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Supporting Information

An energy band engineering design to enlarge the band gap of $KTiOPO_4$ (KTP)-type sulfates via aliovalent substitution

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and calculated Bond Valence Sums for $RbSnFSO_4$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq} ($Å^2$)	BVS
Sn1	10131(9)	12500	2715(5)	11(2)	2.033
Sn2	5257(9)	2500	2322(5)	11(2)	1.827
Rb1	7682(9)	7500	4548(7)	17(3)	0.979
Rb2	2443(12)	-2500	508(7)	11(2)	0.719
S1	7285(3)	-2500	1394(17)	9(5)	5.980
S2	2840(3)	7500	3497(18)	10(5)	6.457
F1	3010(8)	2500	1518(4)	15(13)	1.119
F2	8995(9)	12500	3969(4)	22(15)	1.092
O1	6170(6)	-138(10)	1184(3)	13(10)	2.076
O2	8670(9)	-2500	755(5)	17(17)	1.786
O3	7884(10)	-2500	2414(5)	16(16)	1.664
O4	3704(11)	7500	2607(6)	27(2)	1.600
O5	1256(12)	9020(2)	3513(8)	17(2)	1.579
O6	3938(10)	7500	4356(6)	27(2)	1.874

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) , and calculated Bond Valence Sums for $RbSbF_2SO_4$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq} ($Å^2$)	BVS
Sb1	-6694(6)	-5817(5)	-9765(2)	22(2)	3.043
Rb1	-5152(9)	-1589(7)	231(3)	27(2)	1.35
S1	-7039(3)	-3654(2)	-5209(6)	26(7)	5.927
F1	-8708(3)	-5629(6)	-9419(18)	29(17)	1.026
F2	-6776(7)	-6558(6)	-6430(14)	29(15)	0.915
O1	-7770(10)	-2601(8)	-6229(18)	31(19)	1.855
O2	-8031(10)	-4393(8)	-3938(19)	34(2)	1.622
O3	-6458(10)	-4237(7)	-762(2)	32(2)	1.933
O4	-5846(9)	-3345(7)	-3586(17)	30(17)	1.691

Table S3. Selected Bond lengths (Å) and angles (deg) for $RbSnFSO_4$.

Sn1—F2	2.008(7)	O1—S1—Rb2^{x}	117.9(2)
Sn2—F1	2.014(6)	O2—S1—Rb2^{x}	58.35(19)
Sn2—O1	2.226(6)	O2—S1—O1	109.0(3)
Sn2—Rb2	4.1099(9)	O2—S1—Rb2	123.4(3)
Sn2—Rb1	4.3410(10)	O2—S1—O3	113.3(5)
Rb1—F2	2.918(3)	O3—S1—O1	109.5(3)
Rb1—O6	2.904(8)	O3—S1—Rb2	123.3(3)
Rb2—F1	2.918(3)	O4—S2—O5	116.9(5)
Rb2—O1	3.218(5)	O4—S2—Rb1	80.5(4)
S1—O3	1.467(8)	O5—S2—Rb1	141.4(4)
S1—O2	1.440(7)	O6—S2—O4	115.7(5)
S1—O1	1.495(5)	O6—S2—Rb1	35.2(4)
S2—O4	1.449(8)	O6—S2—O5	116.7(5)
S2—O5	1.454(10)	Sn2—O1—Rb2	96.36(16)
S2—O6	1.425(8)	Sn2—F1—Rb2	111.57(14)
Sn1—O5^{i}	2.232(10)	S1—O1—Sn2	123.2(3)
Sn2—O1^{v}	2.226(5)	S1—O1—Rb2	105.0(3)
Rb2—O2^{x}	3.174(5)	S2—O6—Rb1	128.3(5)
Rb2—S1^{x}	3.6831(19)	F2—Sn1—O5^{i}	85.3(3)
O2—Rb2^{x}	3.174(5)	O5^{i}—Sn1—Rb1	111.8(3)
S1—Rb2^{x}	3.6831(19)	O1—Sn2—O1^{v}	73.8(3)
S1—O1^{xi}	1.495(5)	O1^{v}—Sn2—Rb2	96.44(13)
S2—O5^{xv}	1.454(10)	O1^{v}—Sn2—Rb1	90.91(13)
F1—Sn2—O1	84.66(19)	F1—Sn2—Rb1^{vi}	135.99(10)
F1—Sn2—Rb2	41.32(6)	F1—Rb2—O2^{x}	171.16(17)
F1—Sn2—Rb1	135.99(10)	F2—Rb1—O3^{iv}	71.19(14)
F2—Sn1—Rb1	38.64(4)	O6—Rb1—O3^{iv}	91.4(2)
F2—Rb1—O6	110.27(14)	S1—O3—Rb1^{vi}	158.5(5)
O1—Sn2—Rb2	51.08(13)	S1—O2—Rb2^{ii}	148.5(5)
O1—Sn2—Rb1	135.79(13)	S2—O4—Rb2^{iv}	133.6(5)
O1—S1—Rb2	53.1(2)	S2—O6—Rb1^{xii}	111.84(16)

Symmetry codes: (i) x+1, −y+5/2, z; (ii) x+1, y, z; (iii) −x+2, −y+2, −z+1; (iv) x, y+1, z; (v) x, −y+1/2, z; (vi) x, y−1, z; (vii) −x+1, y−1/2, −z; (viii) −x+1, −y, −z; (ix) x−1, y, z; (x) −x+1, −y−1, −z; (xi) x, −y−1/2, z; (xii) −x+1, −y+2, −z+1; (xiii) −x+1, y−1/2, −z+1; (xiv) −x+1, −y+1, −z+1; (xv) x, −y+3/2, z.

Table S4. Selected Bond lengths (Å) and angles (deg) for $RbSbF_2SO_4$.

Sb1—F2	1.933(7)	F2—Sb1—F1	85.8(4)
Sb1—F1	1.947(6)	F2—Sb1—O3	84.9(3)
Sb1—O3	2.146(9)	F1—Sb1—O3	87.8(3)
S1—O2	1.436(10)	O2—S1—O1	109.5(6)
S1—O4	1.463(9)	O4—S1—O1	111.8(5)
S1—O1	1.497(9)	O2—S1—O3	111.0(5)
S1—O3	1.525(10)	O4—S1—O3	107.2(6)
Rb1—O4	2.909(8)	O1—S1—O3	103.6(5)
Rb1—F1^{vi}	2.873(9)	O2—S1—O4	113.3(6)
Sb1—Rb1^{v}	4.3355(15)	S1—O3—Sb1	139.6(6)
O1—Sb1^{vi}	2.248(9)	S1—O4—Rb1	137.8(5)
Rb1—F2^{vi}	3.065(7)	F2—Sb1—O1^{i}	83.8(3)
Rb1—O2^{vi}	3.098(9)	F1—Sb1—O1^{i}	84.7(3)
Rb1—O2^{ix}	3.177(10)	O3—Sb1—O1^{i}	166.9(3)
Rb1—F1^{x}	3.185(9)	F2—Sb1—Rb1^{i}	45.8(2)
Rb1—O1^{xi}	3.320(10)	F1—Sb1—Rb1^{i}	39.9(3)
Sb1—O1^{i}	2.248(9)	O3—Sb1—Rb1^{i}	86.1(3)
Sb1—Rb1^{i}	4.0799(16)	O3—Sb1—Rb1^{iii}	62.4(3)
Sb1—Rb1^{ii}	4.0828(16)	F2—Sb1—Rb1^{ii}	116.5(2)
Sb1—Rb1^{iv}	4.3328(16)	F1—Sb1—Rb1^{ii}	49.6(3)
Rb1—O3^{xi}	3.478(9)	O3—Sb1—Rb1^{ii}	126.4(3)
Rb1—S1^{xi}	3.812(3)	F1^{vi}—Rb1—O4	66.8(2)
O2—Rb1^{i}	3.098(9)	S1—O1—Rb1^{xii}	97.3(4)
S1—Rb1^{iii}	3.818(3)	O2—S1—Rb1^{xii}	165.6(4)
F2—Rb1^{iv}	2.949(7)	O4—Rb1—O1^{xi}	87.8(2)
F2—Rb1^{i}	3.065(7)	S1—O1—Sb1^{vi}	136.6(5)
F1—Rb1^{i}	2.873(9)	S1—O3—Rb1^{xii}	90.6(4)
F1—Rb1^{ii}	3.185(9)	Sb1—O3—Rb1^{xii}	127.8(4)
F1—Sb1—Rb1^{iii}	33.88(19)	S1—O2—Rb1^{i}	142.2(6)
F1—Sb1—Rb1^{v}	122.4(2)	O4—Rb1—O3^{xi}	61.9(2)
O3—Sb1—Rb1^{v}	148.5(3)	Sb1—F2—Rb1^{i}	107.3(3)
F1—Sb1—Rb1^{iv}	115.1(2)	Sb1—F1—Rb1^{i}	114.3(4)
F2—Sb1—Rb1^{iv}	34.5(2)	O2—S1—Rb1^{iii}	79.2(4)
O4—Rb1—O1^{vii}	111.5(2)	O4—Rb1—F2^{vi}	66.2(2)
O4—Rb1—O2^{ix}	85.9(3)	O4—Rb1—F1^{x}	139.3(2)
F2—Sb1—Rb1^{v}	104.6(2)	Sb1—F2—Rb1^{iv}	123.8(3)

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

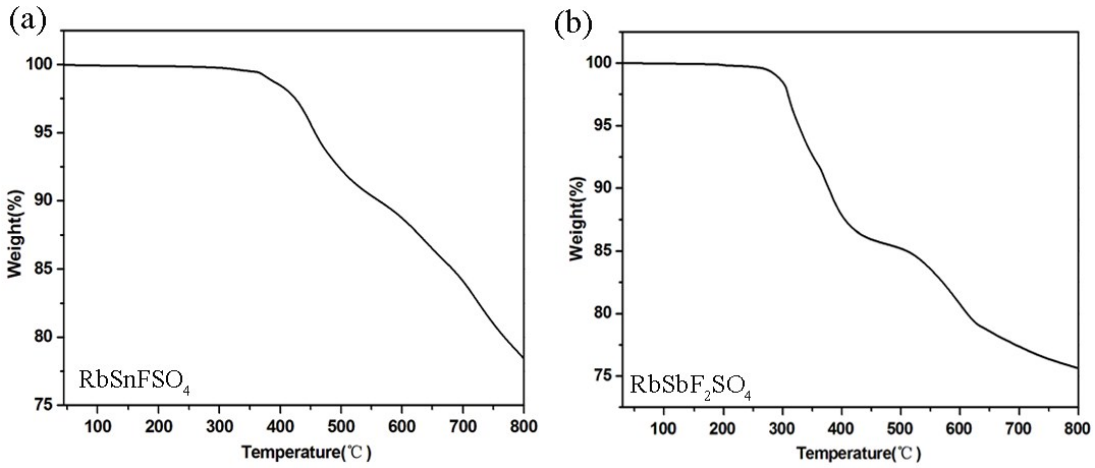

Fig. S1. TGA curves for $RbSnFSO_4$ (a) and $RbSbF_2SO_4$ (b).

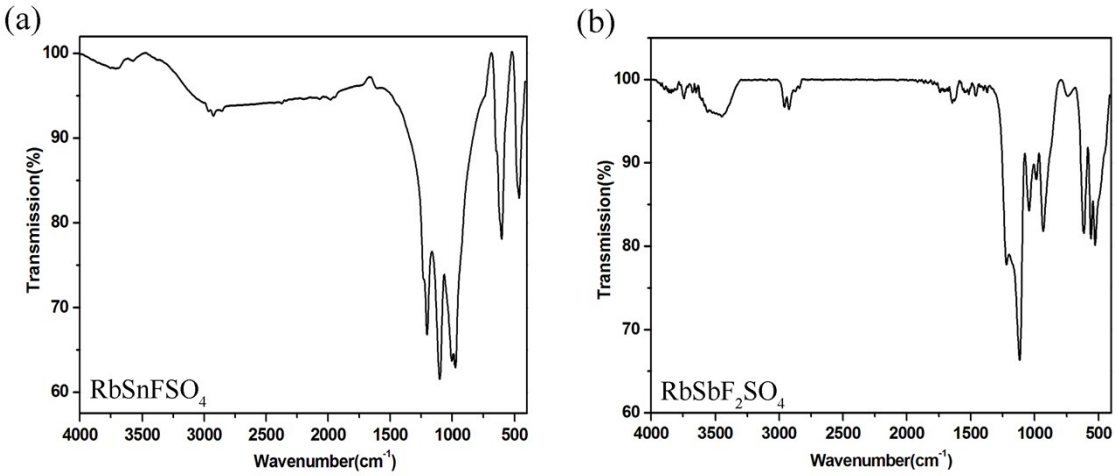

Fig. S2. IR spectra for $RbSnFSO_4$ (a) and $RbSbF_2SO_4$ (b).

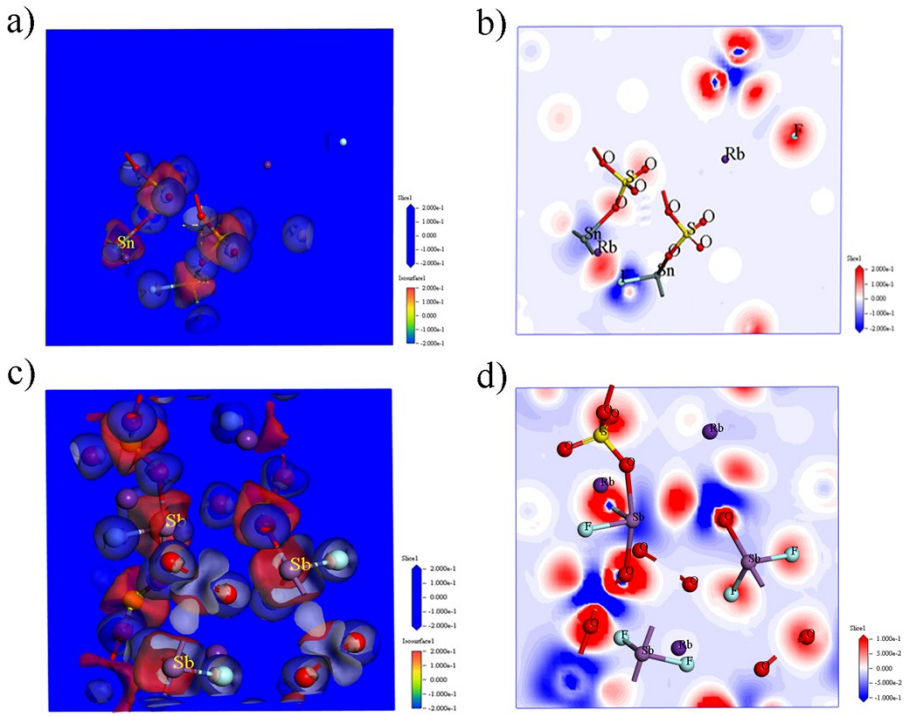

Fig. S3. Electron-density difference maps for $SnRbFSO_4$ (a, b) and $RbSbF_2SO_4$ (c, d).