Electronic Supplementary Information (ESI) for:

Centrosymmetric $K_2SO_4 \cdot (SbF_3)_2$ and Noncentrosymmetric $Rb_2SO_4 \cdot (SbF_3)_2$ Resulting from Cooperative Effects of Lone Pair and Cation Size

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2), and calculated Bond Valence Sum for $K_2SO_4 \cdot (SbF_3)_2$. *U(eq)* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sb1	0.82363 (3)	0.26103 (4)	0.72136 (2)	0.00819 (11)	2.87
Sb2	0.31451 (3)	0.78202 (5)	0.50037 (2)	0.00918 (11)	2.95
K1	0.63949 (11)	0.74910 (13)	0.82655 (5)	0.0126 (2)	1.01
K2	1.01873 (11)	0.24770 (14)	0.92575 (5)	0.0135 (2)	0.93
S1	0.63048 (11)	0.73935 (15)	0.62219 (5)	0.0085 (2)	5.97
F1	0.8624 (3)	0.4739 (4)	0.80384 (11)	0.0165 (5)	1.09
F2	0.9294 (3)	0.0301 (4)	0.79144 (12)	0.0186 (5)	0.91
F3	0.6470 (2)	0.1549 (4)	0.75095 (12)	0.0149 (5)	1.13
F4	0.2645 (2)	0.5580 (4)	0.56661 (11)	0.0147 (5)	1.14
F5	0.1080 (3)	0.7131 (4)	0.44596 (13)	0.0180 (5)	0.90
F6	0.2082 (2)	1.0234 (4)	0.54291 (12)	0.0148 (5)	1.12
O1	0.7634 (3)	0.8914 (6)	0.64463 (15)	0.0206 (7)	1.88
O2	0.4936 (3)	0.8891 (5)	0.60789 (13)	0.0121 (5)	1.90
O3	0.6391 (3)	0.6206 (6)	0.55520 (14)	0.0225 (7)	1.76
O4	0.6236 (3)	0.5680 (6)	0.67873 (16)	0.0237 (7)	1.89

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2), and calculated Bond Valence Sum for $Rb_2SO_4 \cdot (SbF_3)_2$. *U(eq)* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sb1	0.17363 (6)	0.5010 (5)	0.55869 (6)	0.00731 (14)	2.99
Sb2	0.31898 (7)	0.5032 (4)	0.99959 (6)	0.02175 (19)	3.06
Rb1	0.02396 (9)	0.9986 (7)	0.85431 (9)	0.01102 (19)	1.12
Rb2	0.35956 (9)	0.0020 (6)	0.34806 (9)	0.01104 (18)	1.26
S1	0.3706 (2)	−0.0018 (15)	0.7562 (2)	0.0118 (5)	5.97
F1	0.2525 (12)	0.2838 (11)	1.1222 (10)	0.034 (3)*	1.24
F2	0.2244 (10)	0.7570 (16)	1.0886 (9)	0.021 (2)*	1.14
F3	0.1159 (6)	0.501 (3)	0.8857 (6)	0.0162 (11)*	1.11
F4	0.1300 (10)	0.7163 (15)	0.4003 (9)	0.0203 (17)*	1.16
F5	0.0734 (10)	0.2715 (15)	0.4201 (8)	0.0201 (17)*	1.00
F6	0.3456 (8)	0.4126 (15)	0.4977 (9)	0.0233 (18)	1.27
O1	0.2453 (10)	0.1428 (18)	0.7095 (10)	0.020 (2)	2.12
O2	0.5121 (10)	0.1092 (15)	0.7865 (9)	0.0129 (17)*	2.10
O3	0.3556 (11)	−0.1376 (19)	0.8843 (11)	0.025 (2)	1.72
O4	0.3721 (12)	−0.1924 (19)	0.6474 (11)	0.026 (2)	1.65

Table S3. Selected Bond lengths (Å) and angles (deg) for $K_2SO_4 \cdot (SbF_3)_2$.

Sb1—F3	1.935 (2)	K2—O1^{viii}	2.783 (3)
Sb1—F1	1.958 (2)	K2—F2	2.809 (2)
Sb1—F2	1.967 (2)	K2—F6^{ix}	2.827 (2)
Sb1—O4	2.525 (3)	K2—F4^{ii}	2.852 (2)
Sb1—O1^{i}	2.545 (3)	K2—F5^{ii}	2.966 (3)
Sb1—K1^{i}	4.1111 (9)	K2—F5^{ix}	3.157 (3)
Sb1—K1	4.0173 (9)	K2—O3^{viii}	3.167 (3)
Sb1—K1^{ii}	4.1472 (10)	O1—K2^{x}	2.783 (3)
Sb2—F4	1.925 (2)	S1—O4	1.468 (3)
Sb2—F6	1.963 (2)	S1—O3	1.471 (3)
Sb2—F5	1.987 (2)	S1—O1	1.476 (3)
Sb2—O2	2.408 (3)	S1—O2	1.490 (3)
K1—F1	2.687 (2)	F3—K1^{ii}	2.766 (2)
K1—F4^{iii}	2.687 (2)	F4—K1^{ii}	2.687 (2)
K1—F3^{vi}	2.725 (2)	F4—K2^{iii}	2.852 (2)
K1—F3^{iii}	2.766 (2)	F5—K2^{v}	2.732 (3)
K1—O2^{ii}	2.817 (3)	F5—K2^{iii}	2.966 (3)
K1—F6^{ii}	2.879 (2)	F5—K2^{iv}	3.157 (3)
K1—O4	2.994 (3)	F6—K2^{iii}	2.779 (2)
K1—O4^{iii}	3.000 (3)	F6—K2^{iv}	2.827 (2)
K2—F1	2.768 (2)	O3—K2^{x}	3.167 (3)
K2—F6^{ii}	2.779 (2)	O4—K1^{ii}	3.000 (3)
S1—O3—K2^{x}	92.63 (13)	Sb2—F6—K2^{iv}	105.11 (9)
S1—O4—Sb1	122.84 (16)	K2^{iii}—F6—K2^{iv}	94.19 (7)
S1—O4—K1^{ii}	122.82 (16)	S1—O1—Sb1^{vi}	134.71 (16)
Sb1—O4—K1^{ii}	96.90 (10)	S1—O1—K2^{x}	109.16 (15)
K1—O4—K1^{ii}	95.83 (8)	Sb1^{vi}—O1—K2^{x}	115.86 (10)
O2^{ii}—K1—F6^{ii}	57.59 (7)	O4—S1—O3	111.58 (19)

F1—K1—O4	61.39 (7)	O4—S1—O1	109.90 (18)
F4^{iii}—K1—O4	152.20 (8)	O3—S1—O1	108.37 (18)
F3^{vi}—K1—O4	77.45 (8)	O4—S1—O2	109.52 (16)
F3^{iii}—K1—O4	65.71 (7)	O3—S1—O2	108.05 (16)
O2^{ii}—K1—O4	104.26 (8)	O1—S1—O2	109.38 (17)
F6^{ii}—K1—O4	125.82 (8)	O4—S1—K2^{x}	113.34 (12)
S1—O4—K1	118.48 (18)	S1—O2—Sb2	113.52 (14)
Sb1—O4—K1	93.02 (9)	S1—O2—K1^{iii}	139.75 (15)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) *x*−1, −*y*+3/2, *z*−1/2; (v) *x*−1, −*y*+1/2, *z*−1/2; (vi) *x*, *y*+1, *z*; (vii) *x*+1, −*y*+1/2, *z*+1/2; (viii) −*x*+2, *y*−1/2, −*z*+3/2; (ix) *x*+1, −*y*+3/2, *z*+1/2; (x) −*x*+2, *y*+1/2, −*z*+3/2.

Table S4. Selected Bond lengths (Å) and angles (deg) for $Rb_2SO_4 \cdot (SbF_3)_2$.

Sb1—F6	1.923 (8)	Rb1—F5^{x}	2.947 (8)
Sb1—F4	1.957 (8)	Rb1—F2	2.955 (10)
Sb1—F5	1.966 (8)	Rb1—F3	2.969 (17)
Sb1—O1	2.528 (9)	Rb1—F3^{i}	2.996 (17)
Sb1—O4^{i}	2.558 (11)	Rb1—F3^{xi}	3.153 (5)
Sb1—Rb1^{ii}	4.0584 (11)	Rb1—O3^{i}	3.160 (11)
Sb2—F1	1.9482 (10)	S1—O2	1.440 (10)
Sb2—F3	1.971 (6)	S1—O3	1.520 (10)
Sb2—F2	2.012 (8)	S1—O4	1.534 (11)
Sb2—O2^{iv}	2.398 (9)	S1—O1	1.423 (10)
Sb2—O3^{i}	2.414 (10)	Rb2—F4^{vi}	2.852 (9)
Rb2—F5	3.323 (9)	Rb2—F6^{viii}	2.872 (8)
Rb1—F2^{xi}	2.931 (9)	Rb2—F2^{ix}	2.931 (9)
Rb1—F1^{xi}	2.935 (11)	Rb2—O2^{viii}	3.007 (9)
O4—Sb1^{vi}	2.558 (10)	O2—Sb2^{xiv}	2.398 (9)
O2—Rb2^{iii}	3.007 (9)		

F6—Sb1—F4	86.9 (4)	F5—Rb2—Sb1^{vi}	75.76 (15)
F6—Sb1—F5	84.6 (3)	S1—Rb2—Sb1^{vi}	53.60 (10)
F4—Sb1—F5	83.7 (3)	Sb1—Rb2—Sb1^{vi}	86.86 (2)
F6—Sb1—O1	81.1 (3)	F4^{x}—Rb1—O1^{i}	73.5 (3)
F4—Sb1—O1	163.1 (3)	F4^{x}—Rb1—F2^{xi}	72.0 (2)
F5—Sb1—O1	83.4 (3)	O1^{i}—Rb1—F2^{xi}	130.4 (3)
F6—Sb1—O4^{i}	71.8 (3)	F4^{x}—Rb1—F1^{xi}	88.9 (3)
F4—Sb1—O4^{i}	80.7 (4)	O1^{i}—Rb1—F1^{xi}	155.3 (3)
F6—Sb1—Rb2	34.6 (2)	O1—Sb1—Rb2^{iii}	76.0 (2)
F6—Sb1—Rb2^{i}	62.6 (3)	O1^{i}—Rb1—F3^{xi}	152.3 (3)
F1—Sb2—O2^{iv}	81.9 (4)	F4^{x}—Rb1—O3^{i}	118.0 (3)
F3—Sb2—O2^{iv}	148.4 (4)	O1^{i}—Rb1—O3^{i}	46.4 (3)
F2—Sb2—O2^{iv}	72.6 (4)	F2^{xi}—Rb1—O3^{i}	157.0 (3)
F1—Sb2—O3^{i}	160.9 (4)	F1^{xi}—Rb1—O3^{i}	139.7 (3)
F3—Sb2—O3^{i}	88.0 (5)	F5^{x}—Rb1—O3^{i}	93.4 (3)
F4^{vi}—Rb2—O4^{iii}	169.0 (3)	O3—S1—Rb2	148.8 (6)
F6^{viii}—Rb2—O4^{iii}	53.6 (2)	O4—S1—Rb2	45.7 (5)
O1—S1—O2	117.6 (8)	O1—S1—O4	109.4 (6)
O1—S1—O3	109.4 (6)	O2—S1—O4	107.2 (6)
O2—S1—O3	108.5 (5)	O3—S1—O4	103.8 (8)

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

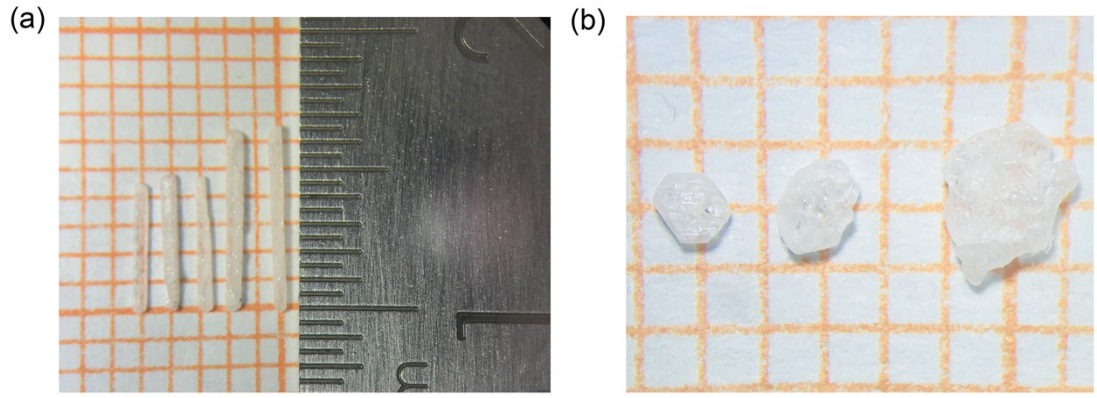

Fig. S1. Crystal photographs of compounds (a) $K_2SO_4 \cdot (SbF_3)_2$ and (b) $Rb_2SO_4 \cdot (SbF_3)_2$.

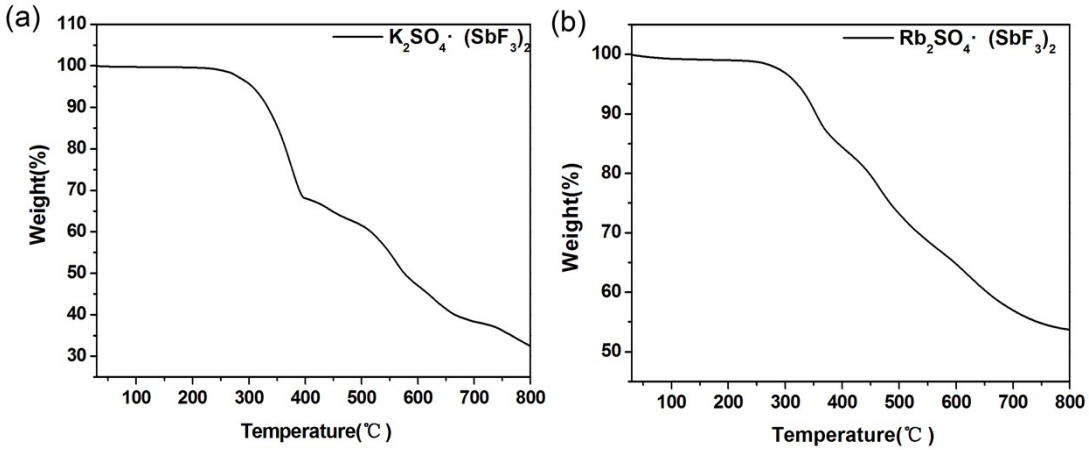

Fig. S2. TGA curves of compounds (a) $K_2SO_4 \cdot (SbF_3)_2$ and (b) $Rb_2SO_4 \cdot (SbF_3)_2$.

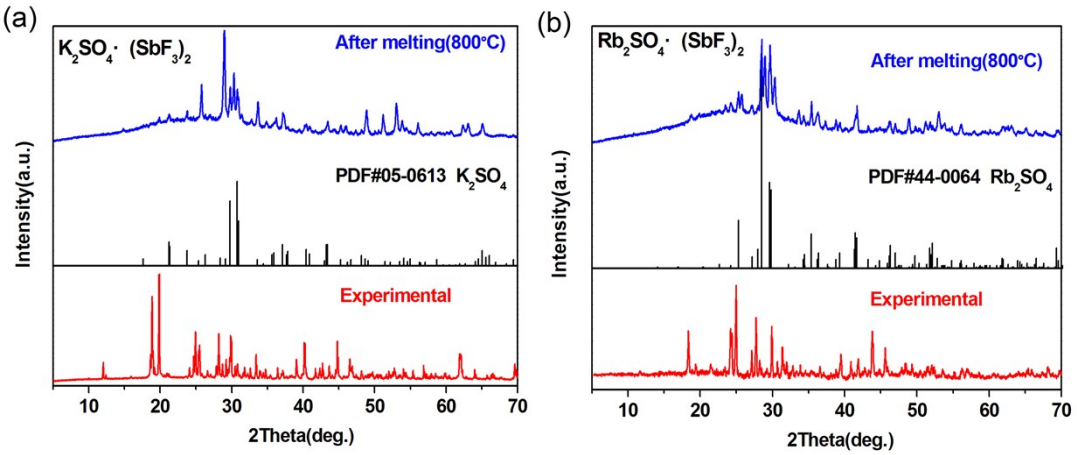

Fig. S3. Experimental XRD patterns for compounds (a) $K_2SO_4 \cdot (SbF_3)_2$ and (b) $Rb_2SO_4 \cdot (SbF_3)_2$ before and after melting.

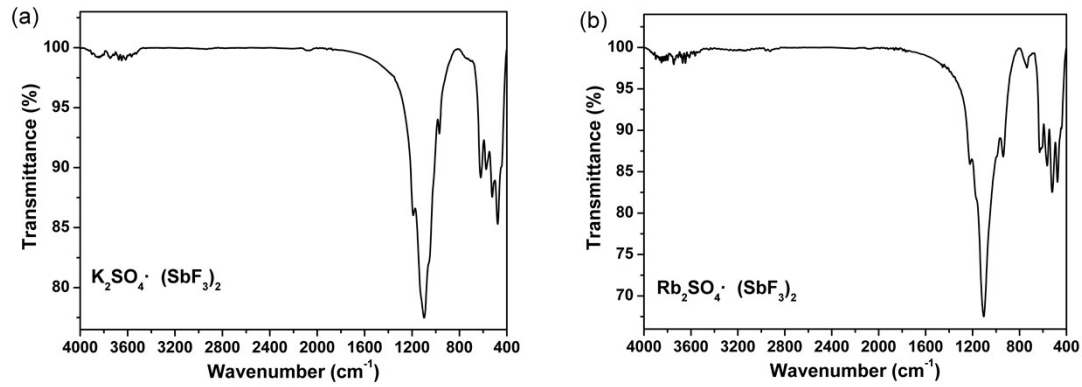

Fig. S4. The IR spectra of compounds (a) $K_2SO_4 \cdot (SbF_3)_2$ and (b) $Rb_2SO_4 \cdot (SbF_3)_2$.

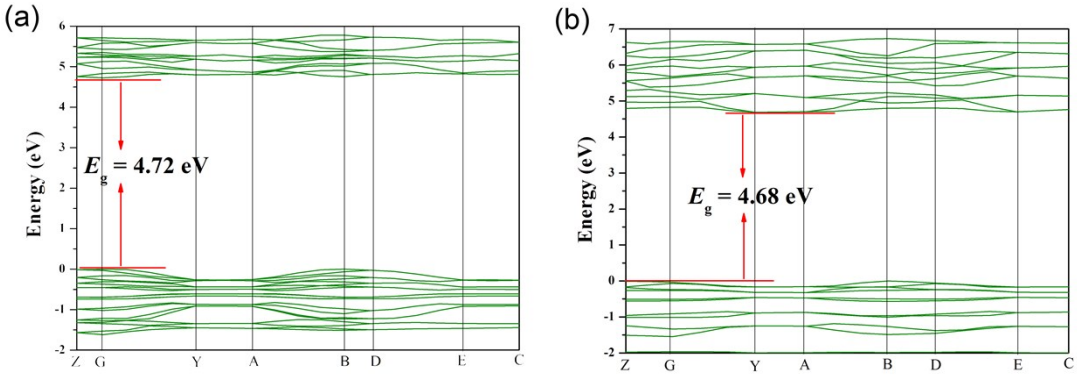

Fig. S5. Calculated band structures of (a) $K_2SO_4 \cdot (SbF_3)_2$ and (b) $Rb_2SO_4 \cdot (SbF_3)_2$.