Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

$A_2Bi_2(SO_4)_2Cl_4$ (A = NH_4, K, Rb): Achieving Subtle Balance of Large Second Harmonic Generation Effect and Sufficient Birefringence in Sulfate Nonlinear Optical Materials

Kaichuang Chen,[ab] Yi Yang,[cd] Guang Peng,[a] Shunda Yang,[ad] Tao Yan,[a] Huixin Fan,[ad] Zheshuai Lin,[cd] and Ning Ye*[a]

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

[b.] College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, P. R. China

[c.] Beijing Center for Crystal R&D, Key Lab of Functional Crystals and Laser Technology of Chinese Academy of Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

[d.] University of Chinese Academy of Sciences, Beijing 100049, China

E-mail: nye@fjirsm.ac.cn

Table of Contents

Table S1. Selected bond lengths (Å) for $A_2Bi_2(SO_4)_2Cl_4$(A = NH_4, K, Rb).

$(NH_4)_2Bi_2(SO_{4)2}Cl_4$		$K_2Bi_2(SO_4)_2Cl_4$		$Rb_2Bi_2(SO_4)_2Cl_4$	
Bi(1)-Cl(1)	2.478(3)	Bi(1)-Cl(1)	2.479(3)	Bi(1)-Cl(1)	2.474(4)
Bi(1)-Cl(2)	2.548(3)	Bi(1)-Cl(2)	2.563(3)	Bi(1)-Cl(2)	2.561(4)
Bi(1)-O(2)	2.334(9)	Bi(1)-O(1)	2.338(9)	Bi(1)-O(3)#2	2.452(12)
Bi(1)-O(3)#1	2.446(9)	Bi(1)-O(3)#2	2.606(10)	Bi(1)-O(1)#1	2.317(13)
Bi(1)-O(4)#2	2.643(9)	Bi(1)-O(4)#3	2.465(9)	Bi(1)-O(2)#3	2.645(13)
S(1)-O(1)	1.461(10)	K(1)-Cl(1)#4	3.419(5)	Rb(1)-Cl(1)#4	3.485(5)
S(1)-O(2)	1.496(10)	K(1)-Cl(1)#5	3.208(4)	Rb(1)-Cl(1)#5	3.293(4)
S(1)-O(3)	1.476(9)	K(1)-Cl(2)#6	3.278(5)	Rb(1)-Cl(1)	3.897(5)
S(1)-O(4)	1.470(10)	K(1)-Cl(2)#7	3.526(5)	Rb(1)-Cl(2)	3.577(5)
N(1)-H(1A)	0.89	K(1)-O(1)#7	2.761(10)	Rb(1)-Cl(2)#6	3.389(5)
N(1)-H(1B)	0.89	K(1)-O(2)	2.754(10)	Rb(1)-O(3)#1	3.203(13)
N(1)-H(1C)	0.89	K(1)-O(2)#6	3.147(10)	Rb(1)-O(3)	2.870(12)
N(1)-H(1D)	0.8899	K(1)-O(4)#7	3.075(9)	Rb(1)-O(1)#1	2.873(13)
		K(1)-O(4)#6	2.772(9)	Rb(1)-O(4)	3.239(13)
		S(1)-O(1)	1.490(9)	Rb(1)-O(4)#6	2.876(13)
		S(1)-O(2)	1.466(10)	S(1)-O(3)	1.476(12)
		S(1)-O(3)	1.486(10)	S(1)-O(1)	1.494(13)
		S(1)-O(4)	1.480(9)	S(1)-O(4)	1.479(13)
				S(1)-O(2)	1.476(13)

Symmetry transformations used to generate equivalent atoms:

For $(NH_4)_2Bi_2(SO_4)_2Cl_4$**:** #1 x+1, y, z; #2 x+1/2, -y+3/2, -z+1; #3 x-1, y, z; #4 x-1/2, -y+3/2, -z+1.

For $K_2Bi_2(SO_4)_2Cl_4$**:** #1 x, y-1, z; #2 x+1/2, -y+1/2, -z+1; #3 x+1, y, z; #4 x-1, y+1, z; #5 x-1/2, -y+1/2, -z+1; #6 -x+1, y+1/2, -z+1/2; #7 x, y+1, z; #8 x+1, y-1, z; #9 -x+1, y-1/2, -z+1/2; #10 x-1, y, z.

For $Rb_2Bi_2(SO_4)_2Cl_4$: #1 -x+1, y+1/2, -z-1/2; #2 -x, y+1/2, -z-1/2; #3 -x+1/2, -y-1, z-1/2; #4 x+1, y, z; #5 x+1/2, -y-3/2, -z-1; #6 -x+1, y-1/2, -z-1/2; #7 x-1/2, -y-3/2, -z-1; #8 x-1,y,z; #9 -x,y-1/2,-z-1/2; #10 -x+1/2, -y-1, z+1/2.

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $(NH_4)_2Bi_2(SO_4)_2Cl_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Bi(1)	9875(1)	8667(1)	6171(1)	6(1)
S(1)	4955(5)	8189(4)	6099(2)	4(1)
Cl(1)	10657(5)	11662(4)	5527(2)	10(1)
Cl(2)	9036(6)	10112(4)	7617(2)	8(1)
O(1)	6203(15)	6754(13)	6497(7)	13(2)
O(2)	6480(15)	9618(13)	5823(6)	8(2)
N(1)	5150(20)	2991(15)	6556(7)	12(2)
O(3)	3459(14)	8969(13)	6723(6)	6(2)
O(4)	3737(16)	7526(14)	5361(6)	9(2)
H(1A)	5037	2563	6024	14
H(1B)	6165	2393	6832	14
H(1C)	3941	2846	6832	14
H(1D)	5477	4163	6536	14

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_2Bi_2(SO_4)_2Cl_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
Bi(1)	9850(1)	1363(1)	3838(1)	5(1)
K(1)	5231(6)	7041(4)	3422(2)	9(1)
Cl(1)	10703(5)	-1697(4)	4488(2)	7(1)
S(1)	4925(5)	1821(4)	3870(2)	2(1)
Cl(2)	8940(5)	-97(4)	2352(2)	6(1)
O(1)	6429(15)	365(13)	4170(6)	4(2)
O(2)	6161(15)	3312(13)	3466(6)	7(2)
O(3)	3635(16)	2474(14)	4624(6)	8(2)
O(4)	3436(14)	984(12)	3236(6)	4(2)

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2Bi_2(SO_4)_2Cl_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Bi(1)	150(1)	-3652(1)	-3841(1)	6(1)
Rb(1)	4724(3)	-7970(2)	-3430(1)	10(1)
S(1)	4947(7)	-8174(5)	-1105(2)	4(1)
Cl(1)	-655(7)	-6632(5)	-4464(2)	8(1)
Cl(2)	990(7)	-5100(5)	-2385(3)	8(1)
O(3)	3445(19)	-8972(17)	-1723(7)	6(2)
O(1)	6460(20)	-9591(17)	-819(8)	7(2)
O(4)	6210(20)	-6748(18)	-1522(8)	9(2)
O(2)	3670(20)	-7505(18)	-377(8)	8(2)

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_2Bi_2(SO_4)_2Cl_4$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$.

	U11	U22	U33	U23	U13	U12
Bi(1)	7(1)	6(1)	5(1)	-1(1)	0(1)	0(1)
S(1)	3(1)	4(1)	5(1)	-1(1)	-3(1)	-2(1)
Cl(1)	14(2)	9(1)	8(1)	4(1)	-2(1)	-3(1)
Cl(2)	12(2)	9(1)	4(1)	-2(1)	2(1)	-2(1)
O(1)	7(4)	8(4)	24(5)	4(4)	-3(4)	-1(4)
O(2)	9(4)	7(4)	8(4)	1(3)	-4(3)	-2(3)
N(1)	20(6)	11(4)	4(5)	-1(4)	-1(5)	-5(5)
O(3)	5(4)	10(4)	5(3)	0(3)	-2(3)	-2(3)
O(4)	10(4)	12(4)	6(4)	-7(3)	-1(3)	0(3)

Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $K_2Bi_2(SO_4)_2Cl_4$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$.

	U11	U22	U33	U23	U13	U12
Bi(1)	5(1)	6(1)	3(1)	0(1)	0(1)	0(1)
K(1)	18(2)	5(1)	4(1)	-2(1)	-1(1)	0(1)
Cl(1)	9(2)	7(1)	5(1)	3(1)	1(1)	3(1)
S(1)	2(1)	4(1)	2(1)	-1(1)	1(1)	-1(1)
Cl(2)	8(2)	8(1)	3(1)	-3(1)	-2(1)	1(1)
O(1)	4(2)	5(2)	4(2)	0(1)	0(1)	0(1)
O(2)	9(5)	4(4)	8(4)	3(4)	0(4)	2(4)
O(3)	6(5)	12(5)	7(5)	-5(4)	-1(4)	-1(4)
O(4)	4(2)	4(2)	4(2)	0(1)	0(1)	0(1)

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2Bi_2(SO_4)_2Cl_4$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$.

	U11	U22	U33	U23	U13	U12
Bi(1)	8(1)	6(1)	4(1)	0(1)	0(1)	0(1)
Rb(1)	16(1)	6(1)	6(1)	1(1)	1(1)	0(1)
S(1)	4(1)	4(1)	3(1)	-1(1)	2(1)	0(1)
Cl(1)	10(1)	8(1)	6(1)	-1(1)	0(1)	-1(1)
Cl(2)	9(1)	8(1)	7(1)	1(1)	-1(1)	0(1)
O(3)	6(3)	6(3)	5(3)	0(1)	0(1)	0(1)
O(1)	7(3)	7(3)	7(3)	0(1)	0(1)	0(1)
O(4)	8(3)	8(3)	9(3)	0(1)	0(1)	0(1)
O(2)	8(3)	8(3)	8(3)	-1(1)	0(1)	0(1)

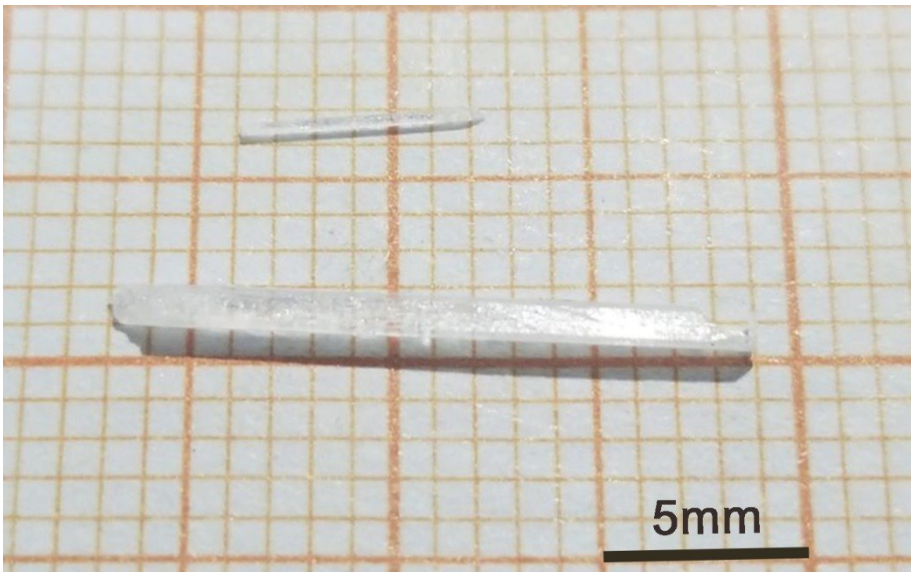

Figure S1. Photograph of $Rb_2Bi_2(SO_4)_2Cl_4$ crystals.

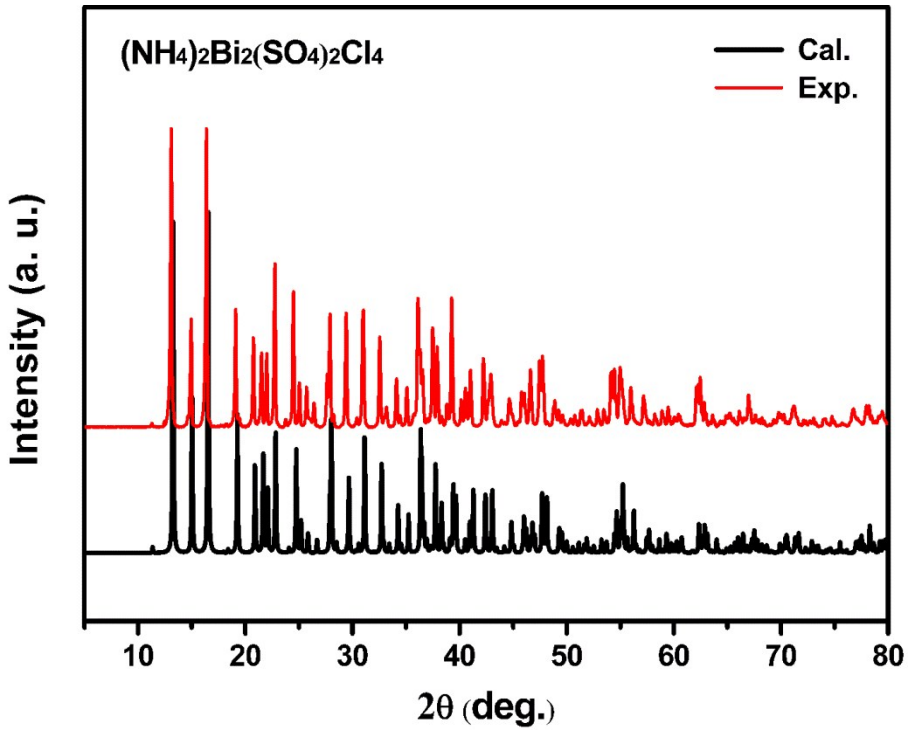

Figure S2. Simulated and experimental powder X-ray diffraction patterns of $(NH_4)_2Bi_2(SO_4)_2Cl_4$.

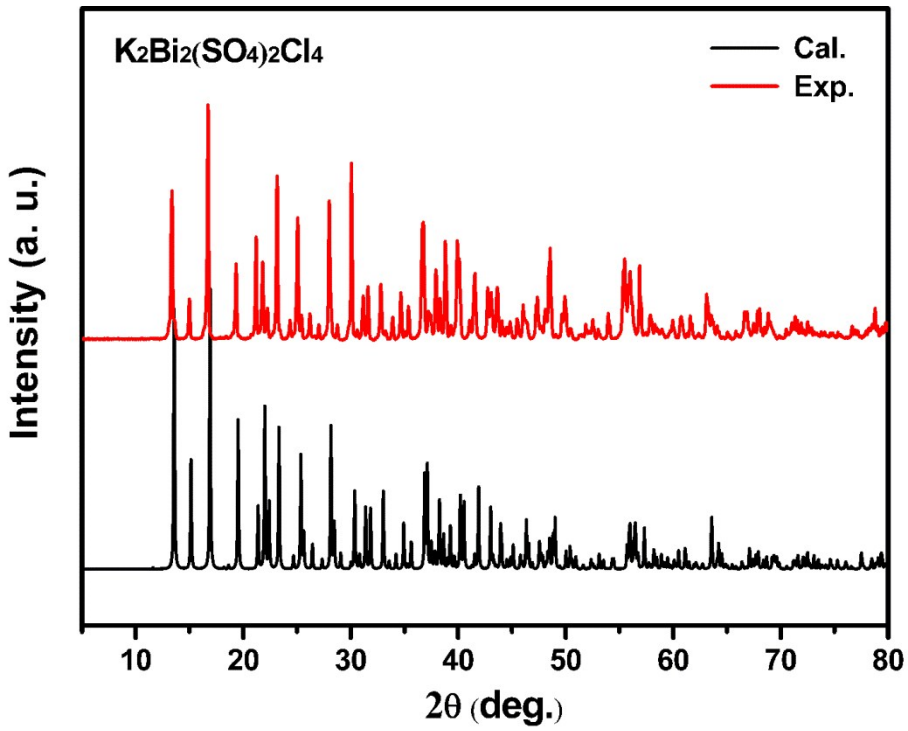

Figure S3. Simulated and experimental powder X-ray diffraction patterns of $K_2Bi_2(SO_4)_2Cl_4$.

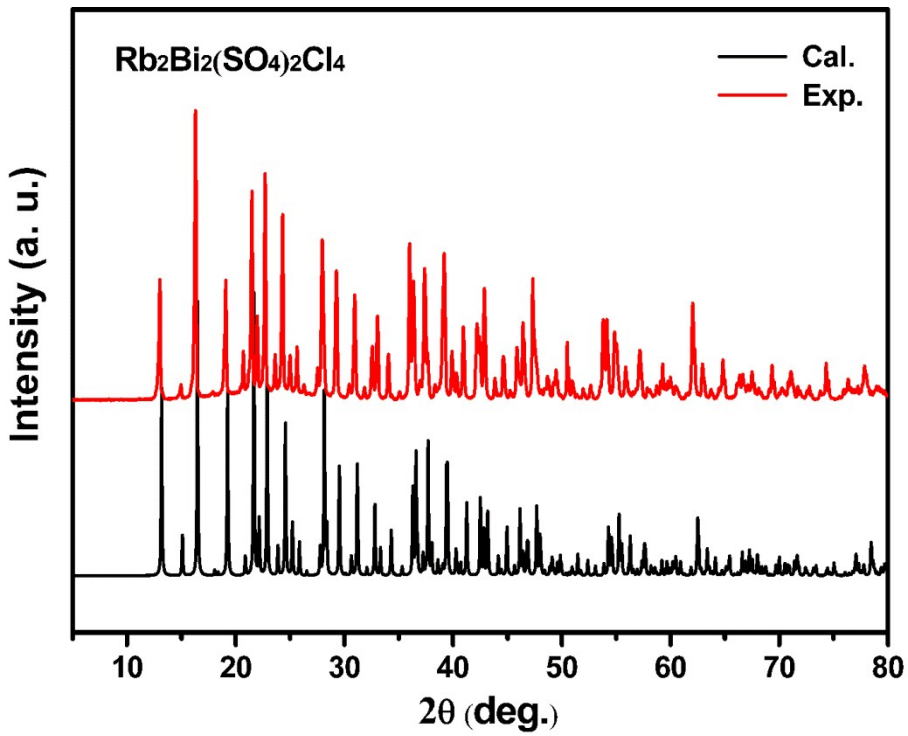

Figure S4. Simulated and experimental powder X-ray diffraction patterns of $Rb_2Bi_2(SO_4)_2Cl_4$.

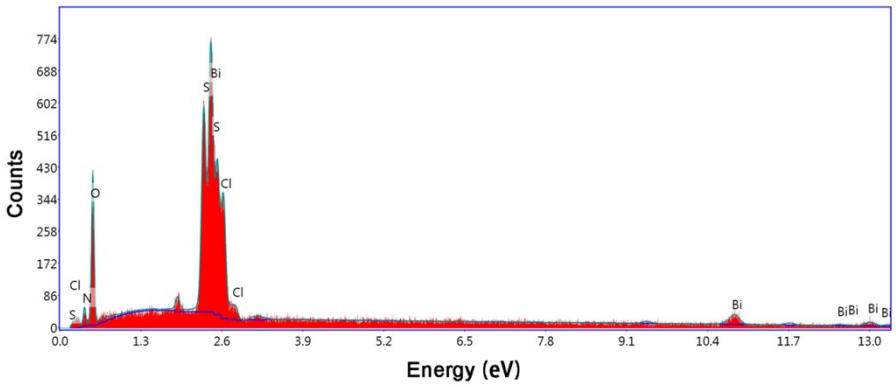

Figure S5. EDS analysis for $(NH_4)_2Bi_2(SO_4)_2Cl_4$.

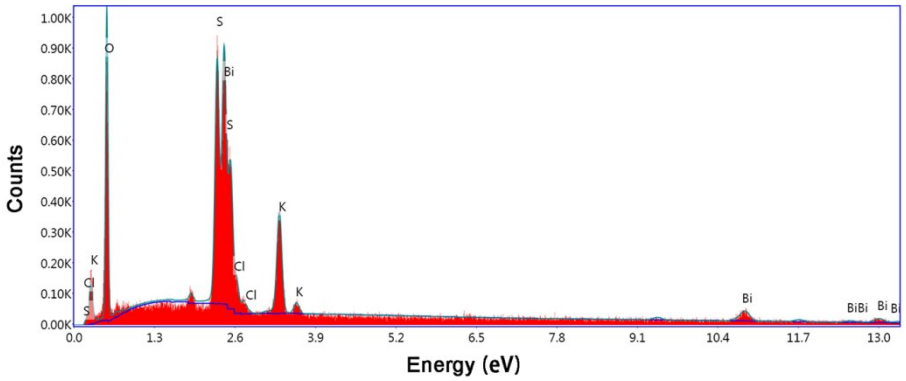

Figure S6. EDS analysis for $K_2Bi_2(SO_4)_2Cl_4$.

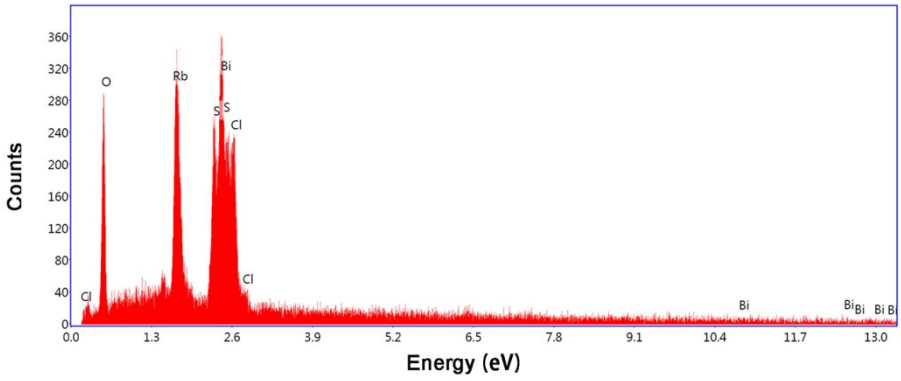

Figure S7. EDS analysis for $Rb_2Bi_2(SO_4)_2Cl_4$.

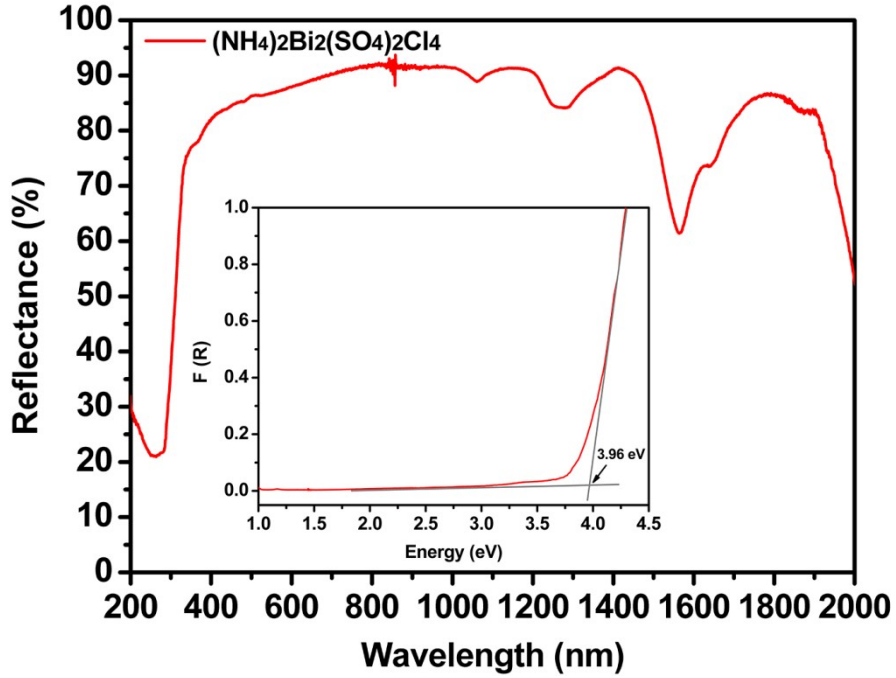

Figure S8. The UV-Vis-NIR reflectance spectrum of $(NH_4)_2Bi_2(SO_4)_2Cl_4$

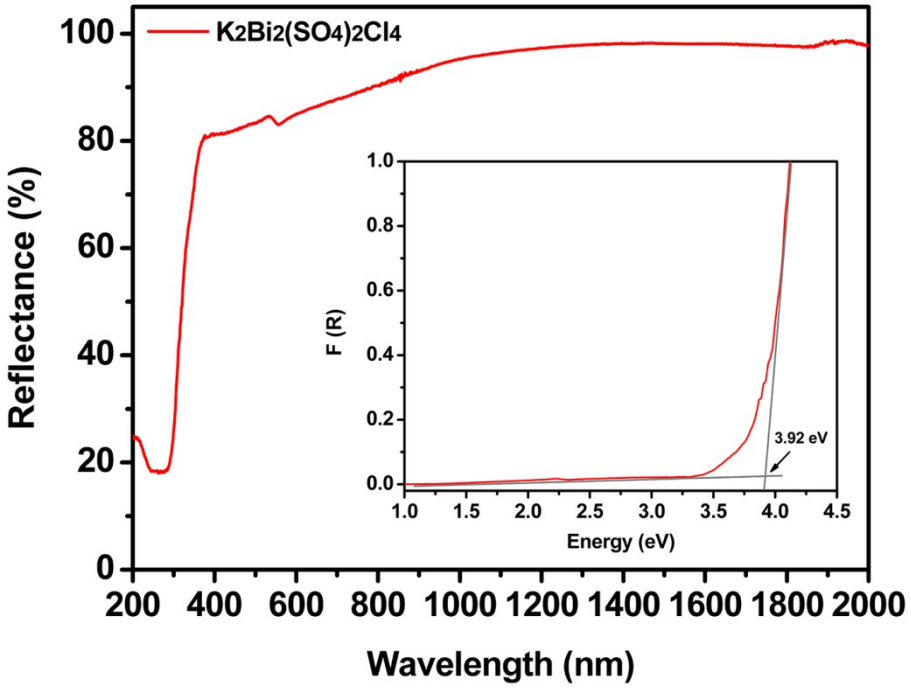

Figure S9. The UV-Vis-NIR reflectance spectrum of $K_2Bi_2(SO_4)_2Cl_4$.

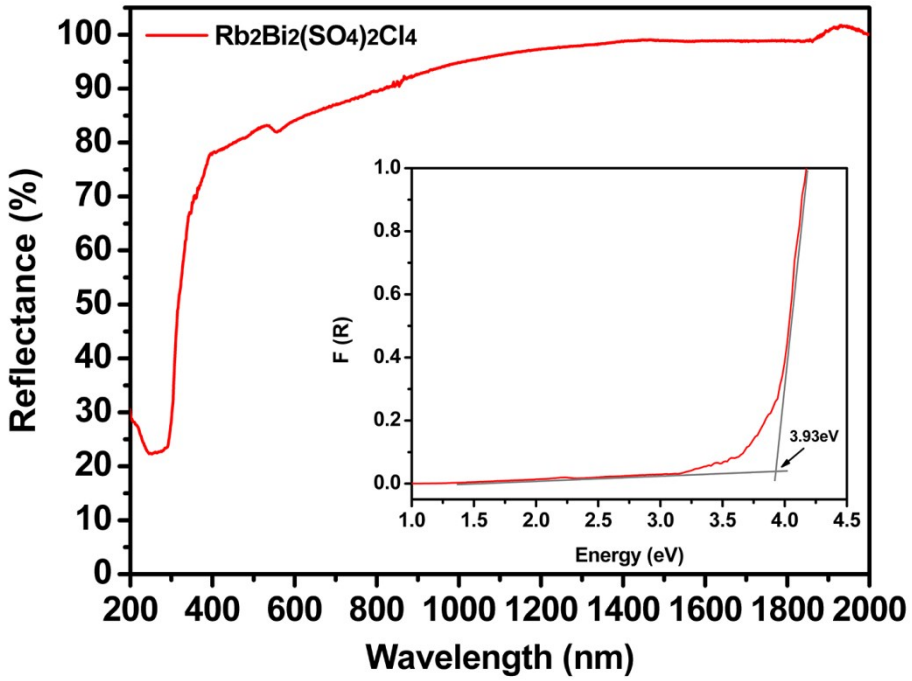

Figure S10. The UV-Vis-NIR reflectance spectrum of $Rb_2Bi_2(SO_4)_2Cl_4$.

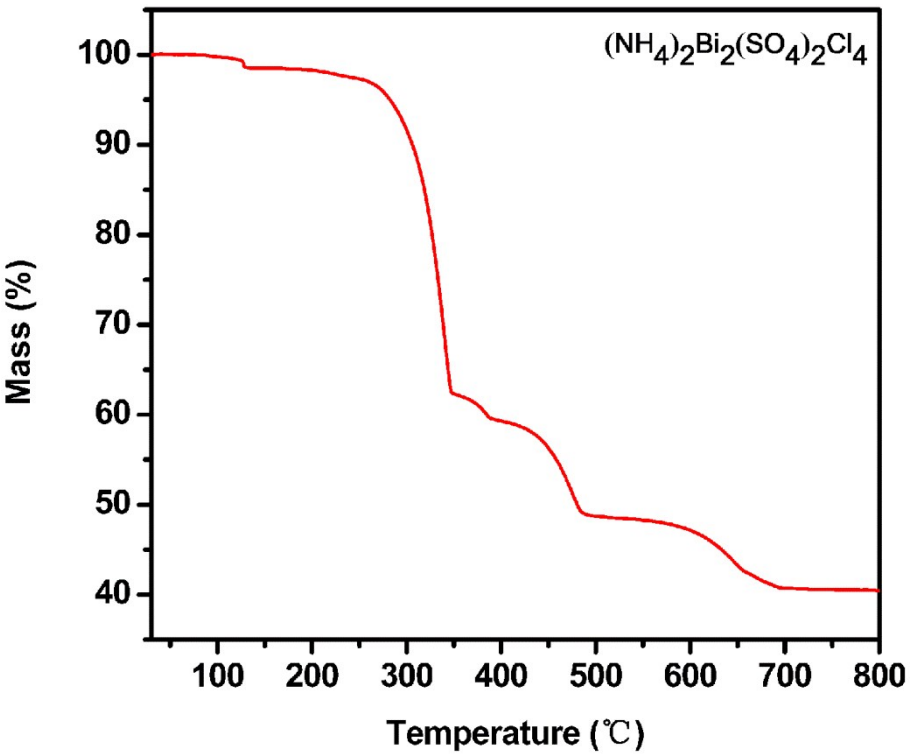

Figure S11. TG curve of $(NH_4)_2Bi_2(SO_4)_2Cl_4$. The slight weight losse at about 120 °C can be attributed to the adsorption water.

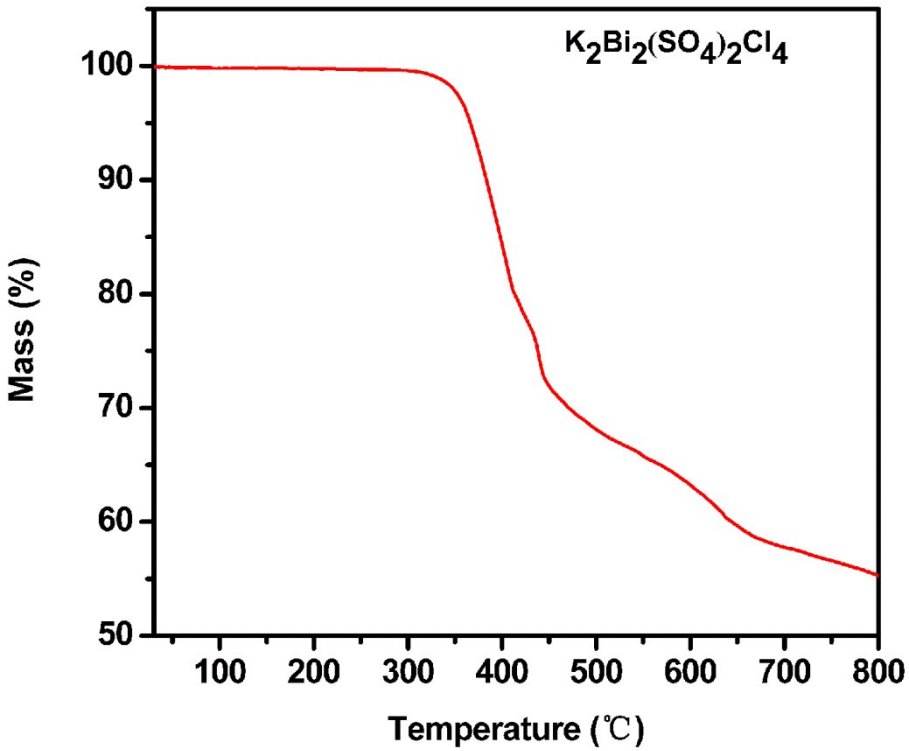

Figure S12. TG curve of $K_2Bi_2(SO_4)_2Cl_4$.

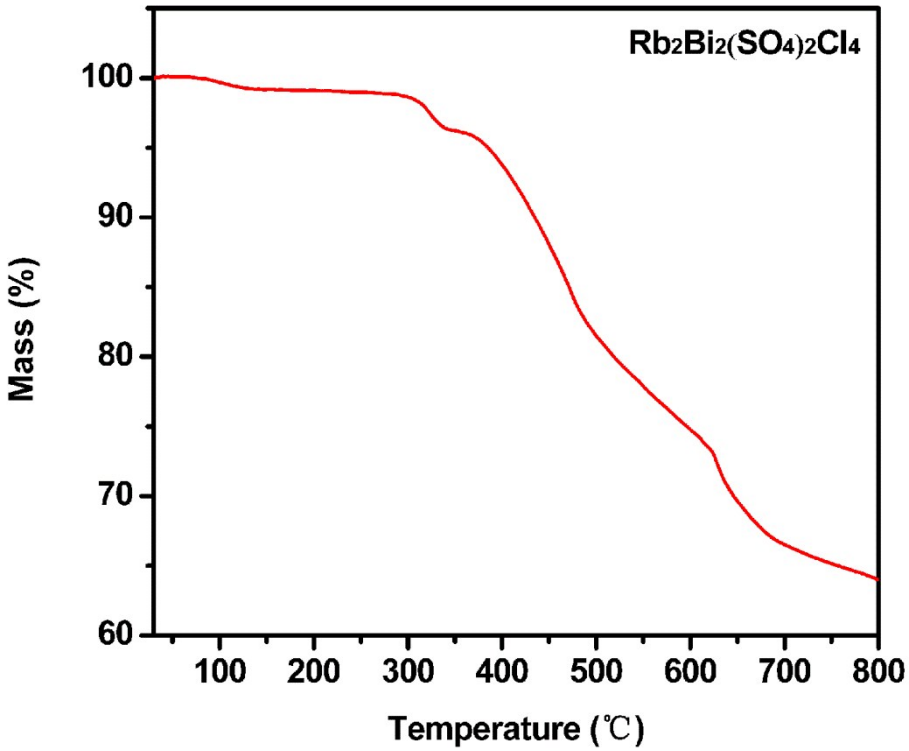

Figure S13. TG curve of $Rb_2Bi_2(SO_4)_2Cl_4$. The slight weight losse at about 120 ^oC can be attributed to the adsorption water.

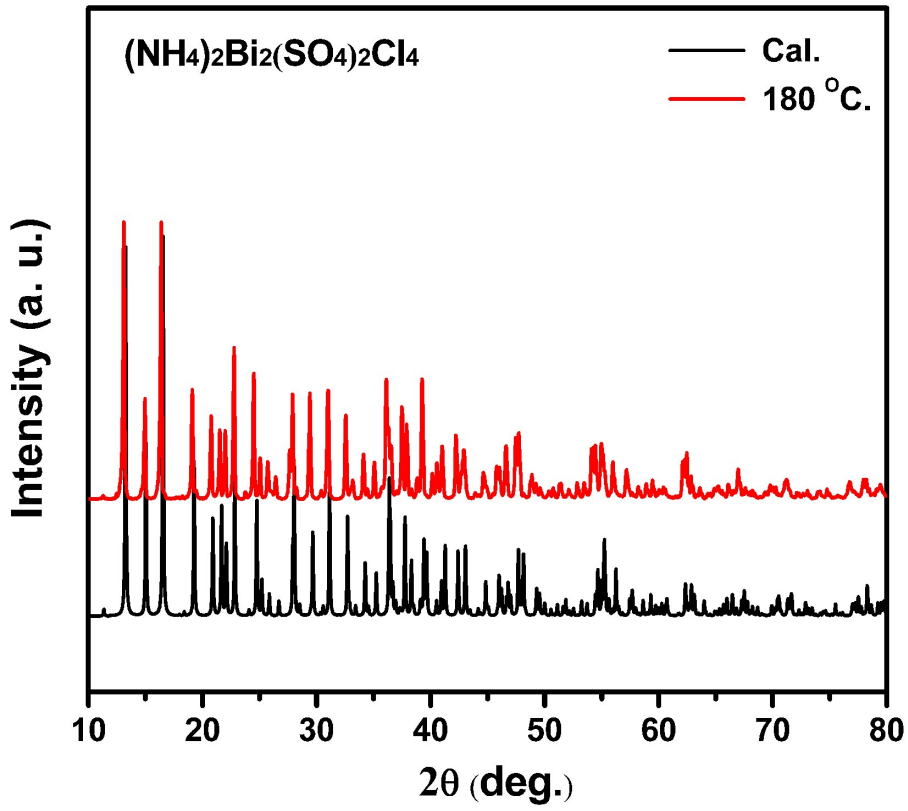

Figure S14. Simulated and experimental powder X-ray diffraction patterns of $(NH_4)_2Bi_2(SO_4)_2Cl_4$ heated at 180 °C.

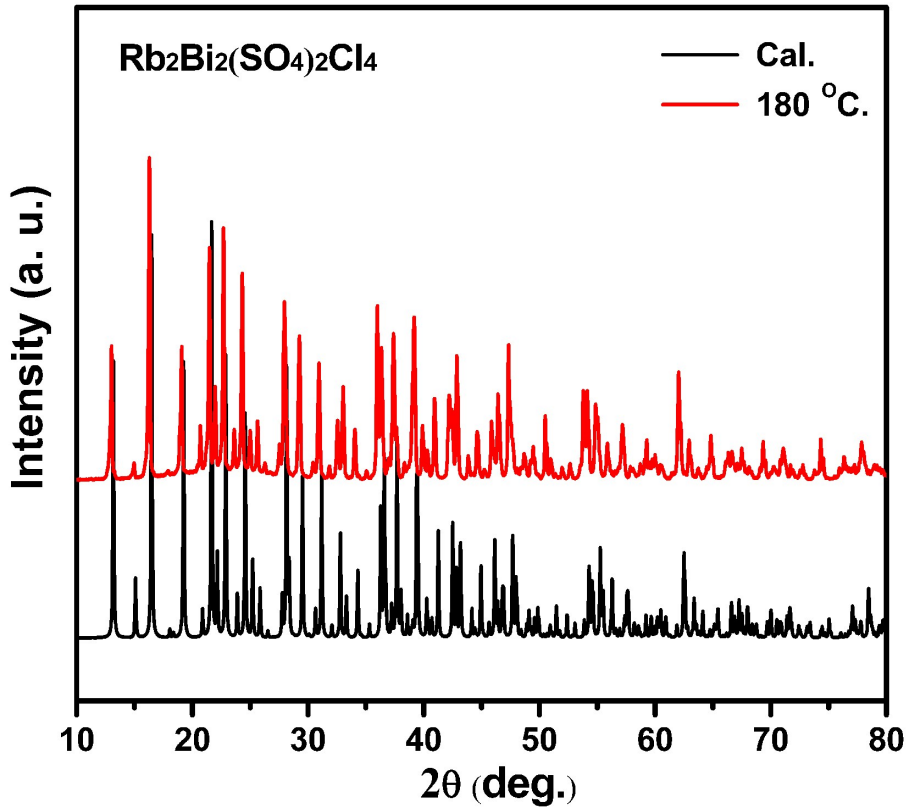

Figure S15. Simulated and experimental powder X-ray diffraction patterns of $Rb_2Bi_2(SO_4)_2Cl_4$ heated at 180 °C.

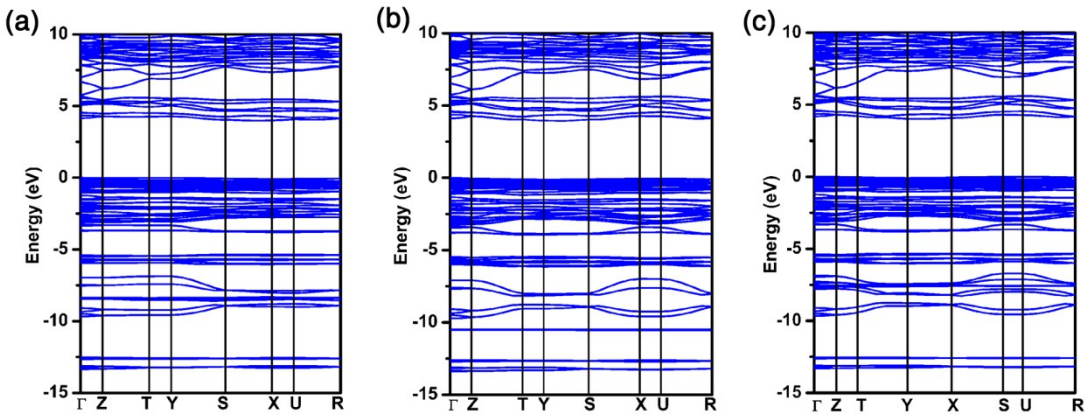

Figure S16. Electronic band structure of $A_2Bi_2(SO_4)_2Cl_4$ (A = NH_4, K, Rb)

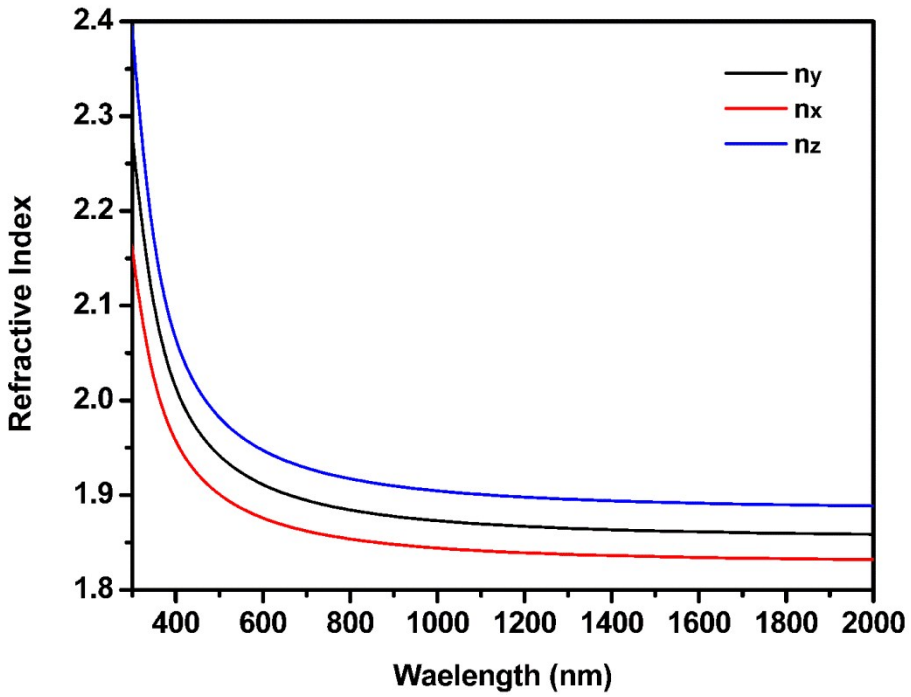

Figure S17. Calculated refractive index of $(NH_4)_2Bi_2(SO_4)_2Cl_4$.

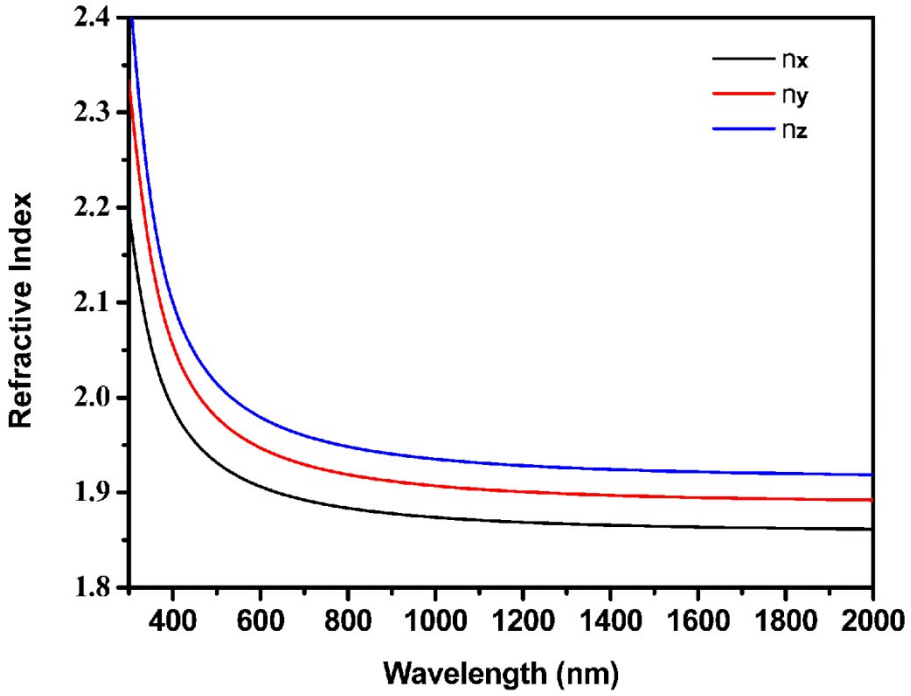

Figure S18. Calculated refractive index of $K_2Bi_2(SO_4)_2Cl_4$.

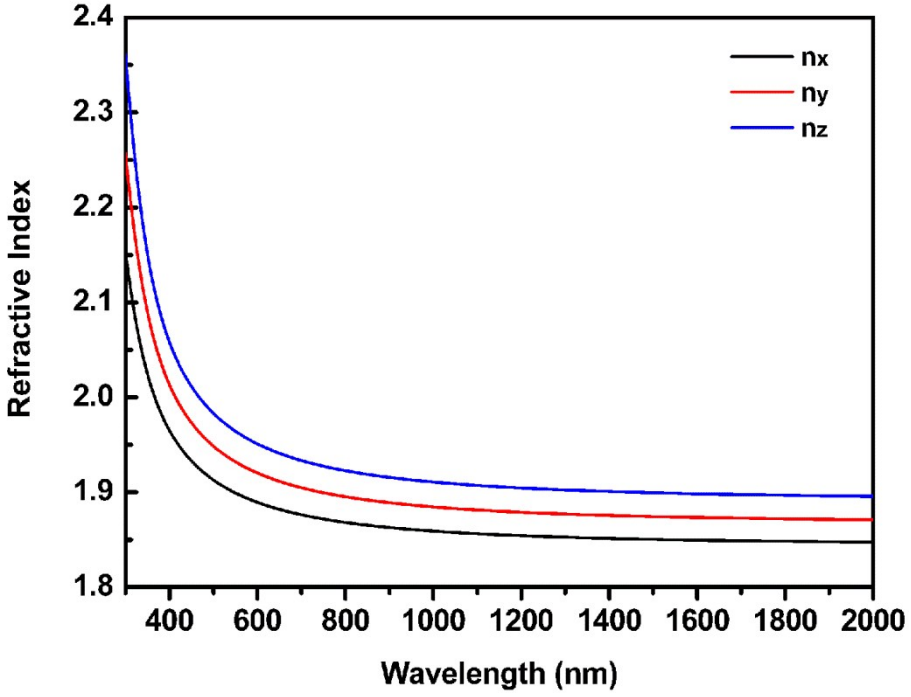

Figure S19. Calculated refractive index of $Rb_2Bi_2(SO_4)_2Cl_4$.

Anionic group theory

The macroscopic second-order susceptibility $\chi^{(2)}$ can be expressed by Eq:[1]

$$\chi_{ijk}^{(2)} = \frac{F}{V}\sum_{p}\sum_{i'j'k'}\alpha_{ii'}\alpha_{jj'}\alpha_{kk'}\beta_{i'j'k'}^{(2)}(P)$$

where *F* is the correction factor of the localized field; $\alpha_{ii'}$, $\alpha_{jj'}$, and $\alpha_{kk'}$ are the direction cosines between the macroscopic coordinates of the crystal and the microscopic coordinates of $[SO_4]^{2-}$ groups, and $\beta_{i'j'k'}^{(2)}$ is the microscopic second-order susceptibility tensors of $[SO_4]^{2-}$ group. According to Kleinman symmetry relations,[2] $[SO_4]^{2-}$ group possesses only one nonvanishing second-order susceptibility $\beta_{123}^{(2)}$. Therefore, the geometrical factor g can be derived to be[3]

$$\chi_{ijk}^{(2)} = \frac{F}{V}\cdot g_{ijk}\cdot\beta_{123}^{(2)}$$

$$g_{ijk} = \sum_{P}^{n}[(\alpha(i1)\alpha(j2)\alpha(k3) + \alpha(i1)\alpha(j3)\alpha(k2)) + \alpha(i2)\alpha(j1)\alpha(k3) + \alpha(i2)\alpha(j3)\alpha(k1)$$

$$g = max(g_{ijk})$$

The structural criterion C is defined as

$$C = \frac{g}{n}$$

Reference

(1) C. T. Chen, Y. C. Wu and R. K. Li, Int. Rev. Phys. Chem., 1989, **8**, 65-91.

(2) D. A. Kleinman, Phys. Rev., 1962, **126**, 1977.

(3) N. Ye, Q. X. Chen, B. C. Wu and C. T. Chen, J. Appl. Phys., 1998, **84**, 555-558.