Electronic Supporting Information

$A_6Sb_4F_{12}(SO_4)_3$ (A = Rb, Cs): Two Novel Antimony Fluoride Sulfates with Unique Crown-like Clusters

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Section S1. Experimental section

Instrumentations. Suitable single crystals were selected under an optical microscope. The intensity data were collected on a Bruker SMART BREEZE diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELX-2014 program package[1, 2]. All of the structures were verified using the ADDSYM algorithm from the program PLATON and no higher symmetries were found[3]. Crystallographic data and structural refinements for the two compounds are summarized in Table S1. Atomic coordinates and isotropic displacement coefficients, and selected bond lengths for the two compounds are listed in Tables S2-S5. IR spectra (KBr pellets) were recorded on a Vertex 70 Fourier transform infrared spectrometer. Thermal analyses were performed in a dynamic nitrogen atmosphere using a Netzsch STA 409 PC thermal analyzer, and with a heating rate of 10℃/min and in the range of RT-800℃. Powder XRD patterns were obtained using a Rigaku Smartlab powder X-ray diffractometer with CuKα radiation (λ = 1.54056 Å), in the angular range of 2θ = 5-50°, and with a scan step width of 0.05° and a fixed time of 0.2 s. The UV transmittance spectroscopy was recorded at room temperature using a UV-2600, Shimadzu in the range of 200-800 nm, and the absorption (*K/S*) data were calculated from the Kubelka-Munk function. The second-harmonic generation (SHG) signal of large particles of $Rb_6Sb_4F_{12}(SO_4)_3$ was measured with a Q-switched Nd:YAG laser using 1064 nm radiation by the Kurtz and Perry method[4]. The microcrystalline crystals of known NLO material KDP was served as the reference with the same particle size ranges.

Computational Descriptions. The first-principles calculations of $Rb_6Sb_4F_{12}(SO_4)_3$ and $Cs_6Sb_4F_{12}(SO_4)_3$ were carried out by using the CASTEP software package[5] to understand the relationship between structure and properties of them. The band structure and density of states (DOS)/partial DOS (PDOS) were computed. The generalized gradient approximation (GGA) with Perdew-Wang 91 (PW91) functional was adopted for all calculations[6]. Ultrasoft pseudopotentials (USP) were employed for all the atoms[7]. Moreover, the kinetic energy cutoff of 500 eV for $Rb_6Sb_4F_{12}(SO_4)_3$ and 550 eV for $Cs_6Sb_4F_{12}(SO_4)_3$ was chosen and the k-point sampling in the Brilliouin zone was used to be 2×2×4 for $Rb_6Sb_4F_{12}(SO_4)_3$ and 2×2×1 for $Cs_6Sb_4F_{12}(SO_4)_3$,

respectively. The rest parameters used in the calculations were set by the default values of the CASTEP.

Table S1 Crystal data and structure refinement for $A_6Sb_4F_{12}(SO_4)_3$ (A = Rb , Cs).

Formula	$Rb_6Sb_4F_{12}(SO_4)_3$	$Cs_6Sb_4F_{12}(SO_4)_3$
Formula Mass(amu)	1516.02	1800.64
Crystal System	trigonal	triclinic
Space Group	$P3$	$P\bar{1}$
***a* (Å)**	16.9490(4)	7.9044(4)
***b* (Å)**	16.9490(4)	10.5139(6)
***c* (Å)**	7.5405(2)	17.3534(6)
***α* (°)**	90	90.350(4)
***β* (°)**	90	90.151(3)
***γ* (°)**	120	104.797(4)
***V*(Å^3)**	1875.94(9)	1394.31(12)
Z	3	2
***ρ*(calcd) (g/cm^3)**	4.026	4.289
Temperature (K)	170	295
***λ* (Å)**	0.71073	1.54184
***F*(000)**	2034	1572
***μ* (mm^{-1})**	16.26	93.89
***R*$_1$, *wR*$_2$ (*I*> 2*σ*(*I*))[a]**	0.020/0.039	0.0702/0.1759
GOF on *F*^{2}	1.05	1.11

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for $Rb_6Sb_4F_{12}(SO_4)_3$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq}(Å^2)	BVS
Sb1	0.64293 (7)	0.46465 (7)	0.44047 (14)	0.0221 (2)	2.98
Sb2	0.6667	0.3333	−0.0513 (2)	0.0219 (4)	2.89
Sb3	0.86543 (7)	0.83733 (7)	0.78790 (13)	0.0211 (2)	3.07
Sb4	1.0000	1.0000	0.3002 (2)	0.0215 (4)	2.91
Sb5	0.3333	0.6667	0.3894 (2)	0.0224 (4)	2.89
Sb6	0.44931 (8)	0.83792 (8)	−0.10225 (15)	0.0265 (2)	2.99
Rb1	0.53391 (10)	0.94319 (10)	0.3984 (2)	0.0223 (3)	1.15
Rb2	0.78879 (11)	0.72605 (10)	1.2832 (2)	0.0229 (3)	1.00
Rb3	0.73175 (10)	0.93997 (10)	1.0782 (2)	0.0222 (3)	0.96
Rb4	0.60304 (11)	0.75777 (12)	0.6202 (2)	0.0307 (4)	1.09
Rb5	0.89029 (13)	0.59864 (11)	0.7224 (2)	0.0319 (4)	0.70
Rb6	0.63091 (14)	0.56440 (14)	0.9249 (2)	0.0350 (4)	0.73
S1	0.2794 (3)	0.8167 (3)	0.1663 (5)	0.0291 (9)	5.83
S2	0.7985 (3)	0.9675 (3)	0.5286 (5)	0.0249 (8)	6.07
S3	0.4686 (3)	0.3047 (3)	0.1725 (5)	0.0251 (8)	6.16
F1	0.5582 (6)	0.4601 (7)	0.6217 (12)	0.025 (2)	1.15
F2	0.8689 (8)	0.7348 (8)	0.8918 (15)	0.038 (3)	1.03
F3	0.6043 (7)	0.5367 (7)	0.3066 (14)	0.031 (2)	1.22
F4	0.4286 (7)	0.9065 (6)	−0.2856 (13)	0.026 (2)	1.13
F5	0.4299 (7)	0.7521 (7)	0.5521 (14)	0.030 (2)	1.04
F6	0.5653 (7)	0.2613 (7)	−0.2151 (14)	0.030 (2)	0.76
F7	0.9459 (8)	1.0507 (8)	0.1395 (13)	0.033 (2)	0.97
F8	0.7327 (7)	0.5806 (6)	0.5491 (12)	0.026 (2)	1.07
F9	0.5709 (7)	0.8899 (8)	−0.2081 (15)	0.039 (3)	0.96
F10	0.5025 (8)	0.9481 (7)	0.0360 (14)	0.036 (2)	1.21
F11	0.7627 (7)	0.7518 (7)	0.6506 (14)	0.031 (2)	1.24

F12	0.7711 (8)	0.8061 (9)	0.9700 (16)	0.042 (3)	1.14
O1	0.3487 (8)	0.8182 (9)	0.2800 (19)	0.033 (3)	2.04
O2	0.5399 (9)	0.3696 (8)	0.0502 (16)	0.029 (3)	1.85
O3	0.7116 (9)	0.9567 (9)	0.4740 (17)	0.032 (3)	2.04
O4	0.1955 (8)	0.7242 (8)	0.1634 (17)	0.029 (3)	1.84
O5	0.2526 (10)	0.8826 (10)	0.237 (2)	0.040 (3)	1.84
O6	0.4698 (8)	0.2185 (8)	0.1749 (15)	0.026 (2)	1.95
O7	0.8283 (8)	0.9220 (9)	0.4113 (18)	0.034 (3)	2.06
O8	0.3143 (9)	0.8451 (10)	−0.0183 (16)	0.036 (3)	1.90
O9	0.3800 (9)	0.2883 (12)	0.1246 (19)	0.044 (4)	2.12
O10	0.4911 (8)	0.3440 (8)	0.3522 (15)	0.027 (2)	2.00
O11	0.7898 (9)	0.9301 (9)	0.7117 (16)	0.031 (3)	1.87
O12	0.8708 (11)	1.0671 (10)	0.5374 (19)	0.043 (3)	1.89

Table S3. Atomic coordinates and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for $Cs_6Sb_4F_{12}(SO_4)_3$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Cs1	0.68453 (12)	0.84832 (9)	0.49010 (5)	0.0367 (3)	1.15
Cs2	−0.16856 (10)	0.66364 (7)	0.00496 (4)	0.0281 (2)	1.34
Cs3	0.99588 (10)	1.15992 (8)	0.32196 (5)	0.0293 (2)	1.28
Cs4	0.75298 (11)	1.05521 (8)	0.08400 (5)	0.0318 (2)	1.08
Cs5	0.74286 (11)	0.42151 (9)	0.41325 (5)	0.0346 (2)	1.07
Cs6	0.51357 (13)	0.33634 (9)	0.16958 (6)	0.0402 (3)	0.88
Sb1	0.29848 (11)	0.56264 (8)	0.34815 (5)	0.0265 (2)	3.16
Sb2	0.44056 (11)	0.98508 (8)	0.29733 (5)	0.0262 (2)	3.26
Sb3	−0.13345 (10)	0.74638 (8)	0.25056 (4)	0.0253 (2)	2.99
Sb4	0.34888 (10)	0.69801 (8)	0.10393 (5)	0.0256 (2)	3.16
S1	0.1824 (4)	0.9796 (3)	0.13171 (17)	0.0249 (6)	6.34
S2	0.1181 (4)	0.8083 (3)	0.42770 (17)	0.0250 (6)	6.11
S3	0.0074 (4)	0.4555 (3)	0.19128 (17)	0.0254 (6)	6.01
F1	−0.2755 (13)	0.7735 (10)	0.1619 (5)	0.042 (2)	1.03
F2	0.3590 (12)	1.1414 (8)	0.3048 (5)	0.0354 (17)	1.29
F3	0.6481 (10)	1.1025 (9)	0.2501 (5)	0.0378 (19)	1.25
F4	0.1928 (11)	0.6281 (8)	0.0199 (5)	0.0338 (17)	1.25
F5	0.4784 (11)	0.5818 (9)	0.4298 (5)	0.0360 (18)	1.20
F6	0.4740 (11)	0.5694 (8)	0.0742 (5)	0.0335 (17)	1.29
F7	0.3513 (13)	0.3960 (9)	0.3257 (6)	0.044 (2)	1.16
F8	0.5598 (14)	1.0467 (11)	0.3949 (6)	0.045 (2)	1.14
F9	0.4886 (13)	0.8080 (10)	0.0236 (6)	0.044 (2)	1.10
F10	−0.3370 (13)	0.6052 (10)	0.2805 (6)	0.046 (2)	1.00
F11	−0.2434 (14)	0.8664 (10)	0.3059 (6)	0.044 (2)	1.05
F12	0.1393 (12)	0.4667 (9)	0.4229 (5)	0.0369 (18)	1.26
O1	−0.0720 (19)	0.3224 (12)	0.1662 (7)	0.046 (3)	2.06

O2	−0.0906 (17)	0.5460 (13)	0.1612 (6)	0.043 (2)	1.90
O3	0.1440 (16)	0.8536 (11)	0.0900 (7)	0.039 (2)	2.13
O4	0.0588 (17)	0.9714 (12)	0.1944 (7)	0.044 (3)	1.99
O5	0.2674 (15)	0.7466 (11)	0.4291 (7)	0.038 (2)	1.92
O6	0.0797 (17)	0.8423 (13)	0.5043 (7)	0.045 (3)	2.10
O7	0.1660 (16)	0.9277 (12)	0.3776 (7)	0.041 (2)	1.84
O8	0.1906 (16)	0.4943 (13)	0.1615 (7)	0.046 (3)	1.89
O9	−0.0345 (16)	0.7147 (11)	0.3944 (7)	0.041 (2)	1.92
O10	0.1663 (17)	1.0791 (13)	0.0787 (7)	0.044 (3)	2.08
O11	0.3614 (15)	1.0105 (12)	0.1630 (7)	0.041 (2)	2.11
O12	0.0132 (16)	0.4619 (13)	0.2769 (6)	0.043 (3)	1.91

Table S4. Bond lengths (Å) and angles (deg) for $Rb_6Sb_4F_{12}(SO_4)_3$.

Sb1—F1	1.957 (9)	S2—O7	1.423 (13)

Sb2—F6^{iv}	1.968 (10)	S3—O9	1.429 (14)
Sb3—F11	1.920 (10)	F2—Rb3^{vii}	3.206 (12)
Sb4—F7^{vii}	1.959 (10)	F3—Rb6^{iii}	2.917 (11)
Sb5—F5	1.979 (10)	F4—Rb1^{iii}	2.855 (9)
Sb6—F4	1.948 (9)	F6—Rb5^{vi}	3.106 (10)
Sb1—O6^{i}	2.544 (12)	F7—Rb2^{x}	3.001 (11)
Sb3—O11	2.544 (12)	F8—Rb2^{iii}	2.944 (10)
Sb6—O8	2.435 (14)	F9—Rb4^{iii}	2.867 (12)
Rb1—F1^{xi}	3.080 (10)	F10—Rb6^{xii}	2.880 (12)
Rb2—F11^{xiii}	2.875 (11)	F11—Rb2^{iii}	2.875 (11)
Rb2—F2	3.224 (12)	O1—Rb4^{xi}	3.300 (15)
Rb3—F12	2.789 (12)	O2—Rb6^{iii}	3.014 (12)
Rb4—F11	2.767 (11)	O3—Rb3^{iii}	3.035 (13)
Rb5—F9^{xiv}	3.303 (12)	O4—Rb1^{xi}	2.911 (11)
Rb6—F1	2.776 (10)	O5—Rb2^{xii}	2.912 (14)
Rb1—O1	2.915 (12)	O7—Rb3^{iii}	3.097 (14)
Rb2—O9^{xvi}	3.524 (17)	O8—Rb6^{xii}	3.285 (15)
Rb3—O3^{xiii}	3.035 (13)	O9—Rb3^{xviii}	2.781 (13)
Rb4—O5^{ii}	2.949 (16)	O10—Rb1^{ii}	3.033 (13)
Rb5—O9^{xvi}	3.053 (14)	O12—Rb2^{x}	2.857 (14)
Rb6—O6^{xvi}	3.007 (11)	O6—Sb1^{iv}	2.544 (12)
F1—Sb1—F8	86.2 (4)	F1^{xi}—Rb1—F9^{xiii}	79.0 (3)
F2—Sb3—F12	82.0 (5)	F3^{xi}—Rb1—F5	128.2 (3)
F4—Sb6—F9	84.5 (5)	F4^{xiii}—Rb1—F5	58.8 (3)
F5^{xi}—Sb5—F5^{ii}	85.6 (5)	F5—Rb1—F1^{xi}	117.0 (3)
F7^{vii}—Sb4—F7^{viii}	85.7 (5)	F12—Rb2—F11^{xiii}	132.4 (3)
F1—Sb1—F8	86.2 (4)	F1^{xi}—Rb1—F9^{xiii}	79.0 (3)
F2—Sb3—F12	82.0 (5)	F3^{xi}—Rb1—F5	128.2 (3)
F8—Sb1—O10	156.1 (4)	O5^{ii}—Rb4—O11	99.1 (4)
F9—Sb6—O8	152.4 (5)	O8^{xv}—Rb4—O11	101.4 (4)

F10—Sb6—O8	78.9 (5)	$O9^{xvi}$—Rb5—$F6^{xvi}$	87.3 (3)
$F1^{xi}$—Rb1—$O9^{xi}$	93.5 (3)	O11—Rb4—$O1^{ii}$	141.2 (3)
F2—Rb2—$O9^{xvi}$	51.4 (3)	$O2^{xiii}$—Rb6—$F4^{xv}$	102.9 (3)
F5—Rb1—$O9^{xi}$	146.0 (3)	$O3^{vii}$—Rb5—$F9^{xiv}$	58.0 (3)
$F7^{xiv}$—Rb2—$O6^{xvi}$	121.9 (3)	$O6^{xvi}$—Rb6—$F4^{xv}$	168.5 (3)
$F8^{xiii}$—Rb2—$O6^{xvi}$	58.9 (3)	$O8^{xv}$—Rb6—F2	103.2 (3)
$F9^{xiii}$—Rb1—$O9^{xi}$	121.7 (3)	O1—S1—O5	108.9 (8)
F12—Rb2—$O12^{xiv}$	127.9 (4)	O3—S2—O11	109.2 (8)
O10—Sb1—$O6^{i}$	111.6 (4)	O5—S1—O4	107.6 (8)
O3—Rb1—$O10^{xi}$	81.1 (3)	O8—S1—O5	108.1 (9)
$O4^{ii}$—Rb1—O1	68.9 (4)	O9—S3—O10	109.3 (8)
$O5^{xv}$—Rb2—$O7^{xiii}$	68.5 (4)	O11—S2—O12	106.6 (8)
$O6^{xvi}$—Rb2—$O7^{xiii}$	177.4 (3)	S1—O1—Rb1	140.0 (7)
$O7^{xiii}$—Rb2—$O9^{xvi}$	139.4 (3)	S2—O3—Rb1	174.0 (8)
$O9^{xvii}$—Rb3—$O3^{xiii}$	73.6 (4)	S3—O2—$Rb6^{iii}$	142.2 (7)
O1—Rb1—$F3^{xi}$	77.1 (3)	Rb1—O1—$Rb4^{xi}$	97.2 (4)
$O4^{ii}$—Rb1—$F3^{xi}$	124.7 (3)	$Rb6^{iii}$—O2—$Rb5^{vi}$	94.5 (3)
$O10^{xi}$—Rb1—F5	163.8 (3)		

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

Table S5. Bond lengths (Å) and angles (deg) for $Cs_6Sb_4F_{12}(SO_4)_3$.

Cs1—$F2^{ii}$	3.580 (9)	Sb1—F5	1.978 (8)
Cs1—F5	3.037 (9)	Sb2—F2	1.916 (8)
Cs1—$F8^{ii}$	3.164 (11)	Sb3—F10	1.964 (9)
Cs3—F3	2.933 (8)	Sb3—F11	1.954 (9)
Cs4—$F1^{i}$	3.219 (10)	Sb4—F4	1.925 (8)

Cs5—F5^{ix}	3.236 (9)	Sb4—F6	1.937 (8)
Cs6—F2v^{iii}	3.162 (9)	S1—O10	1.428 (12)
Cs1—O7^{ii}	3.273 (12)	S1—O11	1.470 (12)
Cs1—O9^{i}	3.353 (14)	S2—O5	1.484 (11)
Cs2—O1^{iii}	3.514 (14)	S2—O6	1.428 (12)
Cs2—O2	3.111 (11)	S3—O12	1.487 (11)
Cs3—O1^{vi}	3.321 (12)	F8—Cs1^{ii}	3.164 (11)
Cs3—O4^{i}	3.087 (12)	F9—Cs2^{i}	3.442 (11)
Cs4—O1^{vi}	3.130 (11)	F10—Cs5^{iv}	3.179 (11)
Cs4—O3^{vii}	3.217 (12)	F11—Cs3^{iv}	3.191 (11)
Cs5—O5^{ix}	3.256 (12)	F12—Cs5^{iv}	3.051 (9)
Cs5—O6^{ix}	3.705 (14)	O1—Cs2^{iii}	3.514 (13)
Cs6—O1^{i}	3.317 (15)	O4—Cs4^{iv}	3.373 (14)
F5—Cs1—F2^{ii}	109.3 (2)	F2—Sb2—F8	84.3 (4)
F8—Cs1—F2^{ii}	118.4 (2)	F2—Sb2—O7	73.3 (4)
F11^{i}—Cs1—F2^{ii}	174.1 (2)	O5—Sb1—O12	110.2 (4)
F4^{iii}—Cs2—F1	122.0 (2)	O11—Sb2—O7	109.1 (4)
F5—Cs1—O6^{ii}	161.5 (3)	O3—S1—O11	110.1 (7)
F8—Cs1—O5	65.3 (3)	O4—S1—O11	109.4 (7)
F8—Cs1—O9^{i}	112.6 (3)	O10—S1—O4	110.3 (8)
F11^{i}—Cs1—O5	81.7 (3)	O5—S2—O7	108.5 (7)
F11^{i}—Cs1—O6^{ii}	85.3 (3)	O6—S2—O5	109.7 (7)
F1—Cs2—O1^{iii}	155.2 (3)	Cs2—F1—Cs4^{iv}	90.4 (2)
F4—Cs2—O10^{v}	111.1 (3)	Cs4^{vii}—F9—Cs2^{i}	139.2 (3)
F6^{iv}—Cs2—O1^{iii}	144.1 (3)	Cs5^{iv}—F10—Cs6^{iv}	89.0 (3)
F2^{i}—Cs3—O12^{vi}	104.0 (3)	Cs2—O3—Cs4^{vii}	81.3 (3)
F11^{i}—Cs3—O1^{vi}	107.4 (3)	Cs3^{xi}—O1—Cs2^{iii}	123.8 (4)
O5—Cs1—F2^{ii}	102.9 (3)	Cs4^{xi}—O1—Cs6^{iv}	80.4 (3)
O6^{i}—Cs1—F2^{ii}	91.6 (3)	Cs6^{iv}—O1—Cs2^{iii}	123.0 (4)
O7^{ii}—Cs1—F2^{ii}	46.0 (2)	Sb1—F5—Cs1	122.5 (4)

O9^{i}—Cs1—F2^{ii}	125.7 (2)	Sb2—F2—Cs1^{ii}	98.3 (3)
O2—Cs2—F1	59.4 (3)	Sb3—F1—Cs2	113.9 (4)
O2—Cs2—F6^{iii}	104.3 (3)	Sb4—F4—Cs2^{iii}	110.8 (4)
O4^{i}—Cs4—F4^{vii}	125.8 (2)	S1—O3—Cs2	139.0 (7)
O10^{i}—Cs4—F1^{i}	85.2 (3)	S2—O5—Cs1	133.7 (6)
O8—Cs6—F9^{x}	103.9 (3)	S3—O1—Cs6^{iv}	98.1 (7)
O11v^{iii}—Cs6—O2^{i}	135.2 (3)	Sb2—O11—Cs4	99.0 (4)
F11^{i}—Cs1—S2^{i}	64.23 (18)	Sb4—O8—Cs6	99.7 (4)
F9^{iv}—Cs2—S3^{iii}	125.07 (17)	S1—O11—Sb2	125.7 (7)
O3—Cs2—S3^{iii}	109.9 (2)	S3—O8—Sb4	129.5 (8)
F12—Sb1—F5	85.7 (4)		

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

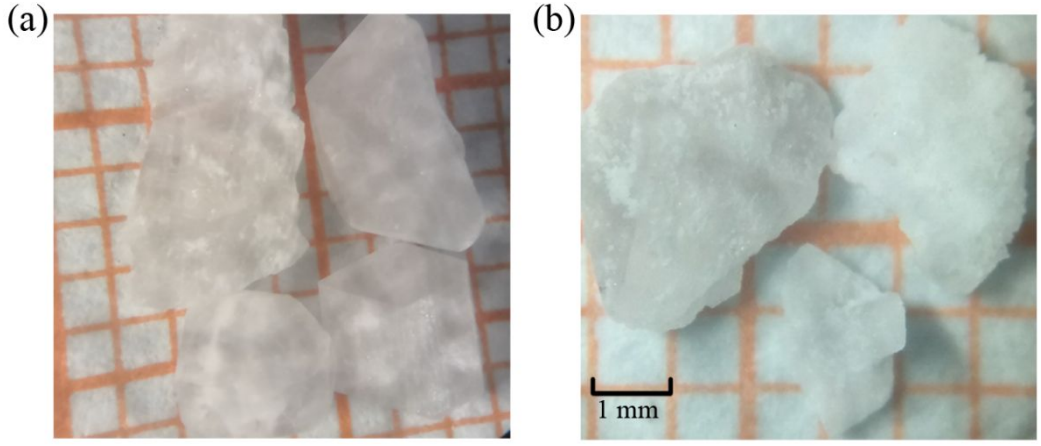

Figure S1. The crystal photographs of $Rb_6Sb_4F_{12}(SO_4)_3$ (a), $Cs_6Sb_4F_{12}(SO_4)_3$ (b).

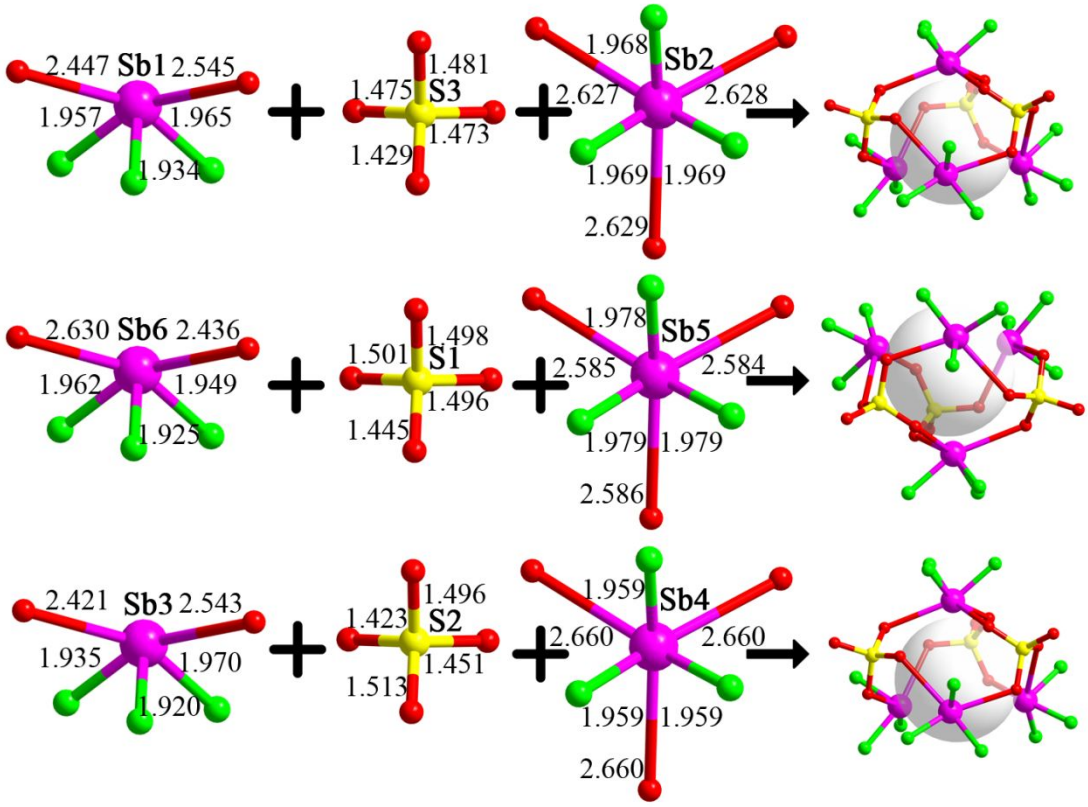

Figure S2. The bond lengths of $[SbF_3O_3]^{6-}$, $[SbF_3O_2]^{4-}$ and $[SO_4]^{2-}$ polyhedra in $Rb_6Sb_4F_{12}(SO_4)_3$.

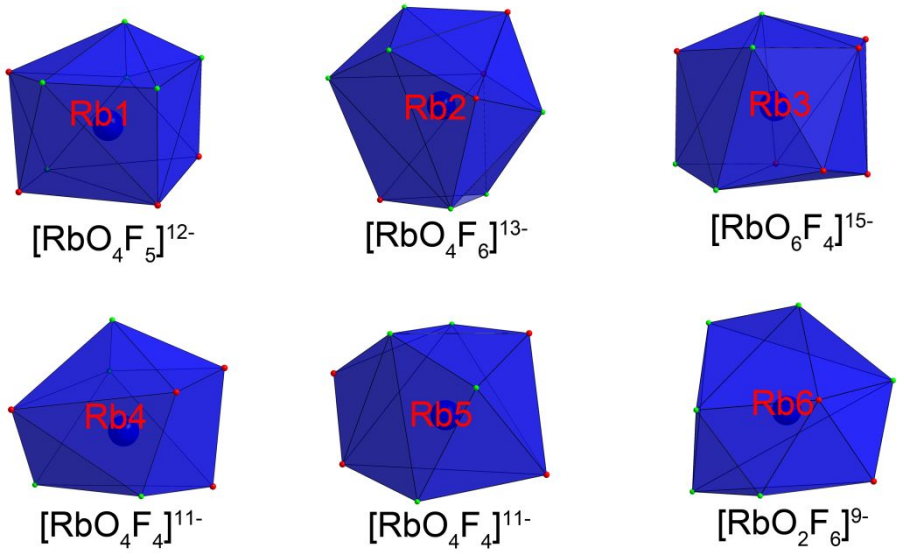

Figure S3. The coordination mode of Rb^+ cations in $Rb_6Sb_4F_{12}(SO_4)_3$.

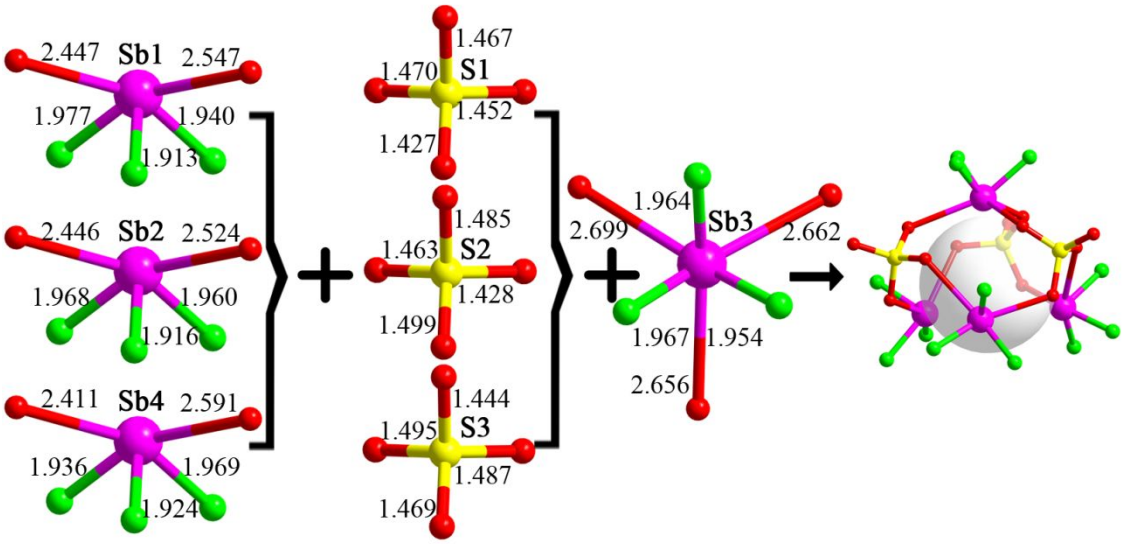

Figure S4. The bond lengths of $[SbF_3O_3]^{6-}$, $[SbF_3O_2]^{4-}$ and $[SO_4]^{2-}$ polyhedra in $Cs_6Sb_4F_{12}(SO_4)_3$.

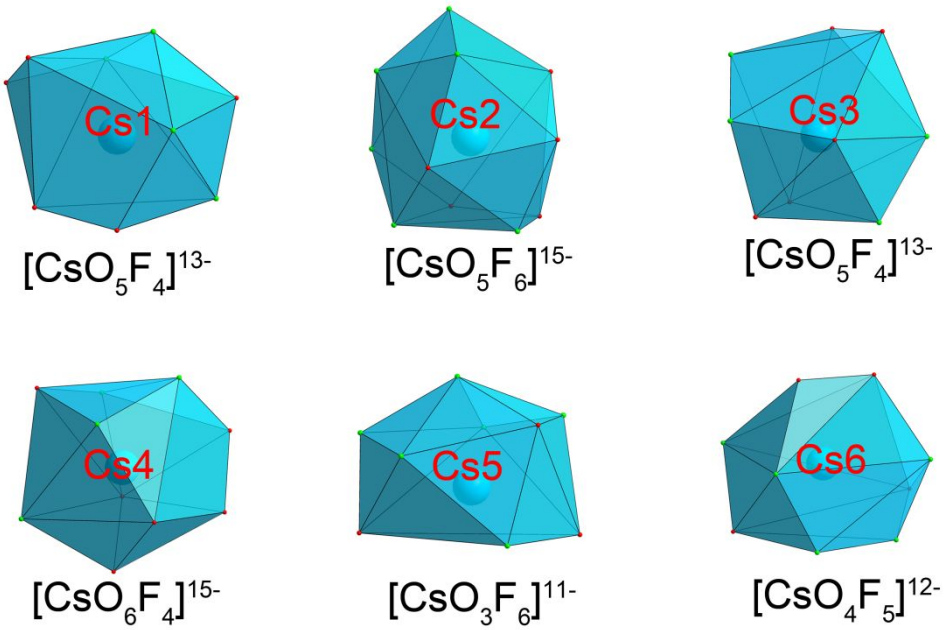

Figure S5. The coordination mode of Cs^+ cations in $Cs_6Sb_4F_{12}(SO_4)_3$.

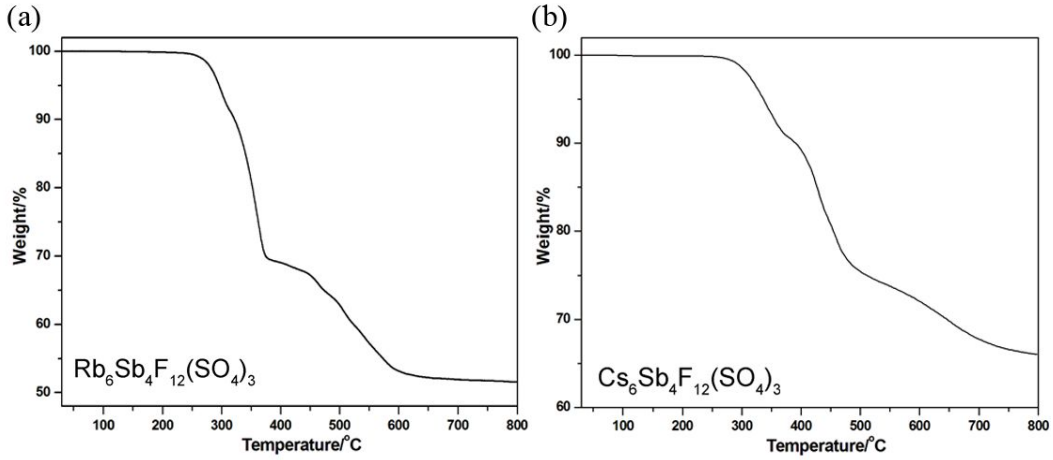

Figure S6. TGA curves for compounds $A_6Sb_4F_{12}(SO_4)_3$ (A = Rb , Cs) under N_2 atmosphere.

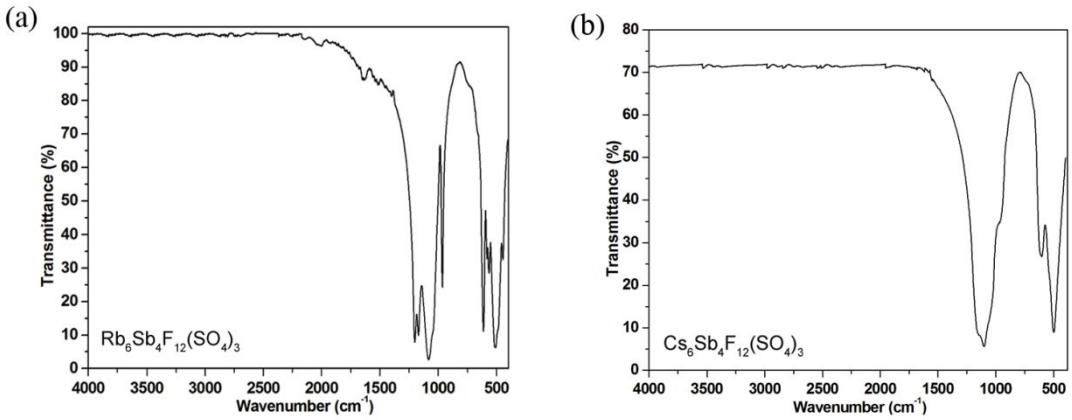

Figure S7. The IR spectra for compounds $A_6Sb_4F_{12}(SO_4)_3$ (A = Rb, Cs).

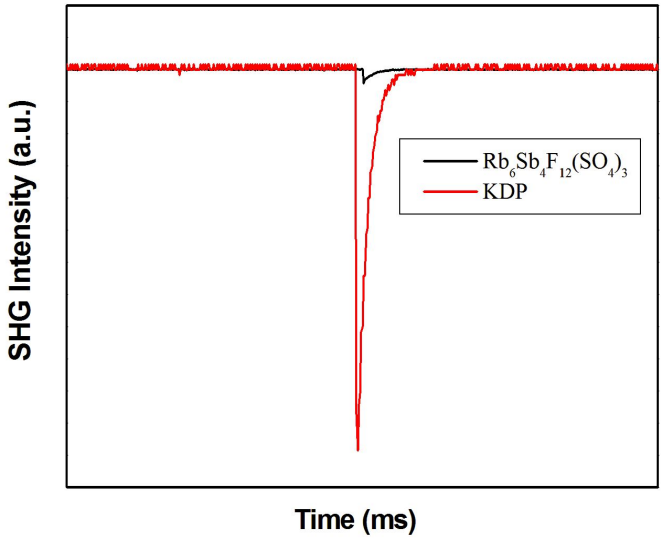

Figure S8. The SHG intensities for $Rb_6Sb_4F_{12}(SO_4)_3$ with KDP as a reference.

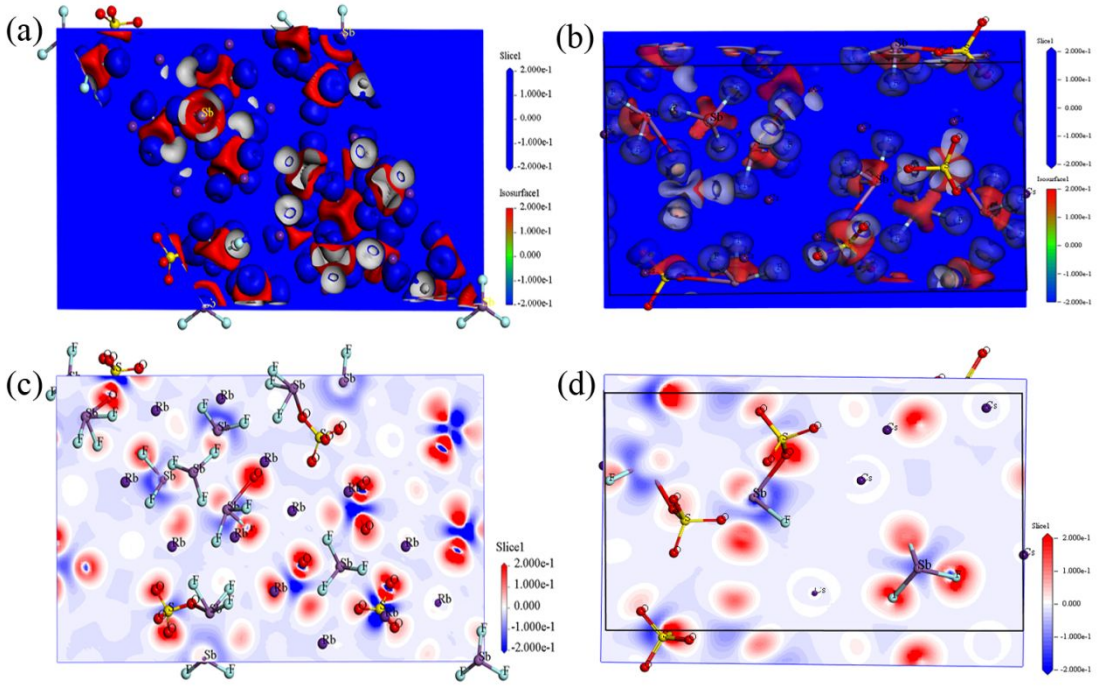

Figure S9. The plot of electronic density difference for $Rb_6Sb_4F_{12}(SO_4)_3$ (a), (c) and $Cs_6Sb_4F_{12}(SO_4)_3$ (b), (d).

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