Synthesis and crystal structure of a new potassium fluorotellurate(IV): KTe$_2$F$_9$ [1]

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Abstract

KTe$_2$F$_9$ was prepared by solid state reaction at 200 °C between KF and TeF$_4$ in a sealed platinum tube. KTe$_2$F$_9$ crystallizes with triclinic symmetry (space group P-1) with the following unit cell parameters: $a = 475.7(2)$ pm, $b = 933.3(5)$ pm, $c = 946.7(4)$ pm, $\alpha = 108.82(3)°$, $\beta = 95.79(5)°$, $\gamma = 96.11(2)°$, $Z = 2$ and $V = 391.5(3) \times 10^6$ pm^3. Its crystal structure was solved and refined to $R1 = 0.054$ and $wR2 = 0.147$ on the basis of 2276 independent reflections registered from a single crystal with a four-circle diffractometer. One-half of the Te(IV) atoms are five-fold coordinated, and the other half are six-fold coordinated. In each case, the lone pair E is stereochemically active. The corresponding Te(1)F$_6$E and Te(2)F$_5$E polyhedra form, by sharing corners, independent pseudo-molecular Te$_4$F$_{18}$ units. The crystal structure corresponds to a regular repetition along the c axis of planar $4^2 \times 3^3$ layers of K atoms separated by Te$_4$F$_{18}$ units. Structural relationships with the BaTe$_2$F$_{10}$ crystal structure have been established and are discussed. © 1997 Elsevier Science S.A.

Keywords: Crystal structure; Potassium fluorotellurate(IV); KTe$_2$F$_9$; Structural relationships

1. Introduction

Only one potassium fluorotellurate(IV) has been identified so far: KTeF$_5$. It was prepared for the first time in 1966 by the reaction of stoichiometric amounts of KF and TeO$_2$ in an aqueous hydrofluoric acid solution [1]. Its crystal structure was determined in 1969 by single-crystal X-ray diffraction analysis [2], its standard enthalpy of formation in 1983 [3] and its polymorphism in 1989 [4].

A solid state re-investigation of the KF–TeF$_4$ system has led to the isolation of a new crystalline compound with the composition KTe$_2$F$_9$. This paper reports the synthesis and crystal structure determination of this new potassium fluorotellurate(IV).

2. Synthesis and characterization of KTe$_2$F$_9$

KTe$_2$F$_9$ was prepared by heating a mixture of KF and 2TeF$_4$ at 200 °C for 24 h in a sealed platinum tube, followed by slow cooling to room temperature. KF was a commercial high purity product (Aldrich) which was dried before use at 140 °C for 12 h under vacuum. TeF$_4$ was prepared by the thermal decomposition of sodium pentafluorotellurate(IV) (NaTeF$_5$) as described previously [5].

Because of their air sensitivity, all the starting products and compounds obtained were handled and stored in a glove box under a strictly dried and deoxygenated argon atmosphere. KTe$_2$F$_9$ was obtained as a very hygroscopic white powder, whose X-ray diffraction pattern (see Table 1) could be indexed on the basis of a triclinic system (space group P-1). KTe$_2$F$_9$ melts at about 120 °C. Rapid cooling of the melt leads to a glassy phase.

3. Determination of the crystal structure

Single crystals of this new phase were obtained by melting at 150 °C a mixture of KF and 4TeF$_4$ in a closed Teflon pot; the melt was very slowly cooled to 100 °C, held at this temperature for 12 h and then slowly cooled to room temperature.

A crystal, 0.15 mm × 0.10 mm × 0.10 mm in size, was selected for crystallographic study. In order to avoid hydrolysis, it was coated with a highly viscous perfluoropolyether oil (RS3000) and sealed inside a glass capillary. The record-

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Table 1
Powder X-ray pattern of KTe$_2$F$_9$

h	k	l	d_{cal} (pm)	d_{obs} (pm)	I/I_0
0	1	0	764.3	762.5	6
0	-2	1	457.8	458.2	11
0	0	2	443.4	443.3	69
1	-1	0	440.6	440.6	67
0	2	0	436.9	437.0	30
0	-2	2	382.2	382.2	100
0	2	1	348.2	348.2	43
1	-2	0	345.9	345.9	25
1	-2	1	341.3	341.5	25
1	1	1	325.7	325.8	7
0	-3	1	309.3	309.2	9
1	2	0	298.2	298.2	58
0	-2	3	295.3	295.4	21
0	3	0	291.3	291.2	76
1	-3	1	271.7	271.8	8
1	-3	2	254.5	254.5	7
0	-1	4	234.6	234.5	26
2	0	0	234.0	234.0	18
-2	1	2	212.3	212.4	96
2	-3	1	197.0	197.0	22

Table 2
Crystal data and structural refinement for KTe$_2$F$_9$

Formula weight	465.30 g
Wavelength	71.073 pm
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 475.7(2)$ pm, $\alpha = 108.82(3)°$
	$b = 933.3(5)$ pm, $\beta = 95.79(3)°$
	$c = 946.7(4)$ pm, $\gamma = 96.11(2)°$
Volume	$391.5(3) \times 10^6$ pm^3
Z	2
Density (calculated)	3.947 Mg m^{-3}
Absorption coefficient	8.09 mm^{-1}
Absorption correction	Empirical method: psi scan
$F(000)$	408
Crystal size	0.15 mm $\times$ 0.10 mm $\times$ 0.10 mm
2θ range for data collection	2.30° to 29.98°
Index ranges	$-1 \le h \le 6$, $-12 \le k \le 12$,
	$-13 \le l \le 13$
Reflections observed	3030
Independent reflections	2276 ($R(\text{int}) = 0.0414$)
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2276/0/110
Goodness-of-fit on F^2	1.156
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.051$, $wR2 = 0.144$
R indices (all data)	$R1 = 0.054$, $wR2 = 0.147$
Extinction coefficient	0.025(3)
Largest difference peak and hole	32×10^2 and -37×10^2 e nm^{-3}

ing of the integrated intensities was performed with a P4 Siemens four-circle automatic diffractometer using Mo Kα radiation under the conditions reported in Table 2. Because of the high sensitivity to air moisture and despite the precautions taken, the recording time was limited to the minimum acceptable. Absorption corrections were performed by the psi-scan method with the XEMP program [6], considering the crystal to be an ellipsoid.

Table 3
Top: atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors B_{eq} (pm$^2 \times 10^{-4}$) [a]. Bottom: anisotropic displacement factors U_{ij} (pm$^2 \times 10^{-1}$) [b]; estimated standard deviations are given in parentheses

Atom	x	y	z	B_{eq}
Te(1)	1163(1)	5381(1)	8056(1)	1.73(8)
Te(2)	3602(1)	917(1)	8221(1)	2.00(8)
K	3785(4)	2370(2)	4583(2)	2.50(8)
F(1)	1363(12)	5989(7)	3557(7)	3.2(2)
F(2)	121(12)	2975(6)	2362(7)	3.2(2)
F(3)	6201(13)	927(7)	6871(7)	3.2(2)
F(4)	3398(12)	5398(7)	6439(6)	3.2(2)
F(5)	1533(13)	9417(6)	6381(6)	2.9(2)
F(6)	2561(12)	2602(6)	7484(6)	3.2(2)
F(7)	2179(12)	4520(8)	882(7)	3.6(2)
F(8)	4337(14)	709(7)	1566(7)	3.7(2)
F(9)	6890(15)	2363(7)	9603(8)	3.7(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te(1)	21(1)	24(1)	21(1)	9(1)	-1(1)	7(1)
Te(2)	29(1)	23(1)	24(1)	7(1)	1(1)	9(1)
K	34(1)	32(1)	29(1)	5(1)	0(1)	5(1)
F(1)	37(3)	38(3)	46(3)	10(2)	-18(2)	0(2)
F(2)	40(3)	35(3)	47(3)	21(2)	-2(2)	13(2)
F(3)	38(3)	44(3)	41(3)	11(2)	15(2)	9(2)
F(4)	37(3)	54(3)	34(3)	20(2)	10(2)	12(2)
F(5)	39(3)	35(3)	38(3)	8(2)	-4(2)	1(2)
F(6)	45(3)	33(2)	45(3)	20(2)	3(2)	15(2)
F(7)	33(3)	61(4)	44(3)	26(3)	9(2)	9(2)
F(8)	61(4)	36(3)	44(3)	15(2)	1(3)	24(3)
F(9)	56(4)	35(3)	53(4)	0(3)	-14(3)	2(3)

[a] $B_{eq} = 4/3 \times 2\pi^2(U_{11} + U_{22} + U_{33})$.
[b] The exponent takes the form: $-2\pi^2[h^2 a^{*2} 2U_{11} + \ldots + 2hka^* b^* U_{12}]$.
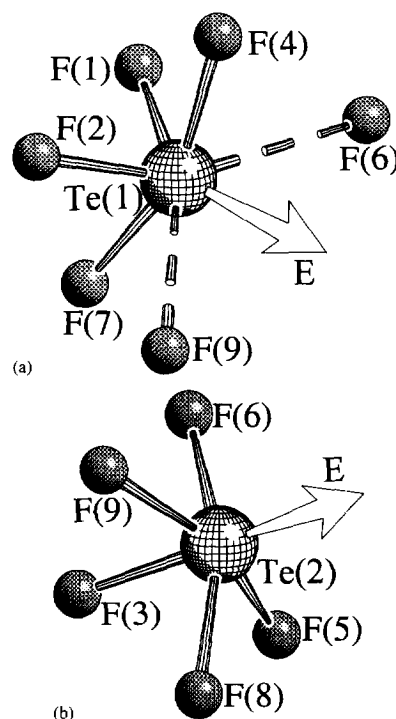

Fig. 1. Anionic polyhedra around Te(1) (a) and Te(2) (b) atoms. Arrows indicate the direction towards which the lone pair E points.

Table 4

Main interatomic distances (pm), angles (°) and bond valences in KTe$_2$F$_9$ (estimated standard deviations are given in parentheses; notations are those indicated in Figs. 1–3)

Te(1)	F(1)	F(2)	F(4)	F(7)	F(9)	F(6)	V_{ij}
F(1)	185.8(5)	264.5(5)	248.6(5)	255.2(5)	432.1(5)	341.4(5)	1.032
F(2)	91.0(3)	185.1(5)	249.1(5)	250.5(5)	274.8(5)	441.1(3)	1.053
F(4)	81.4(3)	81.8(3)	195.3(5)	384.0(5)	367.9(5)	307.7(5)	0.799
F(7)	83.9(3)	82.2(3)	158.0(2)	196.0(6)	323.6(5)	374.2(5)	0.785
F(9)	160.9(3)	76.1(3)	109.9(3)	80.5(3)	252.2(5)	355.0(5)	0.171
F(6)	70.5(3)	157.3(3)	82.5(3)	107.8(3)	124.8(3)	264.5(5)	0.123
V_{ij}							3.963

Te(2)	F(3)	F(5)	F(6)	F(8)	F(9)	V_{ij}
F(3)	186.7(5)	241.5(5)	244.3(5)	245.6(5)	246.8(5)	1.008
F(5)	78.9(3)	193.7(5)	278.4(5)	266.0(5)	385.8(5)	0.835
F(6)	78.3(3)	90.0(2)	200.2(5)	387.6(5)	280.4(5)	0.699
F(8)	80.3(3)	86.5(3)	158.5(3)	194.5(5)	269.2(5)	0.819
F(9)	79.4(3)	157.9(3)	89.2(3)	86.2(3)	199.5(6)	0.714
V_{ij}						4.076

K	F(1)^1	F(1)^2	F(2)	F(3)^1	F(3)^2	F(4)^1	F(4)^2	F(5)^1	F(5)^2	F(5)^3	F(6)	F(8)	V_{ij}
F(1)^1	337.2(7)	475.5(5)	382.7(5)	490.4(5)	563.4(5)	248.6(5)	496.9(5)	343.0(5)	627.8(5)	462.6(5)	267.8(5)	576.9(5)	0.024
F(1)^2	101.9(2)	273.1(6)	508.5(5)	315.0(5)	483.0(5)	292.8(5)	303.9(5)	541.6(5)	343.0(5)	514.8(5)	341.2(5)	475.0(5)	0.135
F(2)	75.6(2)	132.(2)	283.1(6)	584.7(5)	443.3(5)	385.3(5)	320.5(5)	292.2(5)	497.9(5)	583.6(5)	500.2(5)	304.0(5)	0.103
F(3)^1	98.7(2)	65.2(2)	162.1(2)	308.8(7)	341.4(5)	464.0(5)	534.1(5)	446.5(5)	329.3(5)	241.5(5)	244.3(5)	494.5(5)	0.051
F(3)^2	126.3(2)	116.8(2)	100.4(2)	69.0(2)	293.9(6)	575.5(5)	506.2(5)	303.5(5)	241.5(5)	329.3(5)	450.9(5)	245.6(5)	0.077
F(4)^1	46.2(2)	63.4(2)	85.5(2)	102.9(2)	169.2(2)	284.2(6)	317.3(5)	464.3(5)	538.4(5)	553.9(5)	307.7(5)	533.3(5)	0.100
F(4)^2	106.1(2)	66.1(2)	68.9(2)	128.7(2)	122.5(2)	68.0(2)	283.5(6)	510.9(5)	396.0(5)	659.4(5)	510.9(5)	350.0(5)	0.102
F(5)^1	67.1(2)	160.2(2)	62.9(2)	99.2(2)	64.2(2)	111.7(2)	131.6(2)	276.9(6)	475.5(5)	340.0(5)	375.0(5)	357.1(5)	0.122
F(5)^2	164.5(2)	73.9(2)	118.5(2)	65.9(2)	48.3(2)	136.0(2)	86.1(2)	112.1(2)	296.5(6)	465.8(5)	485.5(5)	266.0(5)	0.072
F(5)^3	80.2(2)	102.9(2)	122.8(2)	39.4(2)	56.9(2)	112.3(2)	168.1(2)	60.0(2)	86.2(2)	379.5(5)	278.4(5)	533.2(5)	0.007
F(6)	50.3(2)	76.1(2)	124.9(2)	48.7(2)	103.3(2)	66.0(2)	129.8(2)	84.5(2)	114.5(2)	47.0(2)	281.0(6)	548.7(5)	0.109
F(8)	136.8(2)	117.3(2)	65.0(2)	113.3(2)	50.4(2)	140.1(2)	76.3(2)	79.3(2)	54.6(2)	106.3(2)	153.3(2)	283.1(6)	0.103
V_{ij}													1.004

⟨Te(1)–F⟩ = 190.5 pm (without F(9) and F(6)).
⟨Te(2)–F⟩ = 194.9 pm.
⟨K–F⟩ = 298.4 pm.

The location of K and Te atoms was determined by direct methods using the SHELXS-86 program on the basis of the P-1 space group [7]. After refinement of their positions using the SHELXL-93 program [8], the fluorine atoms were located by Fourier difference calculations. After refinement of the atomic coordinates and isotropic thermal coefficients of all the atoms, anisotropic temperature factors, an extinction coefficient and a weighting scheme were successively introduced. The refinement finally converged to $R1$ and $wR2$ values of 0.054 and 0.147 respectively, when all the reflections were taken into account, and 0.051 and 0.144 respectively, when only reflections with $I > 2\sigma(I)$ were considered. The short recording time explains the rather high values of the R factors and the electron density residuals. However, all of the structural parameters, bond distances and bond valences were normal.

Various refinements on the basis of the non-centrosymmetric space group $P1$ did not lead to significant improvements in the R factors.

The refined parameters are reported in Table 3 and the main interatomic distances, bond angles and bond valences, calculated by Brown's method [9,10], are given in Table 4.

4. Description of the structure

Each Te(1) atom is surrounded by four fluorine atoms (F(1), F(2), F(4) and F(7)) at relatively short distances (185–196 pm) and by two extra fluorine atoms (F(9) and F(6)) at much longer distances (252–264 pm) (Fig. 1(a)). If we consider only the four shortest distances, the coordination polyhedron can be described as a distorted trigonal bipyramid Te(1)F$_4$E whose one equatorial corner is occupied by the lone pair E of Te(1). This kind of polyhedron is frequently observed in tellurium(IV) oxides or oxidefluorides, e.g. the α and β forms of TeO$_2$ [11,12], H$_2$Te$_2$O$_3$F$_4$ [13] and Te$_2$O$_3$F$_2$ [14]. If we take into account the two extra anions F(6) and F(9), the coordination polyhedron then corresponds to a very distorted pentagonal bipyramid
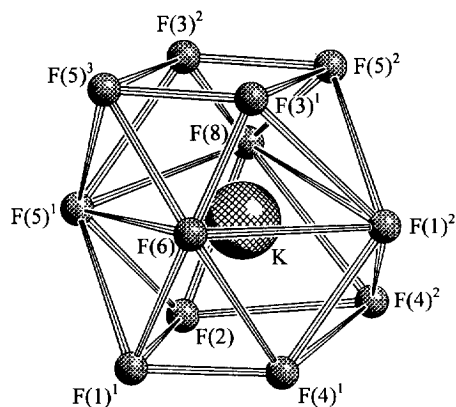
Fig. 2. The KF_{12} polyhedron in KTe_2F_9.

(a)

(b)
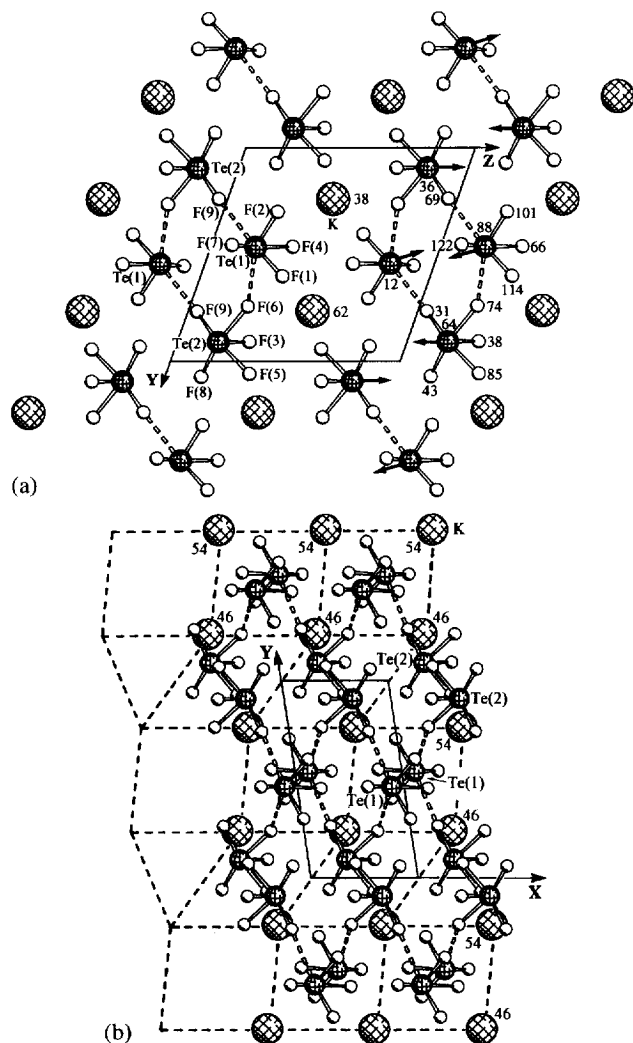
Fig. 3. Projection of the KTe_2F_9 structure: (a) onto the yOz plane (arrows indicate the lone pair E); (b) onto the xOy plane (the broken lines show the $4^2 \times 3^3$ plane net of K cations).

Te(1)F_6E whose one equatorial corner is occupied by the lone pair E.

Each Te(2) atom is surrounded by five fluorine atoms (Fig. 1(b)) at distances ranging from 186 to 200 pm ($\langle Te(2)-F \rangle = 195$ pm). These five anions form a slightly

distorted square pyramid which, in fact, corresponds to a distorted TeF_5E octahedron whose one corner could be occupied by the lone pair E of the central tellurium atom. Such an environment is quite classical in the stereochemistry of Te(IV), mainly in fluorine coordination, as it is observed in all the known alkaline pentafluorotellurates(IV) $MTeF_5$ (M $\equiv$ Na [15], K [2], Rb [16], Cs [17]) and also in TeF_4 [18], $PbTeF_6$ [19] and $BaTe_2F_{10}$ [20].

With regard to the potassium atoms, if we consider only the shortest bonds (i.e. less than 300 pm; see Table 4), they are surrounded by nine anions, forming a rather irregular polyhedron which cannot be related to any simple or regular geometry. The experimental mean bond distance ($\langle K-F \rangle = 294$ pm) is nevertheless in perfect accordance with the sum of the ionic radii calculated on the basis of the values of

(a)

(b)
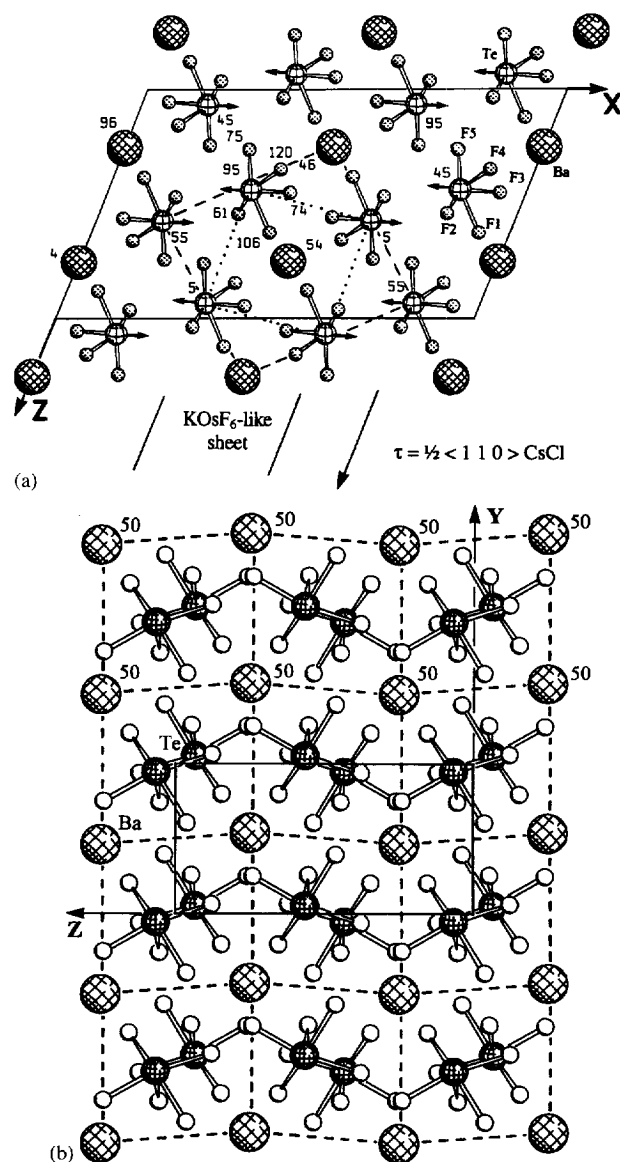
Fig. 4. Projection of the $BaTe_2F_{10}$ structure: (a) onto the xOz plane (the broken and dotted lines show the f.c.c. subcell and the distorted CsCl ($KOsF_6$-like) cell respectively); (b) onto the yOz plane (the broken lines show the square 4^4 plane net of Ba cations).

Shannon and Prewitt [21,22] $(r(K^+(9)) + r(F^-(2))) = 155 + 128.5 = 293.5$ pm). If we take into account the three longer K–F(1)^1, K–F(3)^1 and K–F(5)^3 bonds, the corresponding polyhedron can be described as a highly distorted cuboctahedron represented in Fig. 2.

Projections of the structure along a and c are shown in Fig. 3. Equivalent projections of the $BaTe_2F_{10}$ structure [13] are given, for comparison, in Fig. 4.

If we only take into account the shortest Te–F distances, it is clear from Fig. 3(a) that the KTe_2F_9 structure corresponds to a regular stacking along c of alternate (001) layers of, on the one hand, K atoms and, on the other, $Te(1)F_4E$ and $Te(2)F_5E$ independent polyhedra, according to the sequence: $\cdots$–K–Te–Te–K–$\cdots$ The same sequence of Ba layers and of layers of independent TeF_5E octahedra has been observed in the $BaTe_2F_{10}$ structure, therefore justifying the close geometrical relationships which exist between the two unit cells: $a(BaTe_2F_{10}) \approx 2c(KTe_2F_9)$, $b(BaTe_2F_{10}) \approx a(KTe_2F_9)$, $c(BaTe_2F_{10}) \approx b(KTe_2F_9)$ and $V(BaTe_2F_{10}) \approx 2V(KTe_2F_9)$. The doubling of the a parameter (and therefore of the unit cell volume) results from the periodic shift ($\tau = 1/2\langle 1\ 1\ 0 \rangle$ CsCl; see Fig. 4(a)) of the $KOsF_6$-like sheets [13] not observed in the case of the KTe_2F_9 structure.

Despite this analogy, the two structures are very different. Indeed, in the $BaTe_2F_{10}$ structure, the TeF_5E units are independent, and can therefore form with the Ba atoms slightly distorted cubic close packing and the $KOsF_6$-like (CsCl-like) sheets shown in Fig. 4(a). In the KTe_2F_9 structure, the $Te(1)F_4E$ and $Te(2)F_5E$ units are connected to each other via F(6) and F(9) anions, producing discrete Te_4F_{18} pseudo-molecular units. Such a connection obviously changes the spatial distribution of the basic fluorotellurate units and leads to a distortion of the cationic layers which, from square 4^4 in $BaTe_2F_{10}$ (Fig. 4(b)), become $4^2 \times 3^3$ in KTe_2F_9 (Fig. 3(b)).

In conclusion, the KTe_2F_9 crystal structure should be described as the regular repetition along the Oz axis of planar $4^2 \times 3^3$ layers of potassium atoms separated by independent pseudo-molecular Te_4F_{18} units, built up by the association of two $Te(1)F_6E$ and two $Te(2)F_5E$ polyhedra sharing corners.

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