3PO_4–H_2O$. Here, we present the crystal structure of a new fluorine-rich compound, $K_3[Al_4F_9(PO_4)_2]$.

Three independent aluminium octahedra share common vertices to form a new type of branched chain, $[Al_4F_9O_8]_n$, parallel to the *a* axis of the unit cell (Fig. 1). The habit of the crystal (flat needles along [100]) reflects this structural feature. Four vertices of each aluminium octahedron are occupied by F atoms, and two by O atoms in the *cis* position; these O atoms also belong to PO_4 tetrahedra. The Al2 and Al3 octahedra with C_s symmetry are quite regular (Table 2). The Al2—F and Al3—F distances are in the interval 1.799 (3)–1.838 (2) Å (average 1.826 Å). The two Al—O distances, equivalent by the mirror plane, are Al2—O 1.814 (2) and Al3—O 1.838 (2) Å. The variation of the Al—F distances in the Al1 octahedron in a general position is substantially larger [Al1—F = 1.769 (2)–1.881 (2) Å, average 1.840 Å] whereas the Al1—O distances do not differ significantly [1.833 (3), 1.843 (2) Å]. The very short Al1—F1 distance of 1.769 Å belongs to the sole terminal Al—F bond in the structure.

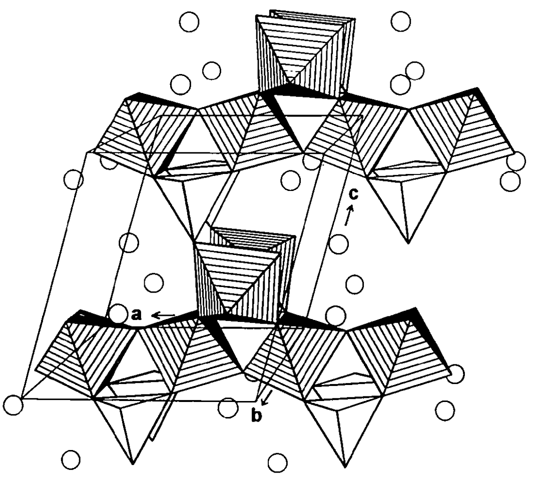

Fig. 1. Perspective view approximately along the *b* axis. K ions are represented by spheres.

The independent fragment of the chain is built by Al2 and Al3 octahedra joined together by F5 on the mirror plane. Two additional Al1 polyhedra are attached to this pair of Al2 and Al3 octahedra through F4 and F3 vertices. These two Al1 octahedra are also linked together by a common F2 atom on the mirror plane (Fig. 2). The centres of these four octahedra thus form a tetrahedron. These tetrahedral units repeat along the *a* axis to form chains parallel to [100] (Fig. 1), which may be considered as a fragment of the pyrochlore structure; there, three such chains intersect according to the cubic symmetry.

In the *b* and *c* directions these octahedral chains are linked by PO_4 tetrahedra to give a three-dimensional framework (Fig. 3). Each of the Al2 and Al3 polyhedra shares four F vertices with four neighbouring octahedra and two O vertices with different PO_4 tetrahedra. The Al1 polyhedra share three F vertices with octahedra,

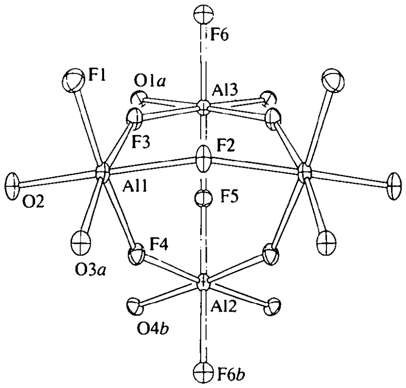

Fig. 2. Independent fragment of the branched octahedral chain. Displacement ellipsoids are drawn at the 50% probability level.

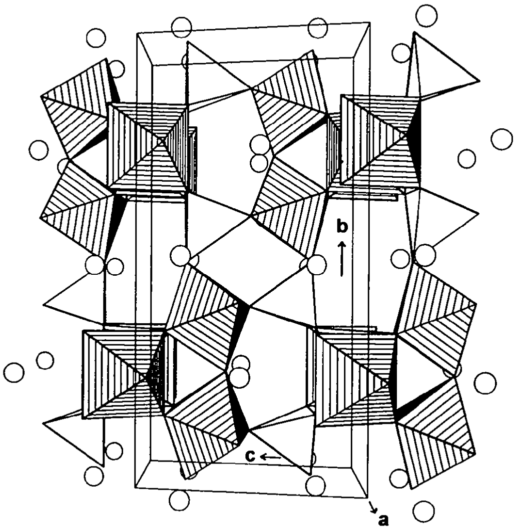

Fig. 3. Perspective view of the mixed anionic framework along the *a* axis, the direction of the octahedral chains.

two O vertices with PO_4 tetrahedra, and one F vertex remains unshared.

Two types of independent K atoms occupy the interstices of this framework. They form a 12-vertex polyhedron $[KO_6F_6]$ (K1, symmetry C_1) and 11-vertex polyhedron $[KO_4F_7]$ (K2, symmetry C_s) (Table 2). The open structure of the anionic framework exhibits several crossed channels (Fig. 1) suggesting possible cationic transport properties.

According to Sandomirskji & Belov (1984), these kinds of crystal structures built by acid and amphoteric complexes and having unshared vertices in the framework are called mixed anionic paraframeworks. A similar classification, particularly for 'aluminofluoride' minerals was proposed by Hawthorne (1984). It is based on the type of polymerization of the aluminium octahedra together with other strongly bonded complex anions. The structure of $K_3[Al_4F_9(PO_4)_2]$, with only corner-sharing polyhedra in the framework, adds a new 'structure motif' to those given by Hawthorne (1984). Other frameworks of corner-sharing aluminium octahedra cross-linked by PO_4 tetrahedra have been found in the minerals ambligonite $LiAlFPO_4$ (Groat *et al.*, 1990), lacroixite $NaAlFPO_4$ (Lahti & Pajunen, 1985) and synthetic $KAlFPO_4$ (Slovokhotova *et al.*, 1991). In all these compounds, the octahedra are linked *via trans* vertices to form linear chains. The type of branched octahedral chains in the $[Al_4F_9(PO_4)_2]^{3-}$ framework has not been found before, to our knowledge, in other fluorine compounds. The increased complexity of the Al:F:P ratio from 1:1:1 in $KAlFPO_4$ {'$K_4[Al_4F_4(PO_4)_4]$'}, closest by composition to our compound, to 2:4.5:1 in $K_3[Al_4F_9(PO_4)_2]$ results in the more complex interconnection within the octahedral chain.

Experimental

Single crystals were obtained by hydrothermal synthesis in the system $KF–Al_2O_3–H_3PO_4–H_2O$ (T = 573 K, P = 1000 atm, 50% aqueous solution of KF). A qualitative X-ray spectral analysis (CAMSCAN 4, AN 10000) revealed the presence of potassium, aluminium and fluorine in the grown material. The amount of phosphorus was too small to be detected in the crystals. The formula of the new compound has been established as a result of its structural investigation.

Crystal data

$K_3[Al_4F_9(PO_4)_2]$
$M_r = 586.16$
Monoclinic
$P2_1/m$
$a = 6.7214\,(6)$ Å
$b = 13.8558\,(7)$ Å
$c = 7.2764\,(4)$ Å
$\beta = 105.927\,(6)^\circ$
$V = 651.64\,(8)$ Å^3
$Z = 2$
$D_x = 2.987$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 18–45^\circ$
$\mu = 15.884$ mm^{-1}
$T = 293\,(2)$ K
Flat needle
0.225 × 0.10 × 0.025 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: nine ψ scans (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{\min} = 0.346$, $T_{\max} = 1.000$
2270 measured reflections
1153 independent reflections

1035 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0796$
$\theta_{\max} = 65^\circ$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 17$
$l = -9 \rightarrow 9$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0333$
$wR(F^2) = 0.0879$
$S = 1.056$
1152 reflections
128 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.2980P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.525$ e Å^{-3}
$\Delta\rho_{\min} = -0.615$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.0032 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K1	0.18928 (14)	0.50856 (6)	−0.20761 (14)	0.0288 (3)
K2	0.0828 (2)	1/4	0.5427 (2)	0.0240 (4)
Al1	0.32780 (15)	0.62254 (6)	0.31890 (15)	0.0089 (3)
Al2	0.4835 (2)	3/4	−0.0383 (2)	0.0093 (4)
Al3	−0.0260 (2)	3/4	−0.0511 (2)	0.0085 (4)
P	0.34670 (13)	0.39792 (5)	0.28523 (13)	0.0088 (3)
F1	0.1557 (3)	0.59180 (12)	0.4550 (3)	0.0164 (5)
F2	0.3235 (4)	3/4	0.3907 (4)	0.0140 (6)
F3	0.0918 (3)	0.65659 (11)	0.1224 (3)	0.0137 (5)
F4	0.4727 (3)	0.66154 (12)	0.1470 (3)	0.0131 (5)
F5	0.2047 (4)	3/4	−0.1309 (4)	0.0130 (6)
F6	−0.2346 (4)	3/4	0.0645 (4)	0.0126 (6)
O1	0.1368 (3)	0.34587 (14)	0.2235 (3)	0.0120 (5)
O2	0.3159 (4)	0.50163 (14)	0.2110 (3)	0.0141 (6)
O3	0.4227 (4)	0.39541 (14)	0.5030 (3)	0.0112 (5)
O4	0.5014 (3)	0.34930 (14)	0.1964 (4)	0.0125 (5)

Table 2. *Selected geometric parameters* (Å, °)

K1···F1^{i}	2.666 (2)	Al1—F1	1.769 (2)
K1···O4^{ii}	2.849 (2)	Al1—O3^{vii}	1.833 (3)
K1···F1^{iii}	2.874 (2)	Al1—O2	1.843 (2)
K1···O2	2.930 (3)	Al1—F2	1.8441 (12)
K1···O1^{iii}	2.958 (2)	Al1—F4	1.864 (2)
K1···F3^{iii}	3.136 (2)	Al1—F3	1.881 (2)
K1···F4^{ii}	3.219 (2)	Al2—F5	1.809 (3)
K1···O2^{ii}	3.336 (2)	Al2—O4^{ii}	1.814 (2)
K1···O3^{i}	3.341 (2)	Al2—O4^{viii}	1.814 (2)
K1···F3	3.356 (2)	Al2—F6^{ix}	1.836 (3)
K1···F5	3.3885 (10)	Al2—F4^{x}	1.838 (2)
K1···O2^{iii}	3.392 (2)	Al2—F4	1.838 (2)
K2···F1^{iv}	2.718 (2)	Al3—F5	1.799 (3)
K2···F1^{v}	2.718 (2)	Al3—F6	1.823 (3)
K2···F6^{v}	2.758 (3)	Al3—F3^{x}	1.830 (2)
K2···O1	2.784 (3)	Al3—F3	1.830 (2)
K2···O1^{vi}	2.784 (3)	Al3—O1^{iii}	1.838 (2)
K2···F2^{v}	2.902 (3)	Al3—O1^{xi}	1.838 (2)
K2···F5^{iii}	3.088 (3)	P—O4	1.524 (2)
K2···O3	3.118 (2)	P—O3	1.526 (3)
K2···O3^{vi}	3.118 (2)	P—O2	1.529 (2)
K2···F3^{v}	3.250 (2)	P—O1	1.537 (2)
K2···F3^{iv}	3.250 (2)		

F1—Al1—O3$^{\text{vii}}$	100.58 (11)	F4$^{\text{x}}$—Al2—F4	83.65 (13)
F1—Al1—O2	93.51 (9)	F5—Al3—F6	171.7 (2)
O3$^{\text{vii}}$—Al1—O2	95.86 (11)	F5—Al3—F3$^{\text{x}}$	88.53 (10)
F1—Al1—F2	90.49 (11)	F6—Al3—F3$^{\text{x}}$	85.61 (10)
O3$^{\text{vii}}$—Al1—F2	90.70 (12)	F3$^{\text{x}}$—Al3—F3	90.04 (14)
O2—Al1—F2	171.56 (13)	F5—Al3—O1$^{\text{iii}}$	90.21 (10)
F1—Al1—F4	171.10 (11)	F6—Al3—O1$^{\text{iii}}$	95.51 (10)
O3$^{\text{vii}}$—Al1—F4	88.20 (10)	F3$^{\text{x}}$—Al3—O1$^{\text{iii}}$	178.24 (11)
O2—Al1—F4	86.96 (9)	F3—Al3—O1$^{\text{iii}}$	88.70 (10)
F2—Al1—F4	87.95 (10)	O1$^{\text{iii}}$—Al3—O1$^{\text{xi}}$	92.5 (2)
F1—Al1—F3	86.63 (10)	O4—P—O3	110.94 (14)
O3$^{\text{vii}}$—Al1—F3	171.25 (10)	O4—P—O2	107.91 (13)
O2—Al1—F3	88.57 (10)	O3—P—O2	111.26 (13)
F2—Al1—F3	84.24 (11)	O4—P—O1	110.30 (13)
F4—Al1—F3	84.50 (10)	O3—P—O1	108.15 (13)
F5—Al2—O4$^{\text{ii}}$	89.77 (11)	O2—P—O1	108.25 (13)
O4$^{\text{ii}}$—Al2—O4$^{\text{viii}}$	98.7 (2)	Al1$^{\text{x}}$—F2—Al1	146.5 (2)
F5—Al2—F6$^{\text{ix}}$	177.92 (15)	Al3—F3—Al1	144.79 (11)
O4$^{\text{ii}}$—Al2—F6$^{\text{ix}}$	91.58 (10)	Al2—F4—Al1	144.94 (11)
F5—Al2—F4$^{\text{x}}$	91.60 (10)	Al3—F5—Al2	140.9 (2)
O4$^{\text{ii}}$—Al2—F4$^{\text{x}}$	172.39 (11)	Al3—F6—Al2$^{\text{xii}}$	130.6 (2)
O4$^{\text{viii}}$—Al2—F4$^{\text{x}}$	88.84 (9)	P—O1—Al3$^{\text{iii}}$	134.89 (14)
F6$^{\text{ix}}$—Al2—F4$^{\text{x}}$	86.86 (10)	P—O2—Al1	135.9 (2)
O4$^{\text{ii}}$—Al2—F4	88.83 (9)	P—O3—Al1$^{\text{vii}}$	135.86 (15)
F6$^{\text{ix}}$—Al2—F4	86.86 (10)	P—O4—Al2$^{\text{ii}}$	140.1 (2)

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, 1-y, -z$; (iii) $-x, 1-y, -z$; (iv) $-x, y-\frac{1}{2}, 1-z$; (v) $-x, 1-y, 1-z$; (vi) $x, \frac{1}{2}-y, z$; (vii) $1-x, 1-y, 1-z$; (viii) $1-x, \frac{1}{2}+y, -z$; (ix) $1+x, y, z$; (x) $x, \frac{3}{2}-y, z$; (xi) $-x, \frac{1}{2}+y, -z$; (xii) $x-1, y, z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *STRUPLO* (Fischer, 1985), *TROMPLEU* (Le Lirzin, Gravereau & Larroche, 1991), *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

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Lists of anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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