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A new layered perovskite, $KSrNb_2O_6F$, by powder neutron diffraction

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The structure of a new layered oxyfluoride, *viz.* potassium strontium diniobium hexaoxide fluoride, $KSrNb_2O_6F$, was refined from powder neutron diffraction data in the orthorhombic space group *Immm*. The oxyfluoride compound is an $n = 2$ member of the Dion–Jacobson-type family of general formula $A[A'_{n-1}B_nX_{3n+1}]$, which consists of double layered perovskite slabs, $[SrNb_2O_6F]^-$, between which K^+ ions are located. Within the perovskite slabs, the NbO_5F octahedra are significantly distorted and tilted about the *a* axis. A bond-valence-sum calculation gives evidence for O/F ordering in $KSrNb_2O_6F$, with the F^- ions located in the central sites of the corner-sharing NbO_5F octahedra along the *b* axis. All atoms lie on special positions, namely Nb on *m*, Sr on *mmm*, K on *m*2*m*, F on *mm*2, and O on sites of symmetry *m* and *m*2*m*.

Comment

Dion–Jacobson type (DJ) compounds with the general formula $A[A'_{n-1}B_nX_{3n+1}]$ have attracted great interest because they have a wide range of properties, including ion exchange, intercalation behavior and ion conductivity (Dion *et al.*, 1981). Among many synthetic approaches developed for the preparation of new DJ phases, the replacement of O^{2-} by F^- could be a promising method (Choy *et al.*, 2001). We describe here the crystal structure of a new oxyfluoride compound, $KSrNb_2O_6F$, based on neutron diffraction analysis. This oxyfluoride compound was obtained by replacement of O^{2-} and La^{3+} ions in the well known oxide $KLaNb_2O_7$ (Gopalakrishnan *et al.*, 1987) by F^- and Sr^{2+} ions.

The crystal structure of $KSrNb_2O_6F$ is closely related to that of $KLaNb_2O_7$, which is an $n = 2$ member of the DJ series. In a previous study (Sato *et al.*, 1992), the structure of $KLaNb_2O_7$ was refined in the space group *C*222, with $a \simeq 3.91$ Å, $b \simeq 21.60$ Å and $c \simeq 3.89$ Å. An attempt to fit the neutron diffraction data for $KSrNb_2O_6F$ using this model was successful only for the major reflections and could not explain some weak reflections, while we found that an orthorhombic unit cell involving doubling of the *c* axis was adequate to fit the phase. Space group *Immm* was chosen from the reflection conditions $h + k + l = 2n$. The starting model was deduced from the structure of $KLaNb_2O_7$ with consideration of the cell doubling. The observed, calculated and difference patterns from the Rietveld refinement of the neutron diffraction pattern are shown in Fig. 1. Selected interatomic distances and angles are summarized in Table 1. This refinement was performed on the assumption that the F^- ions lie in the central positions of the corner-sharing NbO_5F octahedra along the *b* axis (4*j* sites) and the O^{2-} ions occupy the other anionic sites. The ordered O/F distribution was confirmed by bond-valence-sum (BVS) calculations (Brese & O'Keeffe, 1991). The BVS values for the F^- (1.09) and O^{2-} ions (1.93–2.14) are in agreement with the formal charge of both ions within error ranges below 10%. Several models with different O/F distributions were also tested but they gave relatively large deviations of the BVS values from the formal charges for the anions. For example, in the 'random O/F distribution' model, the formal charge of each anion site is 1.86 because the O^{2-} and F^- ions are assumed to occupy all the sites with the statistical proportion (2×6/7 + 1×1/7). The observed BVS values, however, cover the range 1.12–2.06. Noticeably, the anion at the 4*j* site exhibits a significantly small BVS value (1.12). The BVS values for $KSrNb_2O_6F$ deduced from two models with different O/F distributions are summarized in Table 2.

As shown in Fig. 2, the structure of $KSrNb_2O_6F$ is composed of two-dimensional double perovksite layers and interlayer K^+ ions. Adjacent perovskite layers are stacked along the *b* axis with a displacement vector of (**a**+**c**)/2. The K^+ ions are coordinated by six O^{2-} anions to form two short K—O bonds and four long K—O bonds. A similar environment around the K^+ ions has been observed in other K-containing compounds, such as $KCa_2Nb_3O_{10}$ (Fukuoka *et al.*, 2000). The distortion of the trigonal–prismatic coordination of the K^+ ions in $KSrNb_2O_6F$ is attributed to the displacement of the apical O^{2-} ions from their positions in the ideal perovskite structure of

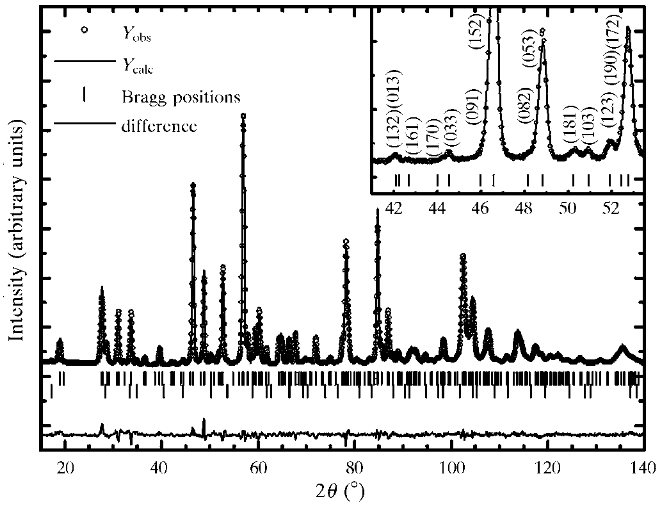

Figure 1
A Rietveld refinement plot of $KSrNb_2O_6F$. The inset shows the indexation of a selected portion of the diffraction pattern.

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the $[SrNb_2O_6F]^-$ moiety. In the perovskite slabs, the NbO_5F octahedra are tilted about the *a* axis, to the left and right alternately (as shown in Fig. 2), giving rise to a diminution of the Nb—F—Nb bond angle. The co-operative tilting of the NbO_5F octahedra results in the corrugation of the perovskite slab along the *c* direction, doubling the *c* axis, which thus becomes twice as long as *a*. Recently, the same tilt was reported for $BaSrNb_2O_7$ (Le Berre *et al.*, 2004).

The Nb^{5+} ion is significantly displaced from the center of the NbO_5F octahedron, leading to four equatorial Nb—O distances of nearly equal length [1.983 (5)–1.995 (5) Å], a short Nb—O bond [1.768 (4) Å] and a long opposite Nb—F bond [2.398 (2) Å]. Such distortion, leading to long and short bonds along the *b* axis, is well known in layered perovskites. However, it is noteworthy that the Nb—F bond in $KSrNb_2O_6F$ is much longer than the $Nb—O_{central}$ bonds (2.25–2.28 Å) found in other DJ-type oxides, such as $KLaNb_2O_7$ and $RbLaNb_2O_7$ (Armstrong & Anderson, 1994). The apical Nb—O bond and equatorial Nb—O bonds in $KSrNb_2O_6F$ show almost the same distances as those of the oxide analogues. The characteristic distribution of interatomic distances also supports the conclusion that the bridging sites of the corner-sharing NbO_5F bi-octahedra aligned with the *b* axis are occupied by F^- ions in the structure of $KSrNb_2O_6F$.

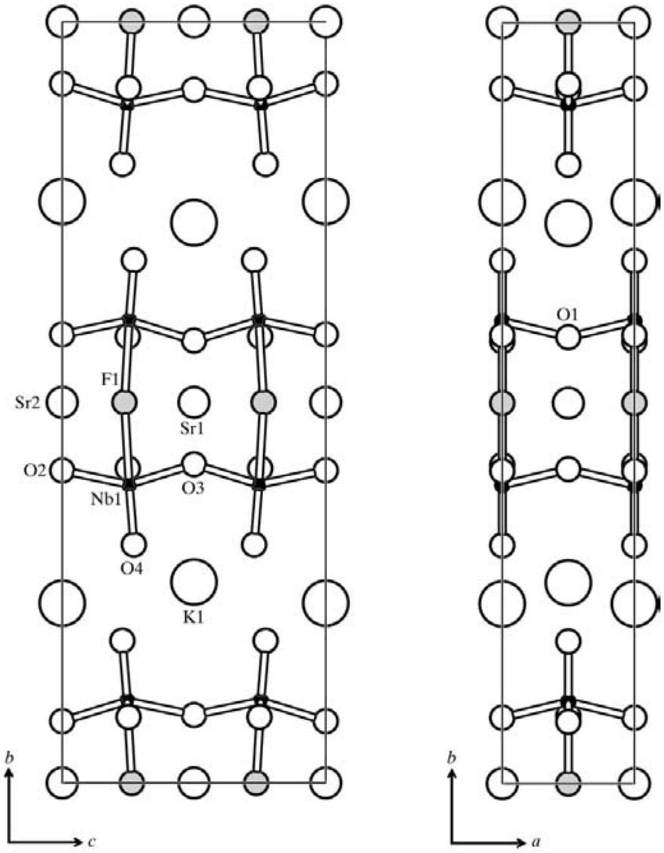

Figure 2
Projections along the *a* axis (left) and the *c* axis (right) of the structure of $KSrNb_2O_6F$.

Experimental

A polycrystalline sample of $KSrNb_2O_6F$ was prepared from $SrNb_2O_6$ and KF. The precursor $SrNb_2O_6$ was prepared by firing a stoichiometric mixture of $SrCO_3$ and Nb_2O_5 at 1373 K for 2 d. The $SrNb_2O_6$ product was thoroughly mixed with KF and pressed into pellets in a glove-box. The pellets were placed inside a sealed gold tube. The tube was heated at a rate of 2 K min^{-1} to the reaction temperature of 1143 K, held at that temperature for 24 h and then cooled at a rate of 2 K min^{-1}. Energy-dispersive X-ray analysis indicated that the ratio of atoms [K:Sr:Nb:O:F = 1.03 (3):1.01 (3):2:5.6 (5):0.97 (3)] matched the nominal composition (1:1:2:6:1) within experimental error.

Crystal data

$KSrNb_2O_6F$
M_r = 427.54
Orthorhombic, *Immm*
a = 3.8604 (2) Å
b = 22.220 (1) Å
c = 7.6932 (3) Å
V = 659.91 (5) $Å^3$
Z = 4
Neutron radiation

λ = 1.8371 Å
μ = 0.87 mm^{-1}
T = 298 K
Specimen shape: cylinder
10 × 10 × 30 mm
Specimen prepared at 101 kPa
Specimen prepared at 1143 K
Particle morphology: plate-like, white

Data collection

HANARO high-resolution powder diffractometer
Specimen mounting: vanadium can
Specimen mounted in transmission mode

Scan method: step
$2\theta_{min}$ = 0°, $2\theta_{max}$ = 160°
Increment in 2θ = 0.05°

Refinement

R_p = 0.049
R_{wp} = 0.063
R_{exp} = 0.032
R_B = 0.039
S = 1.97
Wavelength of incident radiation: 1.8371 Å

Excluded region(s): $2\theta < 15°$, $2\theta > 140°$
Profile function: pseudo-Voigt
39 parameters
Preferred orientation correction: none

Table 1
Selected geometric parameters (Å, °).

$K1—O4^{i}$	2.679 (6)	Sr2—F1	2.647 (4)
K1—O4	2.841 (4)	Nb1—O1	1.9854 (7)
Sr1—O1	2.722 (5)	Nb1—O2	1.995 (5)
Sr1—O3	2.638 (5)	Nb1—O3	1.983 (5)
Sr1—F1	2.805 (4)	Nb1—O4	1.768 (4)
Sr2—O1	2.727 (5)	Nb1—F1	2.398 (2)
Sr2—O2	2.779 (5)		
$Nb1^{ii}—F1—Nb1$	173.1 (3)	$Nb1^{iv}—O2—Nb1$	157.2 (4)
$Nb1—O1—Nb1^{iii}$	152.88 (15)	$Nb1—O3—Nb1^{v}$	145.0 (4)

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

Structure refinement was carried out by the Rietveld method with pseudo-Voigt peak shapes and refined backgrounds. In the Rietveld refinement, isotropic displacement parameters were used for all atoms. The equatorial O atoms were constrained to have a common displacement parameter. Attempts to refine independent values for these parameters led to model instability, which may result from micro-twinning or stacking faults, which are often encountered in powder samples with layered structures. The diffraction pattern also includes peaks from a small amount of KNb_2O_5F ($Fd\overline{3}m$, *a* = 10.58 Å; Subramanian *et al.*, 1983) as an impurity, but the impurity peaks are well separated from those of the $KSrNb_2O_6F$ phase, at least in the low- and medium-scattering angle region. The total concentration of the impurities was estimated to be below 3%.

Table 2
Bond-valence sums (V^*) and the formal charges (V) for $KSrNb_2O_6F$ depending on O/F distribution.

	Ordered			Disordered		
Site	Atom	V^*	V	Atom	V^*	V
4*g*	K1	1.04	1	K1	0.99	1
2*a*	Sr1	2.24	2	Sr1	2.18	2
2*c*	Sr2	2.17	2	Sr2	2.20	2
8*l*	Nb1	4.97	5	Nb1	4.90	5
8*l*	O1	2.02	2	6/7O + 1/7F	1.99	1.86
4*g*	O2	1.93	2	6/7O + 1/7F	1.92	1.86
4*h*	O3	2.14	2	6/7O + 1/7F	2.06	1.86
8*l*	O4	1.99	2	6/7O + 1/7F	1.95	1.86
4*j*	F1	1.09	1	6/7O + 1/7F	1.12	1.86

Data collection: HANARO HRPD beamline software; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 1990); data reduction: *FULLPROF*; program(s) used to solve structure: *FULLPROF*; program(s) used to refine structure: *FULLPROF*; molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *FULLPROF*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3094). Services for accessing these data are described at the back of the journal.

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