
Supporting Information

$K_3Na(TaF_7)(SiF_6)$: A Mixed-anion Pentanary Fluoride with Zero Dimensional Anions Exhibiting Large Band Gap

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Figures and Tables

Table S1. Bond lengths for $K_3Na(TaF_7)(SiF_6)$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si(1)	F(1)	1.665(3)	K(2)	F(1)	2.760(3)
Si(1)	F(1)^{3}	1.665(3)	K(2)	F(2)^{1}	2.772(2)
Si(1)	F(3)^{5}	1.678(3)	K(2)	F(2)^{9}	2.772(2)
Si(1)	F(3)	1.678(3)	K(2)	F(2)^{6}	2.772(2)
Si(1)	F(5)^{5}	1.702(3)	K(2)	F(2)^{15}	2.772(2)
Si(1)	F(5)	1.702(3)	K(2)	F(5)^{10}	2.891(2)
Ta(1)	F(2)	1.925(2)	K(2)	F(5)	2.891(2)
Ta(1)	F(2)^{6}	1.925(2)	K(2)	F(5)^{5}	2.891(2)
Ta(1)	F(2)^{9}	1.925(2)	K(2)	F(5)^{4}	2.891(2)
Ta(1)	F(2)^{10}	1.925(2)	K(2)	F(6)^{1}	2.8475(3)
Ta(1)	F(4)^{6}	1.932(3)	K(2)	F(6)	2.8475(3)
Ta(1)	F(4)	1.932(3)	Na(1)	F(5)^{17}	2.242(3)
Ta(1)	F(6)	2.032(4)	Na(1)	F(5)^{7}	2.242(3)
K(1)	F(1)	2.9870(10)	Na(1)	F(5)^{4}	2.242(3)
K(1)	F(1)^{7}	2.9870(10)	Na(1)	F(5)^{5}	2.242(3)
K(1)	F(2)	2.915(2)	Na(1)	F(6)	2.361(4)
K(1)	F(2)^{9}	2.915(2)	Na(1)	F(6)^{16}	2.361(4)
K(1)	F(2)^{11}	2.729(2)	Na(2)	F(3)^{18}	2.365(3)
K(1)	F(2)^{12}	2.729(2)	Na(2)	F(3)	2.365(3)
K(1)	F(3)^{5}	2.843(2)	Na(2)	F(3)^{5}	2.365(3)
K(1)	F(3)^{7}	2.843(2)	Na(2)	F(3)^{21}	2.365(3)
K(1)	F(4)^{11}	3.028(2)	Na(2)	F(4)^{20}	2.503(3)
K(1)	F(4)^{13}	3.028(2)	Na(2)	F(4)^{19}	2.503(3)
K(1)	F(5)^{7}	3.393(3)	Na(2)	F(4)^{22}	2.503(3)
K(1)	F(5)^{5}	3.393(3)	Na(2)	F(4)^{13}	2.503(3)
K(2)	F(1)^{14}	2.760(3)	Na(2)	F(3)^{21}	2.365(3)

^{1}-1+*x*, +*y*, +*z*; ^{2}-1+*x*, +*y*, -*z*; ^{3}+*x*, +*y*, -*z*; ^{4}-1-*x*, -*y*, -*z*; ^{5}-1-*x*, +*y*, -*z*; ^{6}-*x*, -*y*, +*z*; ^{7}1+*x*, +*y*, +*z*; ^{8}1/2+*x*, -1/2+*y*, 1/2+*z*; ^{9}-*x*, +*y*, +*z*; ^{10}+*x*, -*y*, +*z*; ^{11}1/2-*x*, 1/2-*y*, 1/2-*z*; ^{12}-1/2+*x*, 1/2-*y*, 1/2-*z*; ^{13}-1/2+*x*, 1/2+*y*, 1/2-*z*; ^{14}-1-*x*, -*y*, +*z*; ^{15}-1+*x*, -*y*, +*z*; ^{16}-*x*, -*y*, -*z*; ^{17}1+*x*, -*y*, +*z*; ^{18}-1-*x*, 1-*y*, -*z*; ^{19}-1/2-*x*, 1/2-*y*, 1/2-*z*; ^{20}-1/2+*x*, 1/2+*y*, -1/2+*z*; ^{21}+*x*, 1-*y*, +*z*; ^{22}-1/2-*x*, 1/2-*y*, -1/2+*z*; ^{23}1/2+*x*, -1/2+*y*, 1/2-*z*

Table S2. Selected bond angles for $K_3Na(TaF_7)(SiF_6)$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F(1)[2]	Si(1)	F(1)	178.8(2)	F(2)[6]	Ta(1)	F(2)[9]	81.38(13)
F(1)[2]	Si(1)	F(3)	90.43(8)	F(2)	Ta(1)	F(2)[9]	92.73(13)
F(1)	Si(1)	F(3)[5]	90.43(8)	F(2)	Ta(1)	F(2)[6]	153.87(12)
F(1)	Si(1)	F(3)	90.43(8)	F(2)	Ta(1)	F(2)[10]	81.38(13)
F(1)[2]	Si(1)	F(3)[5]	90.43(8)	F(2)[6]	Ta(1)	F(2)[10]	92.73(13)
F(1)[2]	Si(1)	F(5)[5]	89.56(8)	F(2)[9]	Ta(1)	F(2)[10]	153.87(12)
F(1)	Si(1)	F(5)	89.56(8)	F(2)[9]	Ta(1)	F(4)[6]	125.16(8)
F(1)[2]	Si(1)	F(5)	89.56(8)	F(2)[6]	Ta(1)	(4)[6]	77.48(9)
F(1)	Si(1)	F(5)[5]	89.56(8)	F(2)	Ta(1)	F(4)[6]	125.16(8)
F(3)[5]	Si(1)	F(3)	91.5(2)	F(2)[10]	Ta(1)	F(4)[6]	77.48(9)
F(3)[5]	Si(1)	F(5)[5]	90.13(14)	F(2)[9]	Ta(1)	F(4)	77.48(9)
F(3)	Si(1)	F(5)	90.13(14)	F(2)[10]	Ta(1)	F(4)	125.16(8)
F(3)[5]	Si(1)	F(5)	178.35(17)	F(2)	Ta(1)	F(4)	77.48(9)
F(3)	Si(1)	F(5)[5]	178.35(17)	F(2)[6]	Ta(1)	F(4)	125.16(8)
F(3)	Si(1)	F(5)[5]	88.2(2)	F(2)[10]	Ta(1)	F(6)	76.93(6)
F(4)[6]	Ta(1)	F(4)	74.9(2)	F(2)[9]	Ta(1)	F(6)	76.93(6)
F(4)	Ta(1)	F(6)	142.56(10)	F(2)	Ta(1)	F(6)	76.93(6)
F(4)[6]	Ta(1)	F(6)	142.56(10)	F(2)[6]	Ta(1)	F(6)	76.93(6)

[1]-1+*x*, +*y*, -*z*; [2]+*x*, +*y*, -*z*; [3]-1+*x*, +*y*, +*z*; [4]-1-*x*, -*y*, -*z*; [5]-1-*x*, +*y*, -*z*; [6]-*x*, -*y*, +*z*; [7]1+*x*, +*y*, +*z*; [8]1/2+*x*, -1/2+*y*, 1/2+*z*; [9]+*x*, -*y*, +*z*; [10]-*x*, +*y*, +*z*; [11]1/2-*x*, 1/2-*y*, 1/2-*z*; [12]-1/2+*x*, 1/2+*y*, 1/2-*z*; [13]-1/2+*x*, 1/2-*y*, 1/2-*z*; [14]-1-*x*, -*y*, +*z*; [15]-1+*x*, -*y*, +*z*; [16]-*x*, -*y*, -*z*; [17]1+*x*, -*y*, +*z*; [18]-1-*x*, 1-*y*, -*z*; [19]-1/2+*x*, 1/2+*y*, -1/2+*z*; [20]-1/2-*x*, 1/2-*y*, 1/2-*z*; [21]+*x*, 1-*y*, +*z*; [22]-1/2-*x*, 1/2-*y*, -1/2+*z*; [23]1/2+*x*, -1/2+*y*, 1/2-*z*

Table S3. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement Parameters (Å2×10^3) for $K_3Na(TaF_7)(SiF_6)$.

Atom	***x***	***y***	***z***	U_{eq}/Å^2	**BVS**
Si(1)	-5000	2300.3(14)	0	10.7(3)	4.55(8)
Ta(1)	0	0	2699.2(2)	12.82(8)	5.27(9)
K(1)	0	2872.2(10)	1395.5(7)	24.3(2)	0.91(8)
K(2)	−5000	0	1327.9(9)	17.6(3)	1.28(7)
Na(1)	0	0	0	13.7(7)	1.15(2)
Na(2)	−5000	5000	0	23.0(9)	1.02(4)
F(1)	−5000	2285(3)	1022.9(17)	26.7(7)	1.05(6)
F(2)	2209(4)	1172.3(17)	2431.8(12)	23.0(5)	1.22(5)
F(3)	−7117(5)	3286(2)	0	22.0(6)	1.11(7)
F(4)	2068(6)	0	3641.9(18)	30.4(7)	1.07(8)
F(5)	−7085(5)	1272(2)	0	28.4(7)	1.15(1)
F(6)	0	0	1451(2)	22.1(9)	1.05(8)

[a]U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

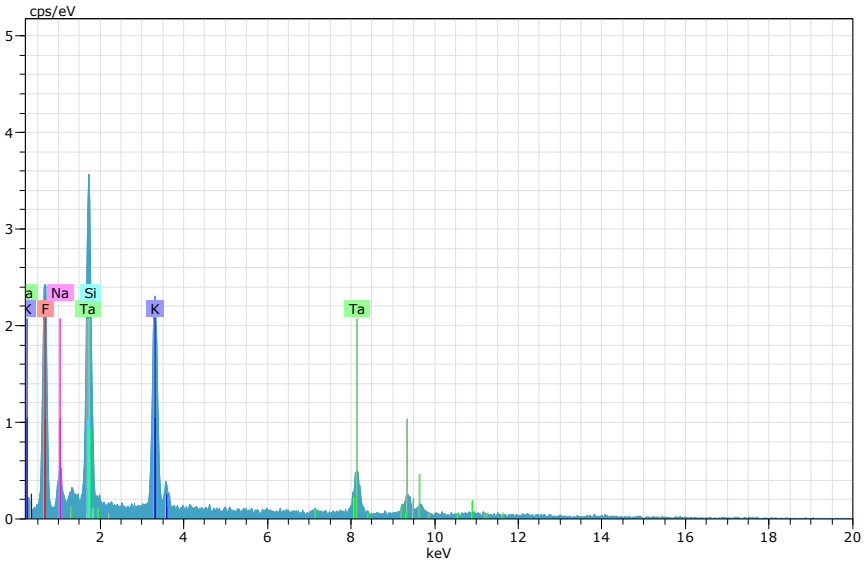

Figure S1. EDS elemental analysis of $K_3Na(TaF_7)(SiF_6)$.

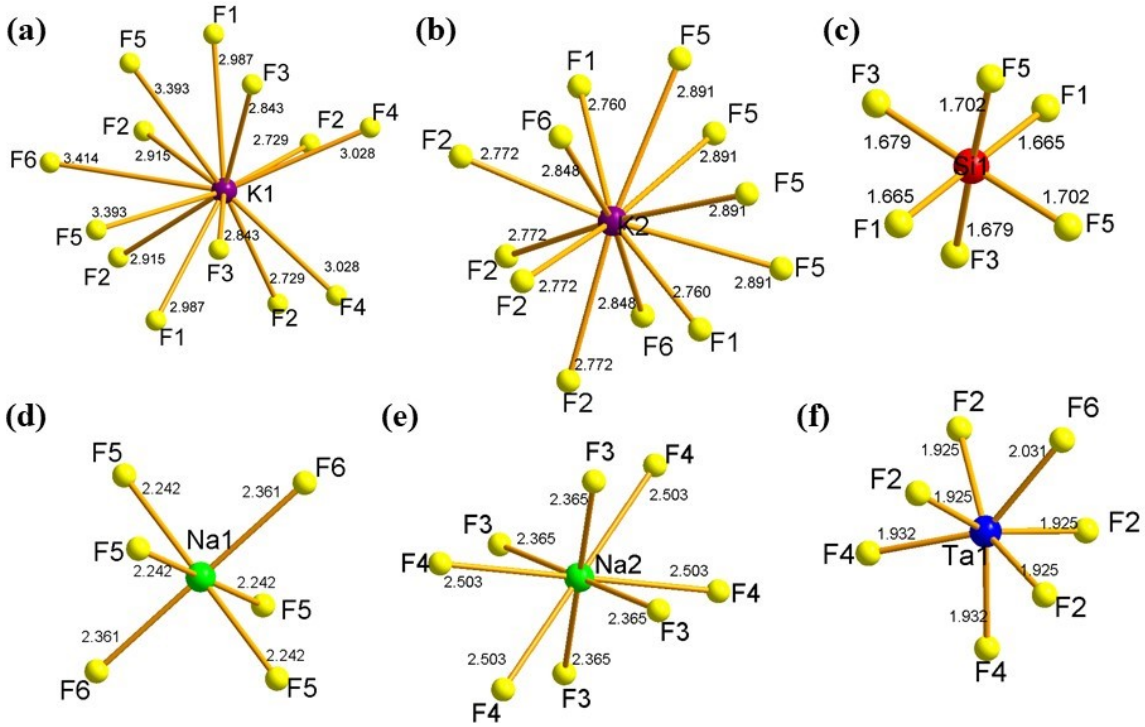

Figure S2. The coordination geometries of K(1) (a), K(2) (b), Na(1) (c), Na(2) (d), Ta(1) (e) and Si(1) (f) in the structure of $K_3Na(TaF_7)(SiF_6)$.

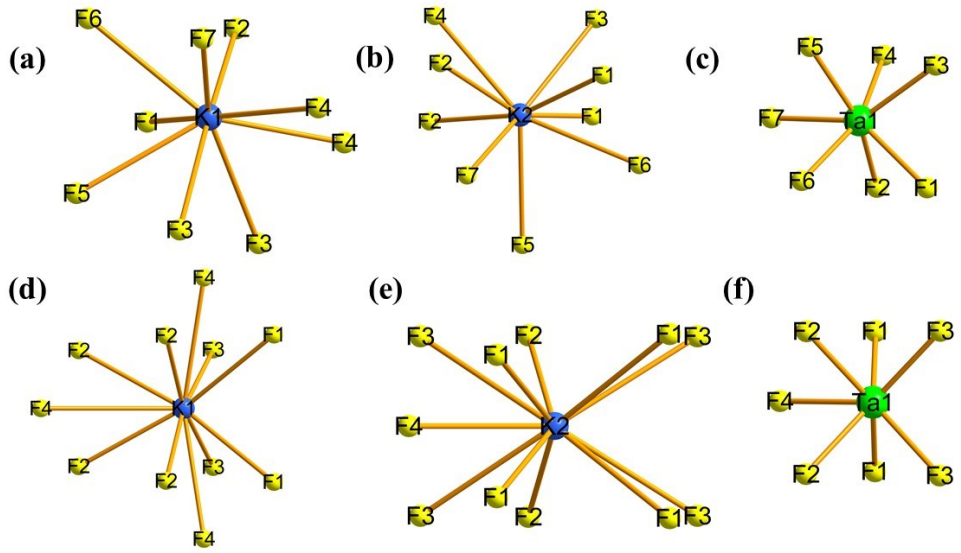

Figure S3. The coordination geometries of K(1) (a), K(2) (b), Ta(1) (c) in the structure of α-K_2TaF_7 and K(1) (d), K(2) (e) and Ta(1) (f) in the structure of β-K_2TaF_7.