$A_2Bi_2(SeO_3)_3F_2$ (A = K and Rb): Excellent Mid-infrared Nonlinear Optical Materials with both Strong SHG Responses and Large Band Gaps

Shuangshuang Shi, [†,‡] Chensheng Lin, [†] Guangsai Yang, [†,§] Liling Cao, [†,‡] Bingxuan Li, [†] Tao Yan, [†] Min Luo, [*,†] Ning Ye[*,†]

[†] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[‡] University of the Chinese Academy of Sciences, Beijing 100049, China

[§] Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, North Wollongong NSW2500, Australia

E-mail: nye@fjirsm.ac.cn

E-mail: lm8901@fjirsm.ac.cn

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Table S1. Crystal Data and Structure Refinement for $A_2Bi_2(SeO_3)_3F_2$ (A= K, Rb).

Formula	$K_2Bi_2(SeO_3)_3F_2$	$Rb_2Bi_2(SeO_3)_3F_2$
Fw	915.04	1007.78
Temperature (K)	293(2)	293(2)
Crystal System	Monoclinic	Monoclinic
Space Group	*Cm*	*Cm*
a (Å)	12.8396(5)	13.096(10)
b (Å)	5.8831(3)	5.955(4)
c (Å)	7.6506(3)	7.727(6)
β (deg)	93.076(3)	92.877(12)
V(Å^3)	577.07(4)	601.8(7)
Z	2	2
Dc (Mg/m^3)	5.266	5.562
λ (Å)	0.71073	0.71073
F (000)	792	864
μ (mm^{-1})	40.697	46.369
R/*wR* (*I*>2*σ* (*I*)) [a]	0.0449/ 0.1132	0.0328/ 0.0605
R/*wR* (all data) [a]	0.0450/ 0.1134	0.0354/ 0.0617
GOF on F^2	1.019	1.025
Absolute Structure Parameter	0.04(2)	0.00

[a] $R(F) = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. $wR(Fo^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

Table S2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (Å^2×10^3) and BVS for $K_2Bi_2(SeO_3)_3F_2$.

Atom	x	y	z	U(eq)	BVS
Bi(1)	5460(1)	0	5223(1)	9(1)	3.02
Bi(2)	9497(1)	0	-1347(1)	9(1)	2.93
Se(3)	8486(3)	-5000	1468(5)	13(1)	4.02
K(1)	2406(7)	0	6996(14)	14(2)	1.15
K(2)	6599(7)	0	403(11)	15(2)	0.94
Se(1)	5525(2)	-5000	2950(5)	11(1)	4.20
Se(2)	8169(3)	0	-5189(5)	11(1)	4.27
F(1)	10684(11)	-2450(30)	-2209(18)	19(3)	1.08
O(1)	8473(13)	-2730(30)	80(20)	25(4)	2.01
O(2)	6272(14)	-2880(30)	3770(20)	15(3)	2.15
O(3)	8904(14)	2180(30)	-4380(20)	19(3)	1.97
O(4)	7233(18)	0	-3770(30)	14(4)	2.16
O(5)	9749(19)	-5000	2250(30)	17(5)	1.78
O(6)	5810(16)	-5000	790(30)	10(5)	2.03

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths [Å] and angles [deg] for $K_2Bi_2(SeO_3)_3F_2$.

Bi(1)-O(2)	2.310(16)	F(1)#4-Bi(1)-O(3)#6	110.4(5)
Bi(1)-O(2)#1	2.310(16)	F(1)#5-Bi(1)-O(3)#6	65.4(5)
Bi(1)-O(4)#2	2.36(2)	O(2)-Bi(1)-O(3)#7	152.3(6)
Bi(1)-O(5)#3	2.40(3)	O(2)#1-Bi(1)-O(3)#7	87.6(5)
Bi(1)-F(1)#4	2.475(14)	O(4)#2-Bi(1)-O(3)#7	133.5(4)
Bi(1)-F(1)#5	2.475(14)	O(5)#3-Bi(1)-O(3)#7	81.7(6)
Bi(1)-O(3)#6	2.626(17)	F(1)#4-Bi(1)-O(3)#7	65.4(5)
Bi(1)-O(3)#7	2.626(17)	F(1)#5-Bi(1)-O(3)#7	110.4(5)
Bi(2)-F(1)	2.225(15)	O(3)#6-Bi(1)-O(3)#7	78.3(7)
Bi(2)-F(1)#1	2.225(15)	F(1)-Bi(2)-F(1)#1	80.9(8)
Bi(2)-O(6)#8	2.29(2)	F(1)-Bi(2)-O(6)#8	73.8(5)
Bi(2)-O(1)#1	2.378(15)	F(1)#1-Bi(2)-O(6)#8	73.8(5)
Bi(2)-O(1)	2.378(15)	F(1)-Bi(2)-O(1)#1	168.3(5)
Bi(2)-O(3)#1	2.727(17)	F(1)#1-Bi(2)-O(1)#1	95.8(6)
Bi(2)-O(3)	2.727(17)	O(6)#8-Bi(2)-O(1)#1	94.4(5)
Se(3)-O(5)	1.70(3)	F(1)-Bi(2)-O(1)	95.8(6)
Se(3)-O(1)#13	1.706(16)	F(1)#1-Bi(2)-O(1)	168.3(5)
Se(3)-O(1)	1.706(16)	O(6)#8-Bi(2)-O(1)	94.4(5)
Se(1)-O(2)	1.671(16)	O(1)#1-Bi(2)-O(1)	85.1(9)
Se(1)-O(2)#13	1.671(16)	F(1)-Bi(2)-O(3)#1	66.8(5)
Se(1)-O(6)	1.71(2)	F(1)#1-Bi(2)-O(3)#1	102.6(5)
Se(2)-O(4)	1.66(2)	O(6)#8-Bi(2)-O(3)#1	140.5(5)
Se(2)-O(3)	1.690(17)	O(1)#1-Bi(2)-O(3)#1	124.9(6)
Se(2)-O(3)#1	1.690(17)	O(1)-Bi(2)-O(3)#1	86.3(5)
F(1)-Bi(1)#11	2.475(14)	F(1)-Bi(2)-O(3)	102.6(5)
O(3)-Bi(1)#12	2.626(17)	F(1)#1-Bi(2)-O(3)	66.8(5)
O(4)-Bi(1)#19	2.36(2)	O(6)#8-Bi(2)-O(3)	140.5(5)
O(5)-Bi(1)#9	2.40(3)	O(1)#1-Bi(2)-O(3)	86.3(5)
O(6)-Bi(2)#20	2.29(2)	O(1)-Bi(2)-O(3)	124.9(6)
O(2)-Bi(1)-O(2)#1	94.6(8)	O(3)#1-Bi(2)-O(3)	56.2(7)
O(2)-Bi(1)-O(4)#2	72.8(5)	O(5)-Se(3)-O(1)#13	101.4(7)
O(2)#1-Bi(1)-O(4)#2	72.8(5)	O(5)-Se(3)-O(1)	101.4(7)
O(2)-Bi(1)-O(5)#3	72.6(6)	O(1)#13-Se(3)-O(1)	102.8(12)

O(2)#1-Bi(1)-O(5)#3	72.6(6)	O(2)-Se(1)-O(2)#13	96.2(12)
O(4)#2-Bi(1)-O(5)#3	128.2(7)	O(2)-Se(1)-O(6)	102.2(8)
O(2)-Bi(1)-F(1)#4	142.3(5)	O(2)#13-Se(1)-O(6)	102.2(8)
O(2)#1-Bi(1)-F(1)#4	84.4(5)	O(4)-Se(2)-O(3)	99.8(8)
O(4)#2-Bi(1)-F(1)#4	70.9(5)	O(4)-Se(2)-O(3)#1	99.8(8)
O(5)#3-Bi(1)-F(1)#4	140.6(4)	O(3)-Se(2)-O(3)#1	98.9(11)
O(2)-Bi(1)-F(1)#5	84.4(5)	Bi(2)-F(1)-Bi(1)#11	125.1(6)
O(2)#1-Bi(1)-F(1)#5	142.3(5)	Se(3)-O(1)-Bi(2)	145.8(9)
O(4)#2-Bi(1)-F(1)#5	70.9(5)	Se(1)-O(2)-Bi(1)	117.5(9)
O(5)#3-Bi(1)-F(1)#5	140.6(4)	Se(2)-O(3)-Bi(1)#12	148.3(9)
F(1)#4-Bi(1)-F(1)#5	74.5(7)	Se(2)-O(3)-Bi(2)	94.5(7)
O(2)-Bi(1)-O(3)#6	87.6(5)	Bi(1)#12-O(3)-Bi(2)	102.4(6)
O(2)#1-Bi(1)-O(3)#6	152.3(6)	Se(2)-O(4)-Bi(1)#19	120.3(12)
O(4)#2-Bi(1)-O(3)#6	133.5(4)	Se(3)-O(5)-Bi(1)#9	129.9(12)
O(5)#3-Bi(1)-O(3)#6	81.7(6)	Se(1)-O(6)-Bi(2)#20	120.2(11)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z; **#2** x,y,z+1; **#3** x-1/2,y+1/2,z; **#4** x-1/2,y+1/2,z+1;
#5 x-1/2,-y-1/2,z+1; **#6** x-1/2,y-1/2,z+1; **#7** x-1/2,-y+1/2,z+1; **#8** x+1/2,y+1/2,z; **#9** x+1/2,y-1/2,z;
#11 x+1/2,y-1/2,z-1; **#12** x+1/2,y+1/2,z-1; **#13** x,-y-1,z;
#19 x,y,z-1; **#20** x-1/2,y-1/2,z.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $K_2Bi_2(SeO_3)_3F_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^* b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
Bi(1)	6(1)	11(1)	9(1)	0	4(1)	0
Bi(2)	4(1)	14(1)	9(1)	0	3(1)	0
Se(3)	6(1)	19(2)	13(2)	0	1(1)	0
K(1)	7(4)	14(3)	21(4)	0	4(3)	0
K(2)	10(4)	18(4)	19(5)	0	6(3)	0
Se(1)	8(2)	15(2)	10(2)	0	2(1)	0
Se(2)	7(2)	16(2)	12(2)	0	1(1)	0
F(1)	11(5)	33(7)	12(6)	-4(5)	-3(5)	5(6)
O(1)	16(9)	26(9)	33(10)	13(8)	3(8)	-9(8)
O(4)	10(10)	24(12)	9(10)	0	1(9)	0
O(6)	10(5)	10(5)	10(5)	0	1(2)	0

Table S5. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $Rb_2Bi_2(SeO_3)_3F_2$.

	x	y	z	U(eq)	BVS
Bi(1)	1210(1)	0	4637(1)	12(1)	2.99
Bi(2)	5270(1)	0	-1891(1)	10(1)	2.82
Rb(1)	3140(2)	-5000	6472(3)	16(1)	1.35
Se(1)	3947(1)	0	4248(2)	11(1)	4.02
Se(2)	-720(2)	0	960(2)	10(1)	4.33
Rb(2)	2379(1)	0	-117(2)	16(1)	1.09
Se(3)	6259(1)	0	2397(2)	10(1)	4.07
O(1)	6991(7)	2151(16)	3212(11)	11(2)	2.11
F(1)	6388(6)	-2442(13)	7232(11)	18(2)	1.16
O(2)	4675(7)	2154(17)	5051(13)	27(3)	1.92
O(3)	478(10)	0	1795(16)	28(4)	2.12
O(4)	-712(7)	-2217(17)	-384(13)	23(3)	2.06
O(5)	2975(9)	0	5653(15)	12(3)	1.96
O(6)	6542(9)	0	285(15)	13(3)	2.10

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S6. Selected bond lengths [Å] and angles [deg] for $Rb_2Bi_2(SeO_3)_3F_2$.

Bi(1)-O(1)#1	2.291(9)	O(1)#2-Bi(1)-F(1)#4	143.5(3)
Bi(1)-O(1)#2	2.291(9)	O(3)-Bi(1)-F(1)#4	139.5(2)
Bi(1)-O(3)	2.351(12)	O(5)-Bi(1)-F(1)#4	72.0(3)
Bi(1)-O(5)	2.404(11)	F(1)#3-Bi(1)-F(1)#4	74.4(4)
Bi(1)-F(1)#3	2.520(8)	O(1)#1-Bi(1)-O(2)#1	86.8(3)
Bi(1)-F(1)#4	2.520(8)	O(1)#2-Bi(1)-O(2)#1	152.6(3)
Bi(1)-O(2)#1	2.660(10)	O(3)-Bi(1)-O(2)#1	80.6(3)
Bi(1)-O(2)#2	2.660(10)	O(5)-Bi(1)-O(2)#1	132.9(3)
Bi(2)-F(1)#7	2.196(8)	F(1)#3-Bi(1)-O(2)#1	109.3(3)
Bi(2)-F(1)#8	2.196(8)	F(1)#4-Bi(1)-O(2)#1	63.9(3)
Bi(2)-O(6)	2.307(12)	O(1)#1-Bi(1)-O(2)#2	152.6(3)
Bi(2)-O(4)#9	2.429(11)	O(1)#2-Bi(1)-O(2)#2	86.8(3)
Bi(2)-O(4)#10	2.429(11)	O(3)-Bi(1)-O(2)#2	80.6(3)
Se(1)-O(2)	1.697(9)	O(5)-Bi(1)-O(2)#2	132.9(3)
Se(1)-O(2)#14	1.697(9)	F(1)#3-Bi(1)-O(2)#2	63.9(3)
Se(1)-O(5)	1.714(12)	F(1)#4-Bi(1)-O(2)#2	109.3(3)
Se(2)-O(3)	1.667(13)	O(2)#1-Bi(1)-O(2)#2	79.1(4)
Se(2)-O(4)	1.680(10)	F(1)#7-Bi(2)-F(1)#8	83.0(4)
Se(2)-O(4)#14	1.680(10)	F(1)#7-Bi(2)-O(6)	75.9(3)
Se(3)-O(6)	1.692(12)	F(1)#8-Bi(2)-O(6)	75.9(3)
Se(3)-O(1)	1.702(9)	F(1)#7-Bi(2)-O(4)#9	167.7(3)
Se(3)-O(1)#14	1.702(9)	F(1)#8-Bi(2)-O(4)#9	94.2(3)
O(1)-Bi(1)#10	2.291(9)	O(6)-Bi(2)-O(4)#9	91.8(3)
F(1)-Bi(2)#6	2.196(8)	F(1)#7-Bi(2)-O(4)#10	94.2(3)
F(1)-Bi(1)#13	2.520(8)	F(1)#8-Bi(2)-O(4)#10	167.7(3)
O(2)-Bi(1)#10	2.660(10)	O(6)-Bi(2)-O(4)#10	91.8(3)
O(4)-Bi(2)#1	2.429(11)	O(4)#9-Bi(2)-O(4)#10	86.0(5)
O(1)#1-Bi(1)-O(1)#2	95.5(5)	O(2)-Se(1)-O(2)#14	98.2(7)
O(1)#1-Bi(1)-O(3)	73.9(3)	O(2)-Se(1)-O(5)	100.9(4)
O(1)#2-Bi(1)-O(3)	73.9(3)	O(2)#14-Se(1)-O(5)	100.9(4)
O(1)#1-Bi(1)-O(5)	73.2(3)	O(3)-Se(2)-O(4)	101.8(4)
O(1)#2-Bi(1)-O(5)	73.2(3)	O(3)-Se(2)-O(4)#14	101.8(4)
O(3)-Bi(1)-O(5)	130.2(4)	O(4)-Se(2)-O(4)#14	103.6(7)
O(1)#1-Bi(1)-F(1)#3	143.5(3)	O(6)-Se(3)-O(1)	102.1(4)

O(1)#2-Bi(1)-F(1)#3	84.8(3)	O(6)-Se(3)-O(1)#14	102.1(4)
O(3)-Bi(1)-F(1)#3	139.5(2)	O(1)-Se(3)-O(1)#14	97.6(6)
O(5)-Bi(1)-F(1)#3	72.0(3)	Bi(2)#6-F(1)-Bi(1)#13	127.5(3)
O(1)#1-Bi(1)-F(1)#4	84.8(3)		

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,y-1/2,z; **#2** x-1/2,-y+1/2,z; **#3** x-1/2,y+1/2,z; **#4** x-1/2,-y-1/2,z; **#5** x,y+1,z; **#6** x,y,z+1; **#7** x,-y,z-1; **#8** x,y,z-1; **#9** x+1/2,-y-1/2,z; **#10** x+1/2,y+1/2,z; **#11** x+1/2,y+1/2,z-1; **#12** x,y+1,z-1; **#13** x+1/2,y-1/2,z; **#14** x,-y,z.

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2Bi_2(SeO_3)_3F_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^* b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
Bi(1)	14(1)	10(1)	10(1)	0	3(1)	0
Bi(2)	10(1)	10(1)	11(1)	0	1(1)	0
Rb(1)	14(1)	14(1)	21(1)	0	1(1)	0
Se(1)	10(1)	12(1)	10(1)	0	1(1)	0
Se(2)	9(1)	9(1)	13(1)	0	1(1)	0
Rb(2)	14(1)	16(1)	18(1)	0	2(1)	0
Se(3)	11(1)	9(1)	10(1)	0	0(1)	0
O(1)	11(3)	9(3)	12(3)	-2(2)	0(2)	1(2)
F(1)	19(4)	18(5)	15(4)	-5(3)	1(3)	2(4)
O(2)	19(5)	27(6)	35(6)	-17(6)	2(5)	-10(5)
O(3)	19(8)	51(11)	14(8)	0	-2(6)	0
O(4)	24(3)	22(3)	24(3)	-3(2)	1(2)	0(2)
O(5)	12(3)	12(3)	12(3)	0	1(2)	0
O(6)	14(7)	18(9)	7(6)	0	6(5)	0

Table S8. The calculated dipole moments of the Bi-O(F) polyhedra and the SeO_3 units for $A_2Bi_2(SeO_3)_3F_2$ (A = K, Rb) (D = Debyes).

Compound	Species	Dipole moment (D)			
		x	y	z	Total
$K_2Bi_2(SeO_3)_3F_2$	$Bi(1)O_6F_2$	-4.208	0	1.096	-4.349
	$Bi(2)O_5F_2$	-3.211	0	0.483	-3.247
	$2\times\sum_{Bi-O}$	-14.839	0	3.158	15.172
	$Se(1)O_3$	9.950	0	-1.327	10.039
	$Se(2)O_3$	2.247	0	10.561	10.798
	$Se(3)O_3$	6.211	0	-5.573	8.345
	$2\times\sum_{Se-O}$	36.816	0	7.321	37.537
$Rb_2Bi_2(SeO_3)_3F_2$	$Bi(1)O_6F_2$	-4.125	0	2.212	-4.680
	$Bi(2)O_5F_2$	-2.500	0	0.439	-2.538
	$2\times\sum_{Bi-O}$	-13.250	0	5.302	14.271
	$Se(1)O_3$	2.210	0	9.186	9.448
	$Se(2)O_3$	7.109	0	-5.934	9.259
	$Se(3)O_3$	9.148	0	-1.5754	9.282
	$2\times\sum_{Se-O}$	36.932	0	3.354	37.084

Table S9. SHG distribution of each element for $A_2Bi_2(SeO_3)_3F_2$ (A = K and Rb).

(%)	A	Bi	Se	O	F	SeO_3	$[BiO_xF_y]$
$K_2Bi_2(SeO_3)_3F_2$	0.85	18.46	19.03	56.54	5.12	47.30	49.29
$Rb_2Bi_2(SeO_3)_3F_2$	1.45	19.31	17.35	57.17	4.73	45.93	50.25

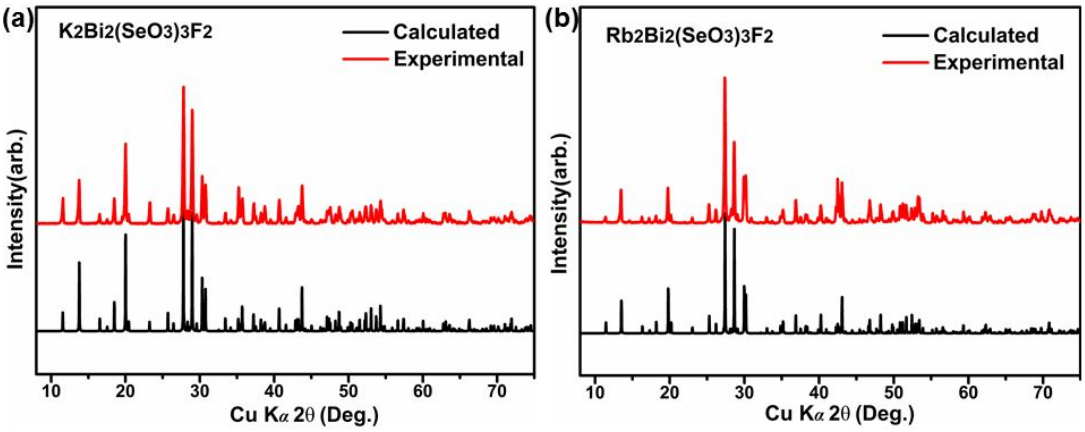

Figure S1. Calculated and experimental powder XRD patterns of $A_2Bi_2(SeO_3)_3F_2$ (A = K**(a)**, Rb**(b)**). The black curve is the calculated one, the red curve is the experimental one.

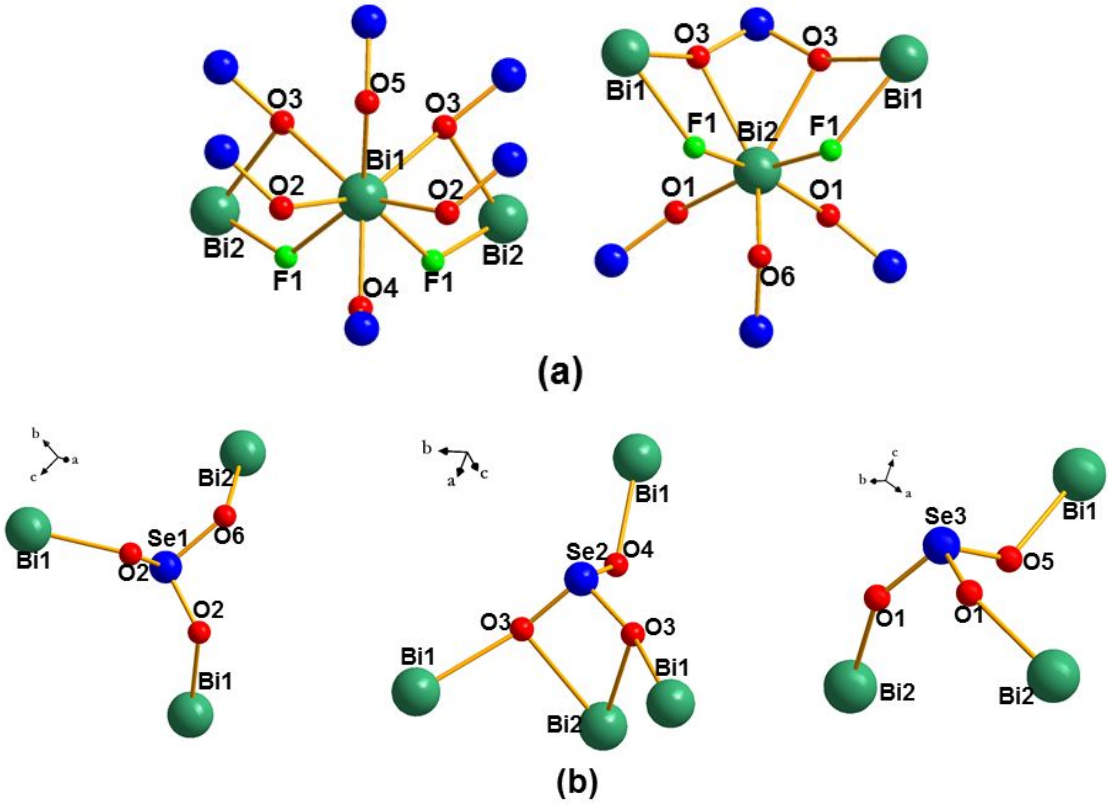

Figure S2. Views of the coordination environment of Bi atoms **(a)** and Se atoms **(b)** for $K_2Bi_2(SeO_3)_3F_2$.

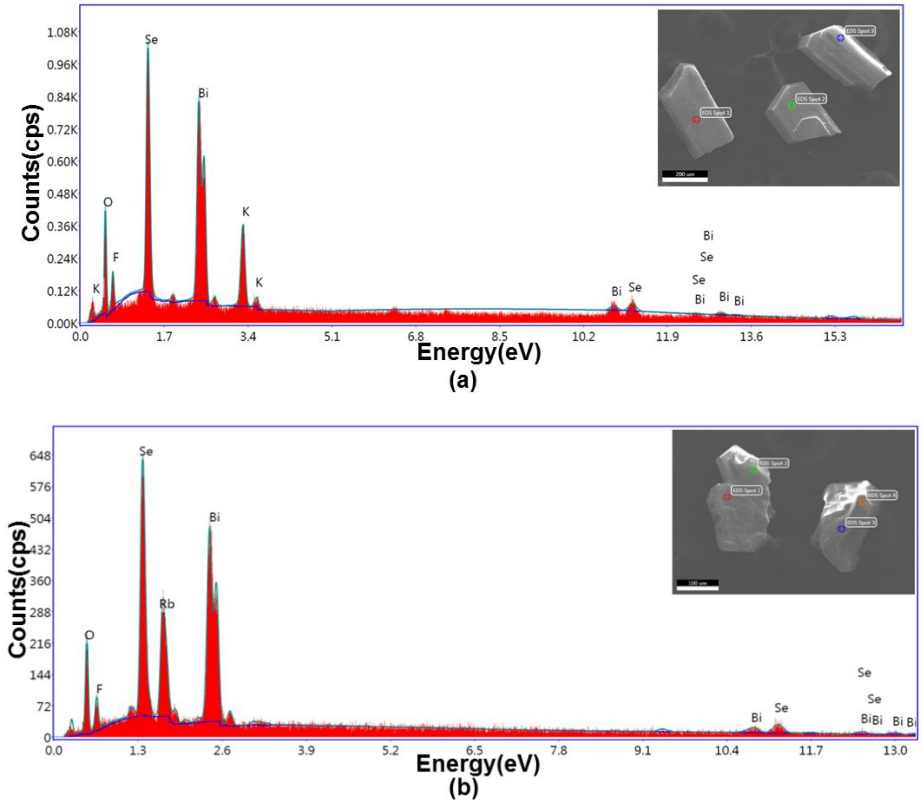

Figure S3. EDS analyses for $A_2Bi_2(SeO_3)_3F_2$ (A = K**(a)**, Rb**(b)**). The inset pictures are the tested crystals.

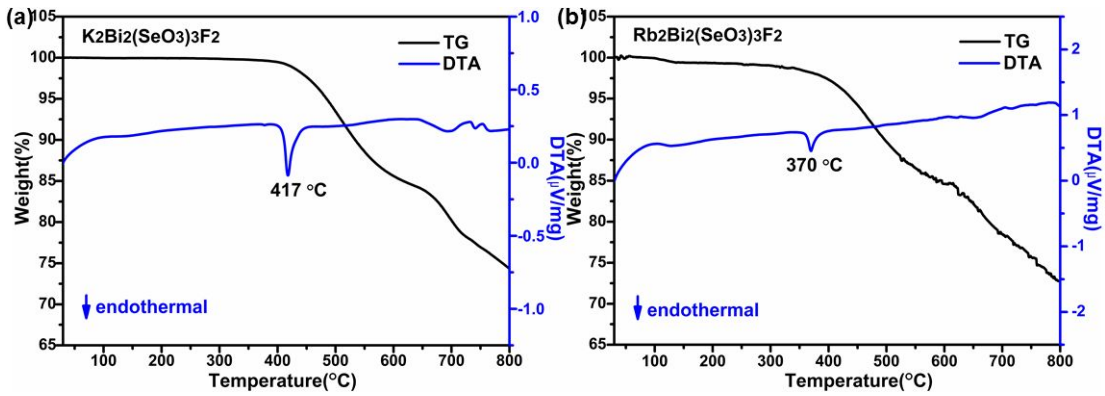

Figure S4. TG and DTA curves of $A_2Bi_2(SeO_3)_3F_2$ (A = K**(a)**, Rb**(b)**).

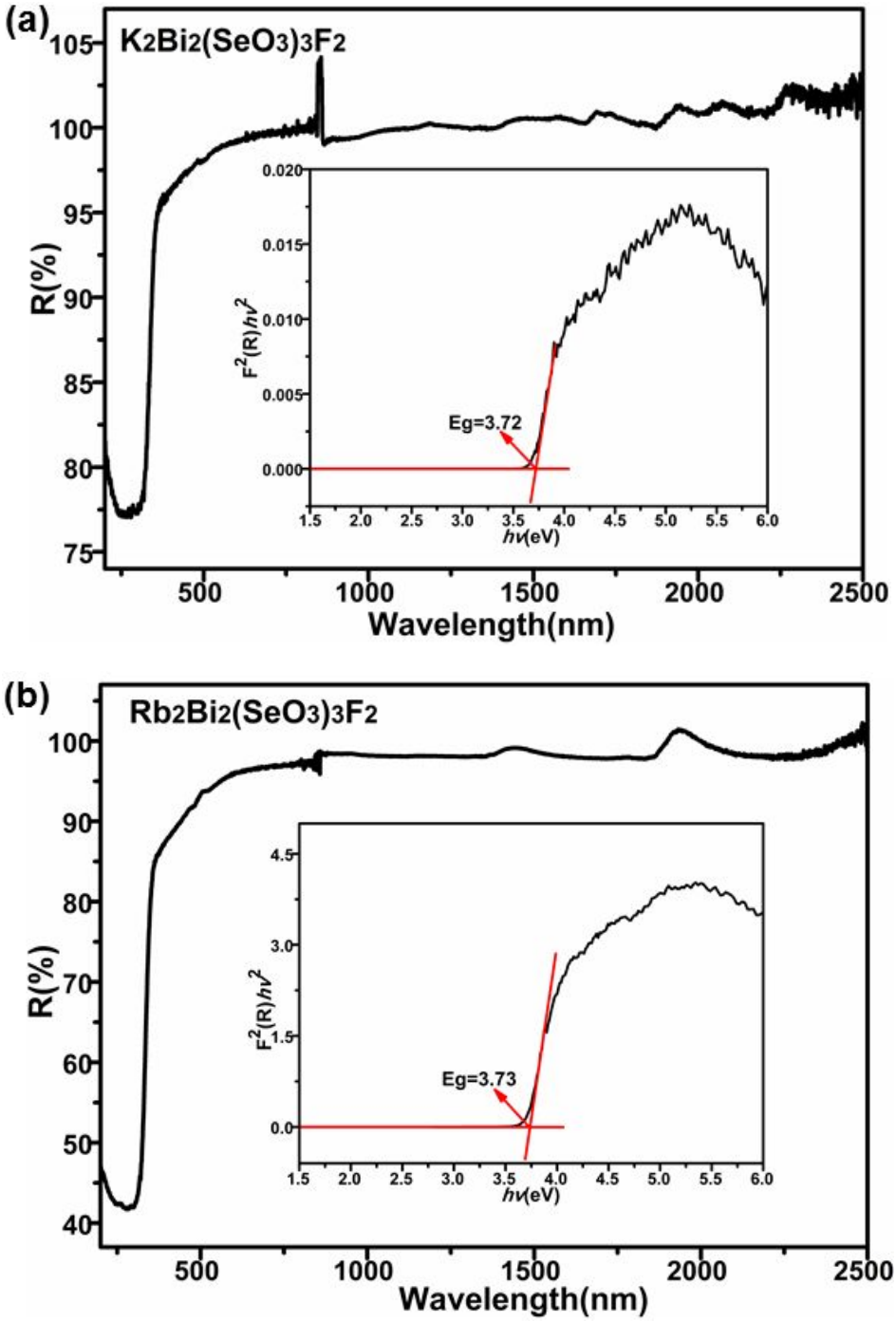

Figure S5. UV-Vis-NIR diffuse reflectance spectra of $A_2Bi_2(SeO_3)_3F_2$ (A = K**(a)**, Rb**(b)**).

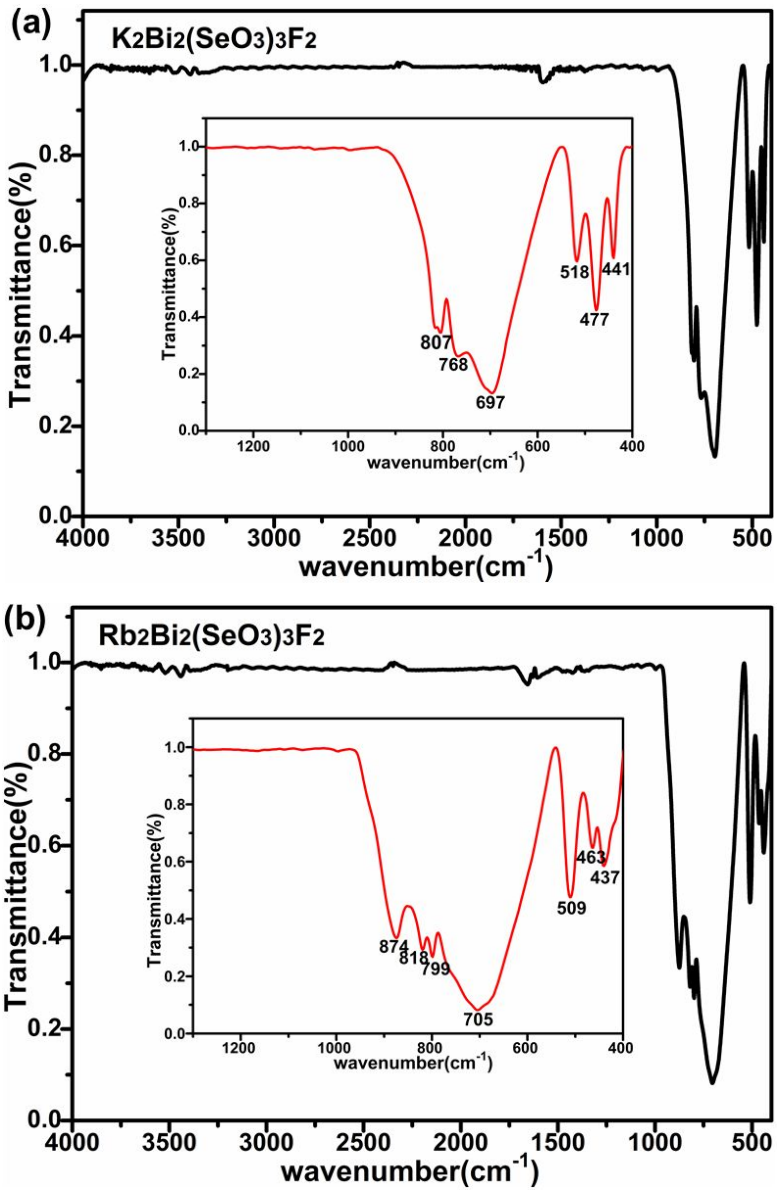

Figure S6. IR transmittance spectra of $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**) (KBr pellet)

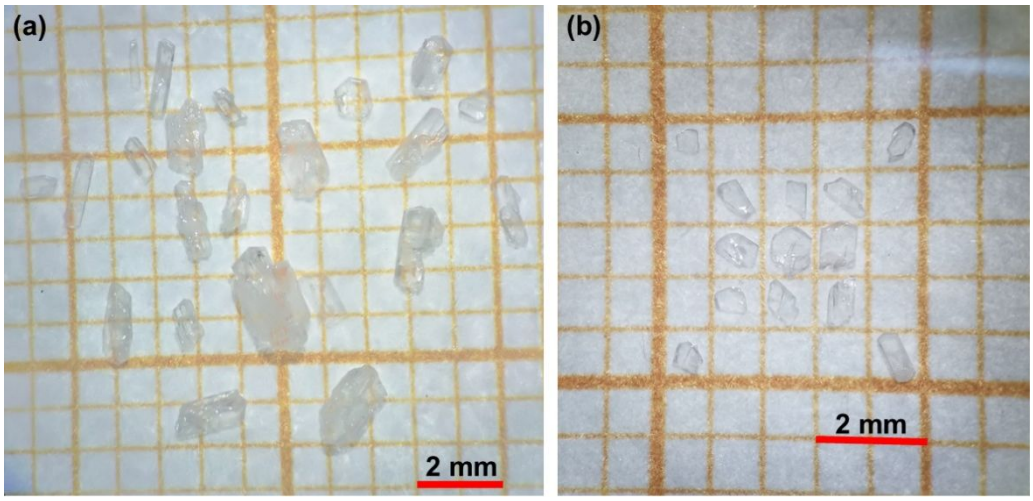

Figure S7. Bulk crystals' photographs of $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**).

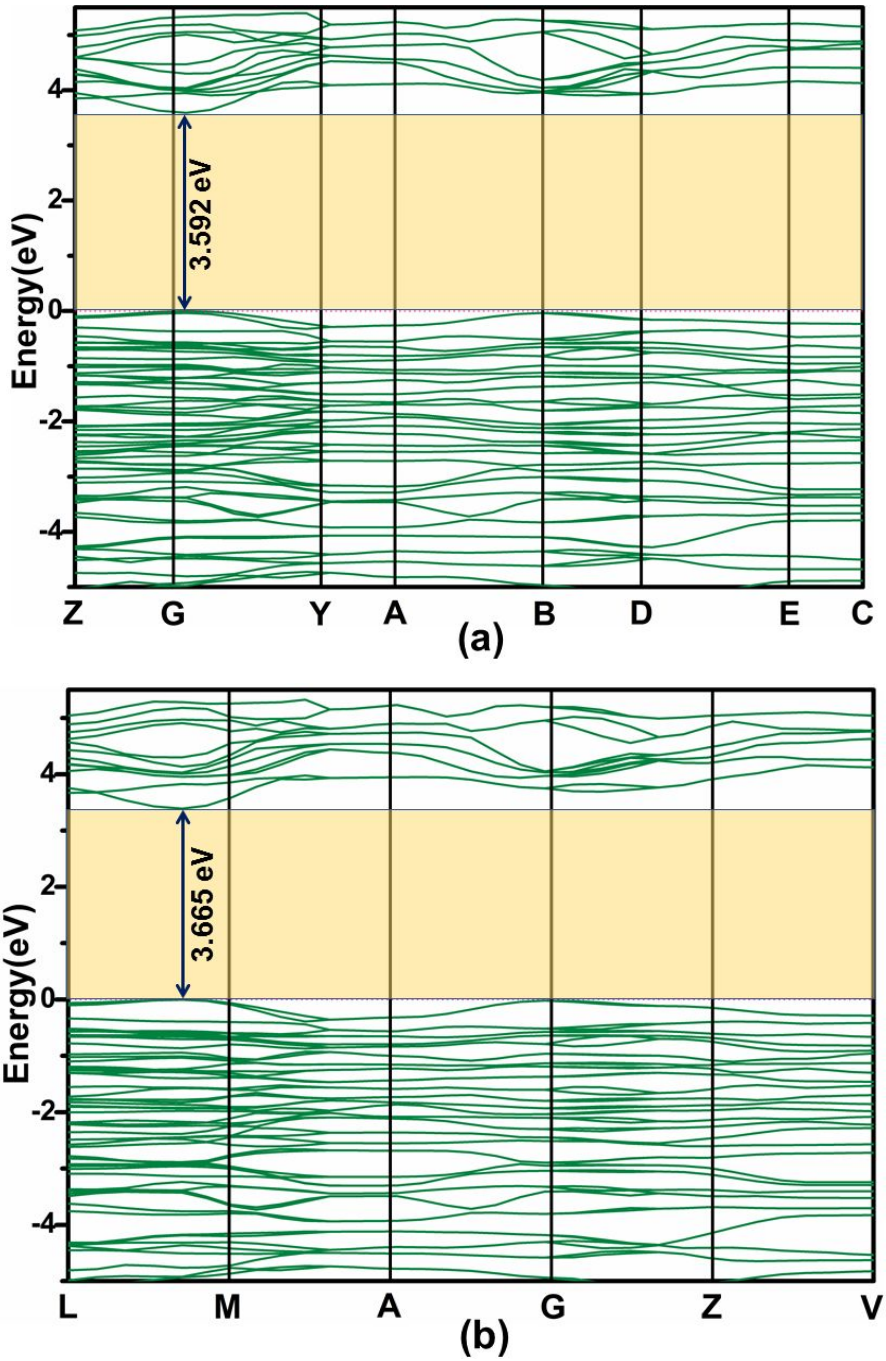

Figure S8. Calculated electronic band structures of $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**).

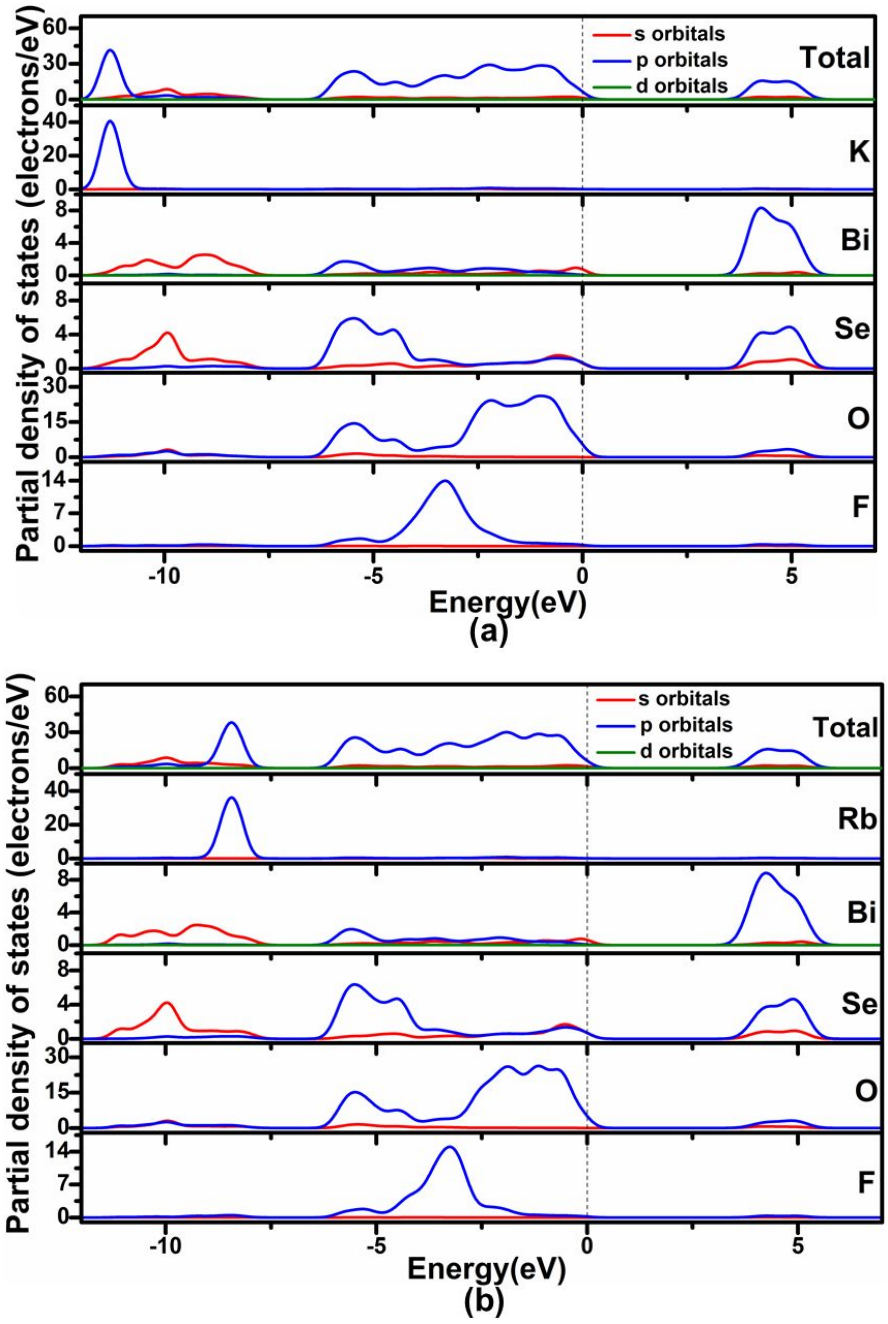

Figure S9. Partial density of states (PDOS) curves for $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**). The dashed vertical line is acted as a reference for all energy values (0 eV)

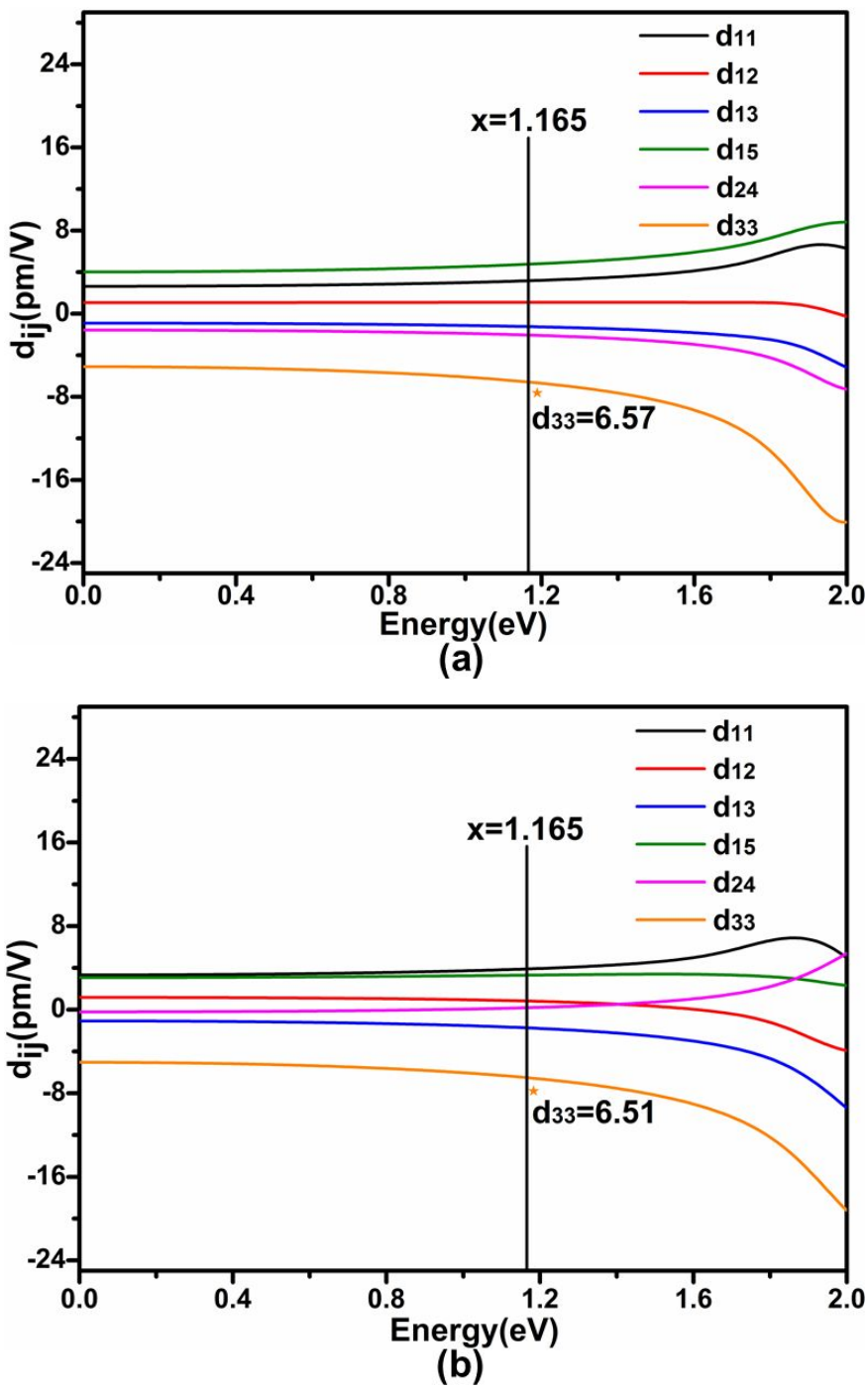

Figure S10. Calculated frequency-dependent SHG coefficients for $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**).

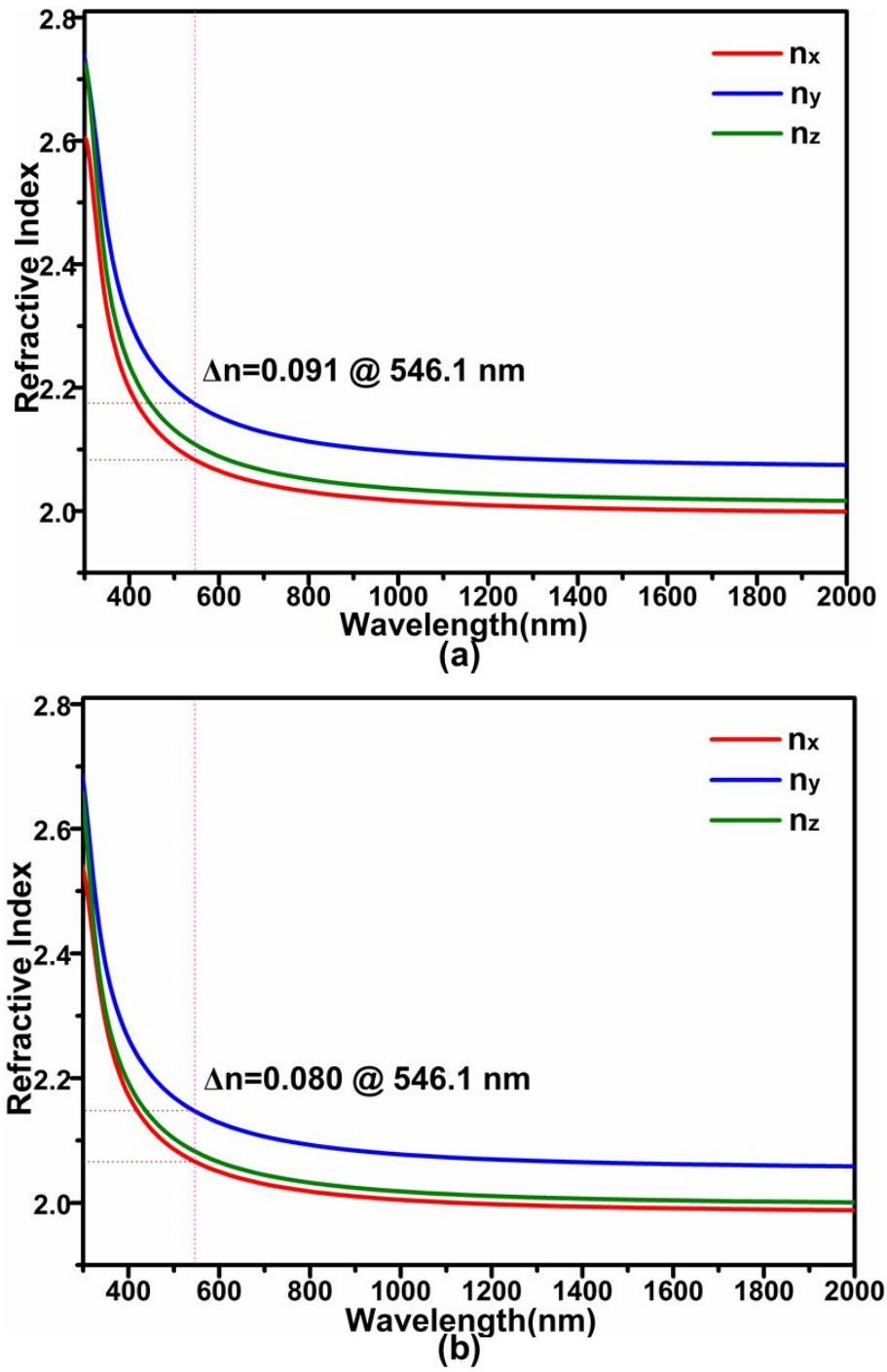

Figure S11. Dispersion curves of calculated refractive index of $A_2Bi_2(SeO_3)_3F_2$ (A= K**(a)**, Rb**(b)**).

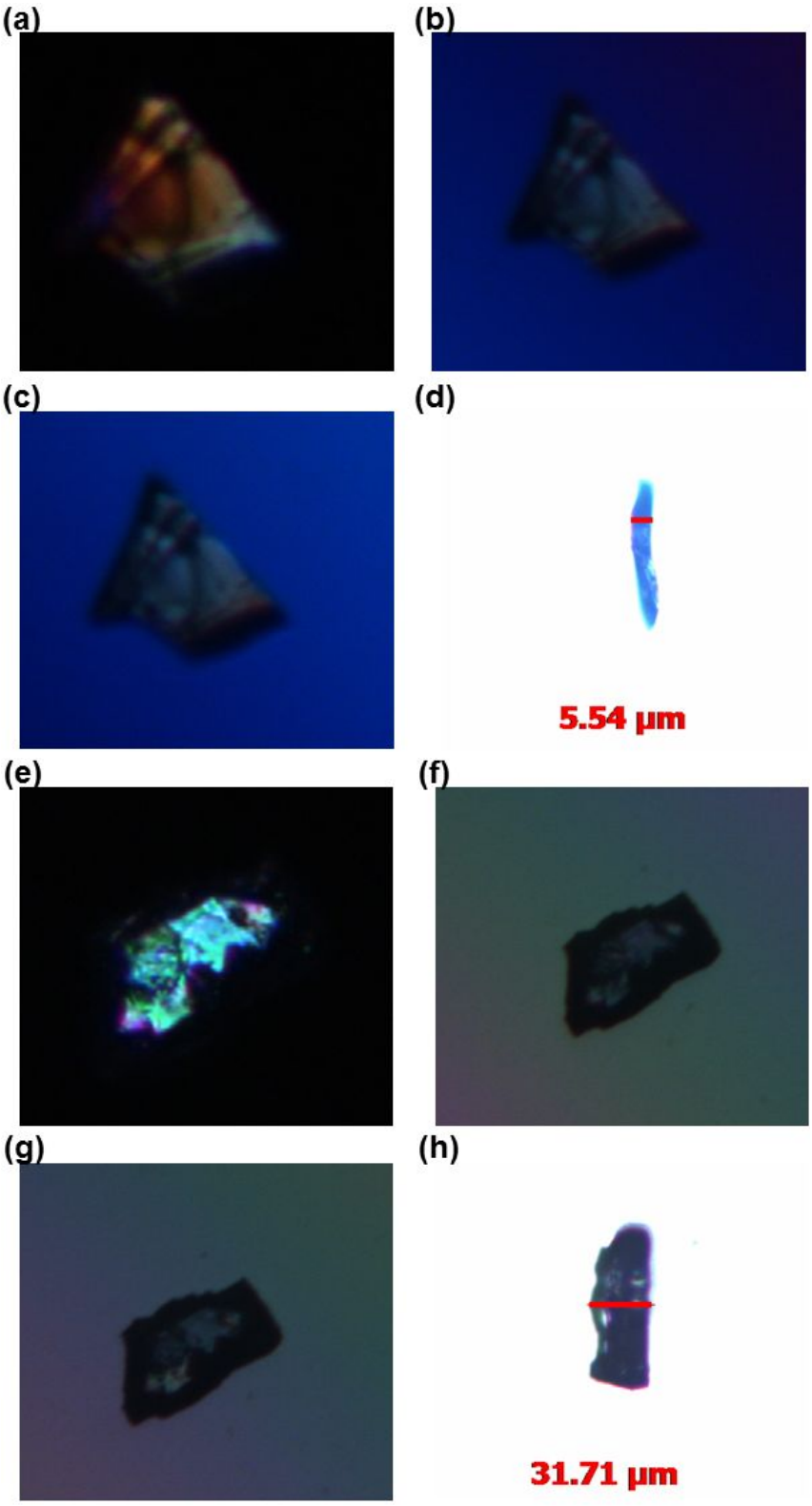

Figure S12. Photographs for measurements of birefringences **(a) (e)**, the positive **(b) (f)** and negative **(c) (g)** rotation of compensatory, the thickness of measured crystals **(d) (h)**, among which **(a-d)** are of $K_2Bi_2(SeO_3)_3F_2$ and **(e-h)** are of $Rb_2Bi_2(SeO_3)_3F_2$.