

KCaNb₂O₆F from a combined synchrotron X-ray and neutron powder diffraction study

Chung-Yul Yoo and Seung-Joo Kim*

Department of Chemistry, Division of Energy Systems Research, Ajou University, Suwon 443-749, Republic of Korea

Correspondence e-mail: sjookim@ajou.ac.kr

Received 27 September 2007; accepted 18 November 2007

Key indicators: powder neutron study; $T = 298$ K; mean $\sigma(\text{Nb}-\text{O}) = 0.0003$ Å; disorder in main residue; R factor = 4.08; wR factor = 5.64; data-to-parameter ratio = 2.0.

Potassium calcium diniobium hexaoxide fluoride, KCaNb₂O₆F, crystallizes in the cubic pyrochlore-type structure. In the crystal structure, NbO₆ octahedra are linked together by common corners to form a three-dimensional [Nb₂O₆]²⁻ network. (K,Ca) and F atoms, which are located in the voids of the [Nb₂O₆]²⁻ network, form zigzag [(K,Ca)F]²⁺ chains. The K and Ca atoms are distributed statistically over the same crystallographic position (site-occupancy factor = 0.5), having an eightfold coordination by six O atoms from the NbO₆ octahedra and by two F atoms. All atoms lie on special positions, *viz.* Nb has $\bar{3}m$, the (K,Ca) site has $\bar{3}m$, O has $2mm$ and F has $\bar{4}3m$ site symmetry.

Related literature

For a general description of structures and physical properties of pyrochlore-type compounds, see Subramanian *et al.* (1983). The oxyfluoride compounds with general composition A₂Nb₂O₆F ($A =$ alkali metal and alkaline-earth metal) crystallize in different structural types, depending on the size of the A cation. The layered perovskite-type structure is the most stable structure for large cations, as observed in KSrNb₂O₆F (Yoo *et al.*, 2007) and RbSrNb₂O₆F (Choy *et al.*, 2001), while the pyrochlore structure is favorable for small A cations, as in NaCaNb₂O₆F (von Gaertner, 1930) and LiCaNb₂O₆F (Le Berre *et al.*, 2007). The structural variation with composition in these oxyfluoride homologues has been discussed in the literature (Kim *et al.*, 2002). For rare earth pyrochlores of composition RE₂Sn₂O₇ (RE = La to Lu), see Kennedy *et al.* (1997). Bond valence parameters were taken from Brese & O'Keeffe (1991), and measured reflections of the title compound were indexed with *DICVOL* (Boultif & Louër, 2004).

Experimental

Crystal data

KCaNb₂O₆F

$M_r = 380$

Cubic, $Fd\bar{3}m$

$a = 10.55376$ (12) Å

$V = 1175.50$ (2) Å³

$Z = 8$

Neutron radiation

$\lambda = 1.8348$ Å

$\mu = 0.09$ mm⁻¹

$T = 298$ K

Specimen shape: cylinder

10 × 10 × 30 mm

Specimen prepared at 101 kPa

Specimen prepared at 1023 K

Particle morphology: particle, white

Data collection

HANARO high-resolution powder diffractometer

Specimen mounting: vanadium can

Specimen mounted in transmission mode

Scan method: step

Absorption correction: for a cylinder mounted on the φ axis

$2\theta_{\min} = 0.0$, $2\theta_{\max} = 160.0^\circ$

Increment in $2\theta = 0.05^\circ$

Refinement

$R_p = 4.08$

$R_{wp} = 5.64$

$R_{exp} = 3.58$

$R_B = 2.53$

$S = 1.57$

Excluded region(s): $2\theta < 15^\circ$, $2\theta > 140^\circ$

Profile function: pseudo-Voigt

51 reflections

25 parameters

Preferred orientation correction:

none

Table 1

Selected bond lengths (Å).

(K,Ca)—F1	2.28500 (10)	Nb1—O1 ⁱⁱ	1.9873 (3)
(K,Ca)—O1 ⁱ	2.7014 (5)		

Symmetry codes: (i) y, z, x ; (ii) $-x + \frac{3}{4}, -y + \frac{1}{4}, z + \frac{1}{2}$.

Data collection: HANARO HRPD beamline software; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: *FULLPROF*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *FULLPROF*.

This work was supported by Ajou University. The authors are also grateful to Pohang Accelerator Laboratory and HANARO Center in the Korea Atomic Energy Research Institute for synchrotron X-ray and neutron diffraction measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2150).

References

- Bergerhoff, G. (1996). *DIAMOND*. Bonn, Germany.
- Boultif, A. & Louër, D. (2004). *J. Appl. Cryst.* **37**, 724–731.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Choy, J. H., Kim, J. Y., Kim, S. J., Sohn, J. S. & Han, O. H. (2001). *Chem. Mater.* **13**, 906–912.
- Gaertner von, H. R. (1930). *Geol. Palaeontol. Beilagen Abt. A*, **61**, 1–30.
- Kennedy, B. J., Hunter, B. A. & Howard, C. J. (1997). *J. Solid State Chem.* **130**, 58–65.
- Kim, J. Y., Chung, I., Kim, S. J. & Choy, J. H. (2002). *J. Mater. Chem.* **12**, 1001–1004.
- Le Berre, F., Crosnier-Lopez, M., Galven, C., Fourquet, J., Legein, C., Body, M. & Buzaré, J. (2007). *Dalton Trans.* pp. 2457–2466.

Rodríguez-Carvajal, J. (2001). *FULLPROF*. Commission on Powder Diffraction (IUCr), Newsletter 26, pp. 12–19.
Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.

Subramanian, M. A., Aravamudan, G. & Subba Rao, G. V. (1983). *Prog. Solid State Chem.* **15**, 55–143.
Yoo, C.-Y., Hong, K.-P. & Kim, S.-J. (2007). *Acta Cryst.* **C63**, i63–i65.

supplementary materials

Acta Cryst. (2007). E63, i203-i204 [doi:10.1107/S1600536807060436]

KCaNb₂O₆F from a combined synchrotron X-ray and neutron powder diffraction study

C.-Y. Yoo and S.-J. Kim

Comment

KCaNb₂O₆F is isotypic with NaCaNb₂O₆F (von Gaertner, 1930), typical examples of cubic pyrochlore-type structures. A general description of structures and physical properties of pyrochlore-type compounds was given by Subramanian *et al.* (1983). Oxyfluoride compounds with general composition $A_2\text{Nb}_2\text{O}_6\text{F}$ (A = alkali metal and alkaline-earth metal) crystallize in different structural types, depending on the size of the A -cation. The layered perovskite-type structure is the most stable structure for large cations as observed in KSrNb₂O₆F (Yoo *et al.*, 2007) and RbSrNb₂O₆F (Choy *et al.*, 2001), while the pyrochlore structure is favorable for small A -cations as in NaCaNb₂O₆F and LiCaNb₂O₆F (Le Berre *et al.*, 2007). The structural variation on composition in these oxyfluoride homologues has been discussed in the literature (Kim *et al.* 2002).

In the title compound, the (K, Ca) atoms are located at 16*d* sites, Nb atoms at 16*c*, O atoms at 48*f* and F atoms at 8*b* sites. (K, Ca) atoms are coordinated to two F atoms and six O atoms, forming a puckered hexagonal bipyramid which is axially compressed with the two F atoms being at considerably shorter distances than the six O atoms. The bond compression inhibits the displacement of the (K, Ca) atoms toward the two closest F atoms, which results in the large anisotropic displacement ellipsoid of the F atom as shown in Fig. 1(*a*). The Nb atoms are bonded to six O atoms at equal distances forming nearly regular octahedra. By neglecting the K/Ca—O interaction, the structure can be regarded as two interpenetrating networks of Nb₂O₆ and (K, Ca)₂F units, the latter with an anti-cristobalite type arrangement (Fig. 1 *b*). The bond valence sums (BVS) calculated from the bond distances using the parameters of Brese and O'Keeffe (1991) are (K⁺, Ca²⁺) = 1.81, Nb⁵⁺ = 4.86, O²⁻ = 1.97 and F⁻ = 1.51. These values imply that the (K, Ca)—F bond is compressed while the Nb—O bond is slightly stretched. Such strong bond compression has been commonly observed in $A_2B_2O_7$ pyrochlores containing large A -cations. For example, the BVS for O at the 8*b* site shows a variation from 2.00 for Lu₂Sn₂O₇ to 2.60 for La₂Sn₂O₇ (Kennedy *et al.*, 1997). Taking into consideration that KCaNb₂O₆F is located near the upper boundary of the stability range for the pyrochlore structures due to the large size of the A -cations, the strong compression of the K/Ca—F bond could be anticipated. The origin of the large variation in BVS for the F ion is, however, still unclear. In this regard, solid state ¹⁹F-NMR spectroscopy may be helpful for further studies.

Experimental

KCaNb₂O₆F was prepared using a solid state reaction between KF and CaNb₂O₆. CaNb₂O₆ was prepared by firing a stoichiometric mixture of CaCO₃ and Nb₂O₅ at 1373 K for 2 d with intermediate grinding. The resulting CaNb₂O₆ was then thoroughly mixed with KF and pressed into pellets in a glovebox under an anhydrous Ar atmosphere. The pellets were placed inside a sealed gold tube and heated at 1023 K for 12 h, before cooled to room temperature at a rate of 2 K min⁻¹. The composition of the product was confirmed with energy-dispersive X-ray analysis (Jeol JSM-5600 scanning electron microscope fitted with a Be window detector, Oxford Instruments). The synchrotron X-ray powder diffraction (SXPDP) measurement was performed on beamline 8 C2-HRPD at Pohang Accelerator Laboratory, Pohang, Korea. The incident X-

supplementary materials

rays were vertically collimated by a mirror, and monochromated to the wavelength of 1.5422 Å by a double-crystal Si(111) monochromator. A dataset was collected in the range of $10^\circ \leq 2\theta \leq 130^\circ$ with a step size of 0.01° (2θ angle). The powder neutron diffraction (PND) data were collected on the high-resolution powder diffractometer with a 32 He-3 multi-detector system and a Ge(331) monochromator, installed at the Korea Atomic Energy Research Institute, Daejeon.

Refinement

Measured reflections were indexed with DICVOL (Boultif & Louër, 2004) and the cubic symmetry was confirmed from both SXRD and NPD data. Additional peaks due to symmetry lowering or impurity phase were not detected. The figures of merit were $M(20) = 49.7$, $F(20) = 24.0$ (0.0083, 100) for NPD and $M(20) = 55.1$, $F(20) = 25.5$ (0.0050, 158) for SXRD measurements. Systematic absences suggested two possible cubic space groups, *viz.* centrosymmetric $Fd\bar{3}m$ (No. 227) and non-centrosymmetric $Fd\bar{3}$ (No. 203). Both space groups turned out later to give basically the same structure solution. Thus, the higher symmetric $Fd\bar{3}m$ was chosen. The positions of the (K/Ca) and Nb atoms were determined employing direct methods using the SXRD data, for which a total of 500 ' F_{obs} ' amplitude factors were converted into structure factors and used as an input for *SHELXS97* (Sheldrick, 1997). The positions of anions were then determined by difference Fourier analyses of both SXRD and PND data. After this step, the anions were removed from the refinement and the residual density was calculated. From the difference Fourier maps it was suggested that all atomic positions are identical with those of the classical pyrochlore structure: $16d$ for (K, Ca), $16c$ for Nb, $48f$ for O and $8b$ for the F atom. The anion positions were confirmed from crystal chemical considerations and from BVS calculations (Brese & O'Keeffe, 1991). Structure refinements were carried out by the Rietveld method using Fullprof (Rodríguez-Carvajal, 2001) with pseudo-Voigt peak shapes and refined backgrounds. Refinement of atomic positions and isotropic displacement parameters gave the goodness of fit, $S = 2.38$. The refinements of the site occupation factors (SOFs) led to 0.502 (1), 0.502 (1) and 1.03 (2) for K, Ca and F atoms, respectively, which were in good agreement with the nominal composition. In the final step, the SOFs were fixed to the ideal values and the anisotropic thermal displacement factors were refined for all atoms, with constraints for the K and Ca atoms. The structure was refined with origin choice 2 of space group $Fd\bar{3}m$. The refinement plots for SXRD and NPD data are shown Fig. 2.

Figures

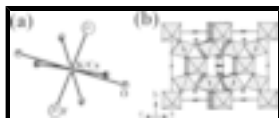


Fig. 1. The local structure around the (K, Ca) site (a), and a schematic view projected along [101] (b). Octahedra represent NbO_6 , large and small ellipsoids represent F and (K, Ca) atoms, respectively.

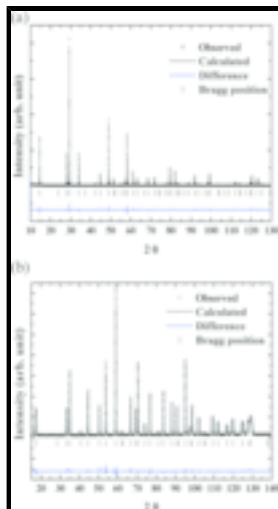


Fig. 2. Rietveld refinement plots of $\text{KCaNb}_2\text{O}_6\text{F}$ based on synchrotron X-ray (a) and neutron (b) powder diffraction data.

Potassium calcium diniobium hexaoxide fluoride

Crystal data

$\text{KCaNb}_2\text{O}_6\text{F}$

$M_r = 380$

Cubic, $Fd\bar{3}m$

Hall symbol: -F 4vw 2vw 3

$a = 10.55376$ (12) Å

$b = 10.55376$ (12) Å

$c = 10.55376$ (12) Å

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 1175.50$ (2) Å³

$Z = 8$

$D_x = 4.294$ Mg m⁻³

Neutron radiation

$\lambda = 1.83480$ Å

$\mu = 0.09$ mm⁻¹

$T = 298$ K

Specimen shape: cylinder

10 × 10 × 30 mm

Specimen prepared at 101 kPa

Specimen prepared at 1023 K

Particle morphology: particle, white

Data collection

HANARO high-resolution powder diffractometer

Radiation source: neutron

Monochromator: Ge(331)

Specimen mounting: vanadium can

Specimen mounted in transmission mode

Scan method: step

$T = 298$ K

$P = 101$ kPa

Absorption correction: for a cylinder mounted on the ϕ axis

(Rodríguez-Carvajal, 1990)

$T_{\min} = ?$, $T_{\max} = ?$

$2\theta_{\min} = 0.000$, $2\theta_{\max} = 160.00^\circ$

Increment in $2\theta = 0.05^\circ$

Refinement

Refinement on I_{net}

$R_p = 4.08$

Excluded region(s): $2\theta < 15^\circ$, $2\theta > 140^\circ$

Profile function: pseudo-Voigt

supplementary materials

$R_{wp} = 5.64$	25 parameters
$R_{exp} = 3.58$	Weighting scheme based on measured s.u.'s ?
$R_B = 2.53$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.57$	Extinction correction: none
Wavelength of incident radiation: 1.83480 Å	Preferred orientation correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	U_{iso}^*/U_{eq}	Occ. (<1)
K	0.25000	0.25000	0.50000	0.0180 (7)	0.50000
Ca	0.25000	0.25000	0.50000	0.0180 (7)	0.50000
Nb	0.50000	0.00000	0.50000	0.0124 (3)	
O	0.31488 (7)	0.12500	0.12500	0.0118 (4)	
F	0.37500	0.37500	0.37500	0.0399 (8)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K	0.0180 (7)	0.0180 (7)	0.0180 (7)	-0.0013 (5)	-0.0013 (5)	-0.0013 (5)
Ca	0.0180 (7)	0.0180 (7)	0.0180 (7)	-0.0013 (5)	-0.0013 (5)	-0.0013 (5)
Nb	0.0124 (3)	0.0124 (3)	0.0124 (3)	-0.0002 (4)	-0.0002 (4)	-0.0002 (4)
O	0.0128 (4)	0.0114 (3)	0.0114 (3)	0.00000	0.00000	0.0046 (4)
F	0.0399 (8)	0.0399 (8)	0.0399 (8)	0.00000	0.00000	0.00000

Geometric parameters (\AA , $^\circ$)

(K,Ca)—F1 ⁱ	2.28500 (10)	(K,Ca)—O1 ^x	2.7014 (5)
(K,Ca)—F1 ⁱⁱ	2.28500 (10)	(K,Ca)—O1 ^{xi}	2.7014 (5)
(K,Ca)—F1 ⁱⁱⁱ	2.28500 (10)	Nb1—O1 ^{xii}	1.9873 (3)
(K,Ca)—F1 ^{iv}	2.28500 (10)	Nb1—O1 ^{xiii}	1.9873 (3)
(K,Ca)—F1 ^v	2.28500 (10)	Nb1—O1 ^{xiv}	1.9873 (3)
(K,Ca)—F1	2.28500 (10)	Nb1—O1 ^{xi}	1.9873 (3)
(K,Ca)—F1 ^{vi}	2.28500 (10)	Nb1—O1 ^{xv}	1.9873 (3)
(K,Ca)—F1 ^{vii}	2.28500 (10)	Nb1—O1 ^{xvi}	1.9873 (3)
(K,Ca)—O1 ^{viii}	2.7014 (5)	Nb1—(K,Ca) ^{xvii}	3.7313 (4)
(K,Ca)—O1 ^{ix}	2.7014 (5)		
F1 ⁱ —(K,Ca)—F1 ⁱⁱ	180.000 (12)	F1 ⁱⁱⁱ —(K,Ca)—O1 ^x	81.59 (1)
F1 ⁱ —(K,Ca)—F1 ⁱⁱⁱ	9.6 (3)	F1 ^{iv} —(K,Ca)—O1 ^x	98.42 (1)
F1 ⁱⁱ —(K,Ca)—F1 ⁱⁱⁱ	180.00	F1 ^v —(K,Ca)—O1 ^x	81.59 (1)
F1 ⁱ —(K,Ca)—F1 ^{iv}	180.00	F1—(K,Ca)—O1 ^x	98.42 (1)
F1 ⁱⁱ —(K,Ca)—F1 ^{iv}	9.6 (3)	F1 ^{vi} —(K,Ca)—O1 ^x	81.6 (2)
F1 ⁱⁱⁱ —(K,Ca)—F1 ^{iv}	180 (4)	F1 ^{vii} —(K,Ca)—O1 ^x	98.42 (1)
F1 ⁱ —(K,Ca)—F1 ^v	9.6 (3)	O1 ^{viii} —(K,Ca)—O1 ^x	62.11 (1)
F1 ⁱⁱ —(K,Ca)—F1 ^v	180.00	O1 ^{ix} —(K,Ca)—O1 ^x	117.89 (1)

F1 ⁱⁱⁱ —(K,Ca)—F1 ^v	9.6 (3)	F1 ⁱ —(K,Ca)—O1 ^{xi}	98.42 (1)
F1 ^{iv} —(K,Ca)—F1 ^v	180.00	F1 ⁱⁱ —(K,Ca)—O1 ^{xi}	81.59 (1)
F1 ⁱ —(K,Ca)—F1	180.00	F1 ⁱⁱⁱ —(K,Ca)—O1 ^{xi}	98.42 (1)
F1 ⁱⁱ —(K,Ca)—F1	9.6 (3)	F1 ^{iv} —(K,Ca)—O1 ^{xi}	81.59 (1)
F1 ⁱⁱⁱ —(K,Ca)—F1	180.00	F1 ^v —(K,Ca)—O1 ^{xi}	98.42 (1)
F1 ^{iv} —(K,Ca)—F1	9.6 (3)	F1—(K,Ca)—O1 ^{xi}	81.59 (1)
F1 ^v —(K,Ca)—F1	180.000 (8)	F1 ^{vi} —(K,Ca)—O1 ^{xi}	98.42 (1)
F1 ⁱ —(K,Ca)—F1 ^{vi}	5.5 (3)	F1 ^{vii} —(K,Ca)—O1 ^{xi}	81.6 (2)
F1 ⁱⁱ —(K,Ca)—F1 ^{vi}	180.00	O1 ^{viii} —(K,Ca)—O1 ^{xi}	117.89 (1)
F1 ⁱⁱⁱ —(K,Ca)—F1 ^{vi}	5.5 (3)	O1 ^{ix} —(K,Ca)—O1 ^{xi}	62.11 (1)
F1 ^{iv} —(K,Ca)—F1 ^{vi}	180.00	O1 ^x —(K,Ca)—O1 ^{xi}	180.000 (13)
F1 ^v —(K,Ca)—F1 ^{vi}	5.5 (3)	O1 ^{xii} —Nb1—O1 ^{xiii}	180.000 (12)
F1—(K,Ca)—F1 ^{vi}	180.00	O1 ^{xii} —Nb1—O1 ^{xiv}	89.04 (2)
F1 ⁱ —(K,Ca)—F1 ^{vii}	180.00	O1 ^{xiii} —Nb1—O1 ^{xiv}	90.96 (2)
F1 ⁱⁱ —(K,Ca)—F1 ^{vii}	5.5 (3)	O1 ^{xii} —Nb1—O1 ^{xi}	90.96 (2)
F1 ⁱⁱⁱ —(K,Ca)—F1 ^{vii}	180.00	O1 ^{xiii} —Nb1—O1 ^{xi}	89.04 (2)
F1 ^{iv} —(K,Ca)—F1 ^{vii}	5.5 (3)	O1 ^{xiv} —Nb1—O1 ^{xi}	180.000 (5)
F1 ^v —(K,Ca)—F1 ^{vii}	180.00	O1 ^{xii} —Nb1—O1 ^{xv}	90.96 (2)
F1—(K,Ca)—F1 ^{vii}	5.5 (3)	O1 ^{xiii} —Nb1—O1 ^{xv}	89.04 (2)
F1 ^{vi} —(K,Ca)—F1 ^{vii}	180.000 (8)	O1 ^{xiv} —Nb1—O1 ^{xv}	89.04 (2)
F1 ⁱ —(K,Ca)—O1 ^{viii}	98.42 (1)	O1 ^{xi} —Nb1—O1 ^{xv}	90.96 (2)
F1 ⁱⁱ —(K,Ca)—O1 ^{viii}	81.59 (1)	O1 ^{xii} —Nb1—O1 ^{xvi}	89.04 (2)
F1 ⁱⁱⁱ —(K,Ca)—O1 ^{viii}	98.42 (1)	O1 ^{xiii} —Nb1—O1 ^{xvi}	90.96 (2)
F1 ^{iv} —(K,Ca)—O1 ^{viii}	81.59 (1)	O1 ^{xiv} —Nb1—O1 ^{xvi}	90.96 (2)
F1 ^v —(K,Ca)—O1 ^{viii}	98.42 (1)	O1 ^{xi} —Nb1—O1 ^{xvi}	89.04 (2)
F1—(K,Ca)—O1 ^{viii}	81.59 (1)	O1 ^{xv} —Nb1—O1 ^{xvi}	180.00 (2)
F1 ^{vi} —(K,Ca)—O1 ^{viii}	98.42 (1)	Nb1 ⁱⁱ —O1—Nb1 ^{xviii}	139.69 (4)
F1 ^{vii} —(K,Ca)—O1 ^{viii}	81.6 (2)	Nb1 ⁱⁱ —O1—(K,Ca) ⁱⁱ	104.44 (1)
F1 ⁱ —(K,Ca)—O1 ^{ix}	81.59 (1)	Nb1 ^{xviii} —O1—(K,Ca) ⁱⁱ	104.44 (1)
F1 ⁱⁱ —(K,Ca)—O1 ^{ix}	98.42 (1)	Nb1 ⁱⁱ —O1—(K,Ca) ^{xviii}	104.44 (1)
F1 ⁱⁱⁱ —(K,Ca)—O1 ^{ix}	81.59 (1)	Nb1 ^{xviii} —O1—(K,Ca) ^{xviii}	104.44 (1)
F1 ^{iv} —(K,Ca)—O1 ^{ix}	98.42 (1)	(K,Ca) ⁱⁱ —O1—(K,Ca) ^{xviii}	87.36 (2)
F1 ^v —(K,Ca)—O1 ^{ix}	81.59 (1)	(K,Ca)—F1—(K,Ca) ^{iv}	109.47
F1—(K,Ca)—O1 ^{ix}	98.42 (1)	(K,Ca)—F1—(K,Ca) ⁱⁱ	109.47
F1 ^{vi} —(K,Ca)—O1 ^{ix}	81.6 (2)	(K,Ca) ^{iv} —F1—(K,Ca) ⁱⁱ	109.47
F1 ^{vii} —(K,Ca)—O1 ^{ix}	98.42 (1)	(K,Ca)—F1—(K,Ca) ^{vii}	109.47
O1 ^{viii} —(K,Ca)—O1 ^{ix}	180.000 (1)	(K,Ca) ^{iv} —F1—(K,Ca) ^{vii}	109.47
F1 ⁱ —(K,Ca)—O1 ^x	81.59 (1)	(K,Ca) ⁱⁱ —F1—(K,Ca) ^{vii}	109.47
F1 ⁱⁱ —(K,Ca)—O1 ^x	98.42 (1)		

Symmetry codes: (i) $x-1/4, -y+1/2, z+1/4$; (ii) $-x+3/4, y, -z+3/4$; (iii) $-x+1/2, y-1/4, z+1/4$; (iv) $x, -y+3/4, -z+3/4$; (v) $-x+1/2, -y+1/2, -z+1$; (vi) $x-1/4, y-1/4, -z+1$; (vii) $-x+3/4, -y+3/4, z$; (viii) $-y+1/2, -z+1/2, -x+1$; (ix) y, z, x ; (x) $y, -x+3/4, -z+3/4$; (xi) $-y+1/2,$

supplementary materials

$x-1/4, z+1/4$; (xii) $-y+1/2, z-1/4, x+1/4$; (xiii) $y+1/2, -z+1/4, -x+3/4$; (xiv) $y+1/2, -x+1/4, -z+3/4$; (xv) $x+1/4, y-1/4, -z+1/2$; (xvi) $-x+3/4, -y+1/4, z+1/2$; (xvii) $-x+3/4, y-1/2, -z+5/4$; (xviii) $-x+3/4, -y+1/4, z-1/2$.

Fig. 1

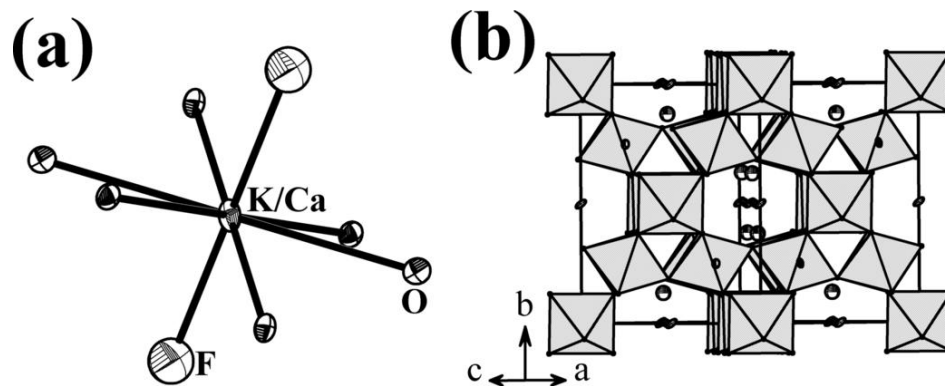


Fig. 2

