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Supporting Information

Ultraviolet Nonlinear Optical Crystals $A_3SrBi(P_2O_7)_2$ (A = K, Rb) with Large Second Harmonic Generation Responses

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Table S1. Crystal data and structure refinement for $A_3SrBi(P_2O_7)_2$ (A = K, Rb).

Empirical formula	$K_3SrBi(P_2O_7)_2$	$Rb_3SrBi(P_2O_7)_2$
Formula weight	761.78	900.89
Temperature / K	299(2)	
Wavelength / Å	0.71073	
Crystal system	Monoclinic	
Space group, Z	$P2_1$, 2	
a / Å	8.6613(7)	8.9637(8)
b / Å	9.6076(7)	9.4920(8)
c / Å	8.8354(8)	9.2113(9)
β / °	106.469(3)	105.995(3)
Volume / Å^3	705.07(10)	753.39(12)
ρ / Mg/m^3	3.588	3.971
μ / mm^{-1}	17.656	25.324
F(000)	700	808
Θ range for data collection / °	2.404 to 27.538	2.300 to 27.534
Limiting indices	-11≤*h*≤11, -12≤*k*≤12, -11≤*l*≤11	-9<=h<=11, -12<=k<=12, -11<=l<=11
Reflections collected / unique	10362 / 3231 [*R*(int) = 0.1080]	7667 / 3370 [R(int) = 0.0357]
Completeness	100%	99.4%
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3231 / 133 / 203	3370 / 1 / 208
Goodness-of-fit on F^2	0.992	1.029
Final *R* indices [$F_o^2>2\sigma(F_o^2)$] [a]	R_1 = 0.0514, wR_2 = 0.0911	R_1 = 0.0580, wR_2 = 0.1558
R indices (all data) [a]	R_1 = 0.0675, wR_2 = 0.1010	R_1 = 0.0641, wR_2 = 0.11623
Absolute structure parameter	0.003(11)	0.042(9)
Largest diff. peak and hole / e·Å^{-3}	1.667 and -1.455	7.541 and -1.370

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and bond valence sum (BVS) for $K_3SrBi(P_2O_7)_2$.

Atom	x	y	z	U(eq) [b]	BVS
Bi(1)	-0.0126(1)	0.8064(1)	0.7239(1)	0.012(1)	2.98
Sr(1)	0.2487(2)	0.5021(2)	1.0252(2)	0.011(1)	2.11
K(1)	0.1798(6)	0.8301(6)	0.3057(6)	0.030(1)	0.91
K(2)	0.4782(6)	0.1702(5)	0.2542(7)	0.024(1)	1.16
K(3)	0.6848(8)	0.7201(7)	0.2843(9)	0.046(2)	0.86
P(1)	0.6773(7)	0.3811(6)	0.0683(7)	0.015(1)	4.84
P(2)	0.3907(7)	0.4906(6)	0.4092(7)	0.016(1)	4.94
P(3)	0.8855(7)	0.6080(6)	0.0174(7)	0.014(1)	5.01
P(4)	0.1469(7)	0.5374(6)	0.5790(7)	0.014(1)	5.09
O(1)	0.2636(18)	0.5839(14)	0.4781(18)	0.017(3)	2.26
O(2)	0.0745(18)	0.3972(15)	0.5174(18)	0.017(2)	2.21
O(3)	1.0119(17)	0.5387(15)	0.1501(18)	0.017(2)	1.97
O(4)	0.7678(17)	0.2750(15)	-0.0030(18)	0.024(3)	1.81
O(5)	0.0147(19)	0.6460(15)	0.5510(20)	0.023(3)	2.09
O(6)	0.7551(18)	0.3819(15)	0.2492(19)	0.022(3)	1.89
O(7)	0.8589(18)	0.7579(14)	0.0496(18)	0.021(3)	1.89
O(8)	0.4991(19)	0.3653(15)	0.0213(19)	0.021(3)	1.97
O(9)	0.7133(17)	0.5363(14)	0.0089(18)	0.017(2)	2.18
O(10)	0.9187(19)	0.5803(15)	-0.1390(20)	0.024(3)	1.86
O(11)	0.2461(18)	0.5306(15)	0.7474(18)	0.020(3)	1.92
O(12)	0.5240(20)	0.4513(17)	0.5480(20)	0.034(4)	1.84
O(13)	0.4220(20)	0.5894(16)	0.2900(20)	0.027(3)	2.03
O(14)	0.2920(18)	0.3654(15)	0.3240(20)	0.022(3)	2.03

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

Table S3. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and bond valence sum (BVS) for $Rb_3SrBi(P_2O_7)_2$.

Atom	x	y	z	U(eq) [b]	BVS
Bi(1)	0.5010(1)	0.4943(1)	0.7270(1)	0.030(1)	3.31
Sr(1)	0.7462(3)	1.1622(3)	1.0006(3)	0.030(1)	2.37
Rb(1)	0.3322(3)	0.9916(4)	0.6852(3)	0.047(1)	0.94
Rb(2)	0.9950(3)	-0.1622(3)	0.2504(3)	0.042(1)	0.91
Rb(3)	1.1393(4)	0.3475(4)	0.2811(4)	0.054(1)	0.79
P(1)	0.6373(8)	0.2047(7)	0.5714(8)	0.033(1)	5.04
P(2)	0.8675(7)	0.0983(7)	0.4277(8)	0.033(1)	5.28
P(3)	0.8331(8)	0.5578(8)	0.9771(8)	0.034(1)	4.81
P(4)	0.5993(8)	0.7715(7)	1.0126(7)	0.033(1)	4.99
O(1)	0.5320(20)	0.7620(20)	1.1450(30)	0.040(5)	1.97
O(2)	0.9960(20)	0.6150(30)	1.0180(30)	0.060(7)	2.01
O(3)	0.8820(20)	0.1480(30)	0.2800(20)	0.051(5)	2.01
O(4)	1.0110(20)	0.0850(30)	0.5480(20)	0.052(6)	1.93
O(5)	0.5010(20)	0.1300(30)	0.4670(20)	0.050(6)	2.19
O(6)	0.7050(30)	0.1370(30)	0.7170(20)	0.054(6)	2.05
O(7)	0.5890(30)	0.3630(20)	0.5810(30)	0.060(6)	2.15
O(8)	0.6730(30)	0.9120(20)	0.9970(30)	0.057(6)	1.82
O(9)	0.7640(20)	0.2190(20)	0.4810(20)	0.039(4)	2.29
O(10)	0.4860(20)	0.7160(20)	0.8700(20)	0.037(4)	1.91
O(11)	0.7630(20)	-0.0300(20)	0.4110(20)	0.042(5)	2.02
O(12)	0.7550(30)	0.5690(30)	0.8060(20)	0.050(5)	1.99
O(13)	0.8110(50)	0.4110(30)	1.0330(30)	0.095(13)	1.89
O(14)	0.7370(30)	0.6580(40)	1.0650(30)	0.074(8)	2.23

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

Table S4. Bond lengths (Å) and angles (°) for $K_3SrBi(P_2O_7)_2$.

Bi(1)-O(2)#1	2.224(15)	K(2)-O(14)	2.656(16)
Bi(1)-O(5)	2.230(16)	K(2)-O(12)#7	2.737(19)
Bi(1)-O(6)#2	2.293(15)	K(2)-O(11)#7	2.742(15)
Bi(1)-O(14)#1	2.404(15)	K(2)-O(9)#9	2.761(16)
Bi(1)-O(3)#2	2.493(14)	K(2)-O(8)	2.827(16)
Bi(1)-O(10)#3	2.637(16)	K(2)-O(1)#7	2.878(16)
Sr(1)-O(11)	2.463(16)	K(2)-O(6)	3.155(16)
Sr(1)-O(13)#6	2.540(17)	K(3)-O(13)	2.612(17)
Sr(1)-O(7)#7	2.541(14)	K(3)-O(2)#2	2.871(16)
Sr(1)-O(8)#6	2.545(15)	K(3)-O(7)	2.912(17)
Sr(1)-O(3)#3	2.614(15)	K(3)-O(8)#8	3.055(17)
Sr(1)-O(4)#2	2.630(14)	K(3)-O(9)	3.072(16)
Sr(1)-O(14)#6	2.875(16)	K(3)-O(11)#2	3.070(16)
Sr(1)-O(10)#3	2.913(16)	K(3)-O(5)#10	3.225(17)
K(1)-O(12)#2	2.778(19)	K(3)-O(6)	3.336(16)
K(1)-O(1)	2.796(15)	P(1)-O(8)	1.487(16)
K(1)-O(10)#8	2.823(16)	P(1)-O(4)	1.527(15)
K(1)-O(4)#8	2.886(16)	P(1)-O(6)	1.549(17)
K(1)-O(2)#1	3.109(15)	P(1)-O(9)	1.640(15)
K(1)-O(7)#5	3.125(16)	P(2)-O(12)	1.477(19)
K(1)-O(13)	3.152(17)	P(2)-O(13)	1.497(17)
K(1)-O(3)#5	3.274(16)	P(2)-O(14)	1.544(16)
K(1)-O(5)	3.409(17)	P(2)-O(1)	1.663(15)
P(4)-O(11)	1.493(16)	P(3)-O(7)	1.499(14)
P(4)-O(5)	1.517(16)	P(3)-O(10)	1.511(17)
P(4)-O(2)	1.519(15)	P(3)-O(3)	1.513(16)
P(4)-O(1)	1.589(16)	P(3)-O(9)	1.625(15)
O(2)#1-Bi(1)-O(5)	70.0(6)	O(14)-K(2)-O(12)#7	106.3(6)
O(2)#1-Bi(1)-O(6)#2	86.5(6)	O(14)-K(2)-O(11)#7	158.9(5)
O(5)-Bi(1)-O(6)#2	90.0(6)	O(12)#7-K(2)-O(11)#7	78.0(5)
O(2)#1-Bi(1)-O(14)#1	77.4(5)	O(14)-K(2)-O(9)#9	105.3(5)
O(5)-Bi(1)-O(14)#1	109.9(6)	O(12)#7-K(2)-O(9)#9	93.9(5)
O(6)#2-Bi(1)-O(14)#1	147.7(5)	O(11)#7-K(2)-O(9)#9	94.8(5)
O(2)#1-Bi(1)-O(3)#2	92.7(5)	O(14)-K(2)-O(8)	82.4(5)
O(5)-Bi(1)-O(3)#2	159.6(5)	O(12)#7-K(2)-O(8)	170.9(5)
O(6)#2-Bi(1)-O(3)#2	77.9(5)	O(11)#7-K(2)-O(8)	94.9(5)
O(14)#1-Bi(1)-O(3)#2	75.1(5)	O(9)#9-K(2)-O(8)	81.0(5)
O(2)#1-Bi(1)-O(10)#3	137.7(5)	O(14)-K(2)-O(1)#7	113.2(5)
O(5)-Bi(1)-O(10)#3	80.1(5)	O(12)#7-K(2)-O(1)#7	53.1(5)
O(6)#2-Bi(1)-O(10)#3	123.5(5)	O(11)#7-K(2)-O(1)#7	52.3(4)
O(14)#1-Bi(1)-O(10)#3	85.8(5)	O(9)#9-K(2)-O(1)#7	134.4(5)
O(3)#2-Bi(1)-O(10)#3	120.3(5)	O(8)-K(2)-O(1)#7	126.4(5)

O(11)-Sr(1)-O(13)#6	135.9(5)	O(14)-K(2)-O(6)	93.5(4)
O(11)-Sr(1)-O(7)#7	86.8(5)	O(12)#7-K(2)-O(6)	130.4(5)
O(13)#6-Sr(1)-O(7)#7	128.5(5)	O(11)#7-K(2)-O(6)	69.4(4)
O(11)-Sr(1)-O(8)#6	79.1(5)	O(9)#9-K(2)-O(6)	124.5(5)
O(13)#6-Sr(1)-O(8)#6	84.2(5)	O(8)-K(2)-O(6)	49.9(4)
O(7)#7-Sr(1)-O(8)#6	76.8(5)	O(1)#7-K(2)-O(6)	77.3(4)
O(11)-Sr(1)-O(3)#3	128.3(5)	O(13)-K(3)-O(2)#2	139.3(6)
O(13)#6-Sr(1)-O(3)#3	84.0(5)	O(13)-K(3)-O(7)	134.8(5)
O(7)#7-Sr(1)-O(3)#3	87.7(5)	O(2)#2-K(3)-O(7)	85.8(4)
O(8)#6-Sr(1)-O(3)#3	148.1(5)	O(13)-K(3)-O(8)#8	89.9(5)
O(11)-Sr(1)-O(4)#2	80.2(5)	O(2)#2-K(3)-O(8)#8	112.0(4)
O(13)#6-Sr(1)-O(4)#2	75.2(5)	O(7)-K(3)-O(8)#8	63.8(4)
O(7)#7-Sr(1)-O(4)#2	153.2(5)	O(13)-K(3)-O(9)	90.3(5)
O(8)#6-Sr(1)-O(4)#2	122.8(5)	O(2)#2-K(3)-O(9)	128.1(4)
O(3)#3-Sr(1)-O(4)#2	82.2(4)	O(7)-K(3)-O(9)	48.2(4)
O(11)-Sr(1)-O(14)#6	158.0(4)	O(8)#8-K(3)-O(9)	72.6(4)
O(13)#6-Sr(1)-O(14)#6	54.2(5)	O(13)-K(3)-O(11)#2	131.5(5)
O(7)#7-Sr(1)-O(14)#6	76.1(5)	O(2)#2-K(3)-O(11)#2	49.7(4)
O(8)#6-Sr(1)-O(14)#6	83.5(5)	O(7)-K(3)-O(11)#2	70.1(4)
O(3)#3-Sr(1)-O(14)#6	65.7(4)	O(8)#8-K(3)-O(11)#2	62.8(4)
O(4)#2-Sr(1)-O(14)#6	120.9(5)	O(9)-K(3)-O(11)#2	115.1(5)
O(11)-Sr(1)-O(10)#3	75.2(5)	O(13)-K(3)-O(5)#10	118.4(5)
O(13)#6-Sr(1)-O(10)#3	127.9(5)	O(2)#2-K(3)-O(5)#10	49.1(4)
O(7)#7-Sr(1)-O(10)#3	82.7(5)	O(7)-K(3)-O(5)#10	91.0(5)
O(8)#6-Sr(1)-O(10)#3	147.8(5)	O(8)#8-K(3)-O(5)#10	151.4(5)
O(3)#3-Sr(1)-O(10)#3	53.0(4)	O(9)-K(3)-O(5)#10	101.4(4)
O(4)#2-Sr(1)-O(10)#3	71.4(4)	O(11)#2-K(3)-O(5)#10	97.2(4)
O(14)#6-Sr(1)-O(10)#3	115.4(5)	O(13)-K(3)-O(6)	73.5(5)
O(12)#2-K(1)-O(1)	92.2(5)	O(2)#2-K(3)-O(6)	120.9(5)
O(12)#2-K(1)-O(10)#8	89.4(5)	O(7)-K(3)-O(6)	84.9(4)
O(1)-K(1)-O(10)#8	176.9(5)	O(8)#8-K(3)-O(6)	115.2(4)
O(12)#2-K(1)-O(4)#8	98.1(5)	O(9)-K(3)-O(6)	46.3(4)
O(1)-K(1)-O(4)#8	105.3(4)	O(11)#2-K(3)-O(6)	153.1(4)
O(10)#8-K(1)-O(4)#8	77.1(5)	O(5)#10-K(3)-O(6)	72.9(4)
O(12)#2-K(1)-O(2)#1	111.8(5)	O(8)-P(1)-O(4)	115.5(9)
O(1)-K(1)-O(2)#1	90.7(4)	O(8)-P(1)-O(6)	113.7(9)
O(10)#8-K(1)-O(2)#1	86.2(4)	O(4)-P(1)-O(6)	107.8(9)
O(4)#8-K(1)-O(2)#1	145.5(4)	O(8)-P(1)-O(9)	106.3(8)
O(12)#2-K(1)-O(7)#5	160.7(5)	O(4)-P(1)-O(9)	108.0(8)
O(1)-K(1)-O(7)#5	104.3(4)	O(6)-P(1)-O(9)	105.0(8)
O(10)#8-K(1)-O(7)#5	74.7(4)	O(12)-P(2)-O(13)	119.4(10)
O(4)#8-K(1)-O(7)#5	68.2(4)	O(12)-P(2)-O(14)	113.7(9)
O(2)#1-K(1)-O(7)#5	78.4(4)	O(13)-P(2)-O(14)	109.7(9)
O(12)#2-K(1)-O(13)	77.8(5)	O(12)-P(2)-O(1)	106.1(10)

O(1)-K(1)-O(13)	47.9(4)	O(13)-P(2)-O(1)	100.7(9)
O(10)#8-K(1)-O(13)	135.1(5)	O(14)-P(2)-O(1)	105.5(8)
O(4)#8-K(1)-O(13)	62.8(4)	O(7)-P(3)-O(10)	115.0(9)
O(2)#1-K(1)-O(13)	138.5(4)	O(7)-P(3)-O(3)	113.1(9)
O(7)#5-K(1)-O(13)	105.8(4)	O(10)-P(3)-O(3)	110.3(8)
O(12)#2-K(1)-O(3)#5	142.7(5)	O(7)-P(3)-O(9)	103.1(8)
O(1)-K(1)-O(3)#5	61.4(4)	O(10)-P(3)-O(9)	107.1(9)
O(10)#8-K(1)-O(3)#5	118.5(4)	O(3)-P(3)-O(9)	107.6(8)
O(4)#8-K(1)-O(3)#5	67.8(4)	O(11)-P(4)-O(5)	112.9(9)
O(2)#1-K(1)-O(3)#5	95.4(4)	O(11)-P(4)-O(2)	112.4(9)
O(7)#5-K(1)-O(3)#5	46.2(4)	O(5)-P(4)-O(2)	109.6(9)
O(13)-K(1)-O(3)#5	64.9(4)	O(11)-P(4)-O(1)	107.1(9)
O(12)#2-K(1)-O(5)	114.9(5)	O(5)-P(4)-O(1)	106.5(9)
O(1)-K(1)-O(5)	46.0(4)	O(2)-P(4)-O(1)	108.2(8)
O(10)#8-K(1)-O(5)	130.9(5)	O(7)#5-K(1)-O(5)	84.1(4)
O(4)#8-K(1)-O(5)	134.2(4)	O(13)-K(1)-O(5)	92.9(4)
O(2)#1-K(1)-O(5)	45.9(4)	O(3)#5-K(1)-O(5)	66.8(4)

Symmetry transformations used to generate equivalent atoms:

#1 -*x*, *y*+1/2, -*z*+1 #2 -*x*+1, *y*+1/2, -*z*+1

#3 *x*-1, *y*, *z*+1 #4 -*x*, *y*+1/2, -*z*+2 #5 *x*-1, *y*, *z*

#6 *x*, *y*, *z*+1 #7 -*x*+1, *y*-1/2, -*z*+1 #8 -*x*+1, *y*+1/2, -*z*

#9 -*x*+1, *y*-1/2, -*z* #10 *x*+1, *y*, *z* #11 -*x*, *y*-1/2, -*z*+2

#12 *x*, *y*, *z*-1 #13 *x*+1, *y*, *z*-1 #14 -*x*, *y*-1/2, -*z*+1

Table S5. Bond lengths (Å) and angles (°) for $Rb_3SrBi(P_2O_7)_2$.

Bi(1)-O(7)	2.14(2)	Rb(3)-O(11)#12	2.97(2)
Bi(1)-O(5)#1	2.20(2)	Rb(3)-O(3)	2.98(2)
Bi(1)-O(12)	2.30(2)	Rb(3)-O(12)#11	2.99(3)
Bi(1)-O(11)#1	2.364(19)	Rb(3)-O(6)#12	3.08(2)
Bi(1)-O(10)	2.51(2)	Rb(3)-O(13)#13	3.25(4)
Bi(1)-O(1)#2	2.55(2)	Rb(3)-O(4)#12	3.25(3)
Rb(1)-O(4)#9	2.948(19)	Rb(3)-O(2)#11	3.47(3)
Rb(1)-O(7)#1	2.99(3)	Rb(3)-O(8)#11	3.49(3)
Rb(1)-O(14)#7	3.00(3)	Rb(3)-O(2)#13	3.50(3)
Rb(1)-O(9)#1	3.01(2)	P(1)-O(6)	1.46(2)
Rb(1)-O(1)#7	3.08(2)	P(1)-O(5)	1.51(2)
Rb(1)-O(5)#5	3.12(2)	P(1)-O(7)	1.58(2)
Rb(1)-O(10)	3.21(2)	P(1)-O(9)	1.591(19)
Rb(1)-O(13)#7	3.29(4)	P(2)-O(4)	1.452(19)
Rb(1)-O(6)#5	3.56(3)	P(2)-O(3)	1.48(2)
Rb(2)-O(14)#10	3.00(3)	P(2)-O(11)	1.520(19)
Rb(2)-O(2)#10	3.01(3)	P(2)-O(9)	1.627(19)
Rb(2)-O(9)#11	3.022(19)	P(3)-O(2)	1.51(2)
Rb(2)-O(4)#11	3.04(2)	P(3)-O(13)	1.52(3)
Rb(2)-O(11)	3.128(19)	P(3)-O(12)	1.54(2)
Rb(2)-O(3)	3.15(3)	P(3)-O(14)	1.64(3)
Rb(2)-O(6)#11	3.24(3)	P(4)-O(1)	1.51(2)
Rb(2)-O(8)#10	3.25(3)	P(4)-O(8)	1.51(2)
Rb(2)-O(12)#11	3.28(2)	P(4)-O(10)	1.52(2)
Sr(1)-O(2)#4	2.40(2)	P(4)-O(14)	1.61(3)
Sr(1)-O(13)#5	2.43(3)	Sr(1)-O(6)#5	2.55(2)
Sr(1)-O(8)	2.46(2)	Sr(1)-O(1)#7	2.66(2)
Sr(1)-O(3)#6	2.53(2)	Sr(1)-O(10)#7	2.71(2)
O(7)-Bi(1)-O(5)#1	75.6(9)	O(14)#10-Rb(2)-O(2)#10	49.3(6)
O(7)-Bi(1)-O(12)	82.8(9)	O(14)#10-Rb(2)-O(9)#11	121.2(7)
O(5)#1-Bi(1)-O(12)	82.1(8)	O(2)#10-Rb(2)-O(9)#11	100.3(6)
O(7)-Bi(1)-O(11)#1	95.3(9)	O(14)#10-Rb(2)-O(4)#11	76.1(7)
O(5)#1-Bi(1)-O(11)#1	80.7(8)	O(2)#10-Rb(2)-O(4)#11	83.4(8)
O(12)-Bi(1)-O(11)#1	162.6(7)	O(9)#11-Rb(2)-O(4)#11	48.1(5)
O(7)-Bi(1)-O(10)	154.6(8)	O(14)#10-Rb(2)-O(11)	89.4(6)
O(5)#1-Bi(1)-O(10)	86.9(8)	O(2)#10-Rb(2)-O(11)	138.6(5)
O(12)-Bi(1)-O(10)	76.7(7)	O(9)#11-Rb(2)-O(11)	100.5(5)
O(11)#1-Bi(1)-O(10)	99.9(6)	O(4)#11-Rb(2)-O(11)	84.4(6)
O(7)-Bi(1)-O(1)#2	84.1(8)	O(14)#10-Rb(2)-O(3)	111.5(7)
O(5)#1-Bi(1)-O(1)#2	154.8(9)	O(2)#10-Rb(2)-O(3)	141.4(7)
O(12)-Bi(1)-O(1)#2	110.5(8)	O(9)#11-Rb(2)-O(3)	116.9(5)
O(11)#1-Bi(1)-O(1)#2	86.4(7)	O(4)#11-Rb(2)-O(3)	128.6(6)

O(10)-Bi(1)-O(1)#2	116.8(6)	O(11)-Rb(2)-O(3)	46.6(5)
O(2)#4-Sr(1)-O(13)#5	89.3(13)	O(14)#10-Rb(2)-O(6)#11	101.9(7)
O(2)#4-Sr(1)-O(8)	94.6(10)	O(2)#10-Rb(2)-O(6)#11	59.2(5)
O(13)#5-Sr(1)-O(8)	173.0(10)	O(9)#11-Rb(2)-O(6)#11	46.9(5)
O(2)#4-Sr(1)-O(3)#6	81.9(7)	O(4)#11-Rb(2)-O(6)#11	68.4(6)
O(13)#5-Sr(1)-O(3)#6	83.9(9)	O(11)-Rb(2)-O(6)#11	146.6(5)
O(8)-Sr(1)-O(3)#6	90.9(8)	O(3)-Rb(2)-O(6)#11	145.1(6)
O(2)#4-Sr(1)-O(6)#5	77.3(8)	O(14)#10-Rb(2)-O(8)#10	47.3(7)
O(13)#5-Sr(1)-O(6)#5	100.3(9)	O(2)#10-Rb(2)-O(8)#10	79.5(6)
O(8)-Sr(1)-O(6)#5	86.2(8)	O(9)#11-Rb(2)-O(8)#10	164.2(5)
O(3)#6-Sr(1)-O(6)#5	158.7(7)	O(4)#11-Rb(2)-O(8)#10	116.6(5)
O(2)#4-Sr(1)-O(1)#7	144.7(7)	O(11)-Rb(2)-O(8)#10	71.1(6)
O(13)#5-Sr(1)-O(1)#7	82.7(10)	O(3)-Rb(2)-O(8)#10	67.5(6)
O(8)-Sr(1)-O(1)#7	97.3(8)	O(6)#11-Rb(2)-O(8)#10	138.1(6)
O(3)#6-Sr(1)-O(1)#7	130.8(7)	O(14)#10-Rb(2)-O(12)#11	138.1(7)
O(6)#5-Sr(1)-O(1)#7	70.5(7)	O(2)#10-Rb(2)-O(12)#11	102.7(6)
O(2)#4-Sr(1)-O(10)#7	158.9(7)	O(9)#11-Rb(2)-O(12)#11	90.8(5)
O(13)#5-Sr(1)-O(10)#7	87.0(11)	O(4)#11-Rb(2)-O(12)#11	138.7(5)
O(8)-Sr(1)-O(10)#7	87.3(8)	O(11)-Rb(2)-O(12)#11	112.3(5)
O(3)#6-Sr(1)-O(10)#7	77.0(6)	O(3)-Rb(2)-O(12)#11	68.8(6)
O(6)#5-Sr(1)-O(10)#7	123.8(7)	O(6)#11-Rb(2)-O(12)#11	79.8(6)
O(1)#7-Sr(1)-O(10)#7	55.2(6)	O(8)#10-Rb(2)-O(12)#11	104.7(6)
O(4)#9-Rb(1)-O(7)#1	101.3(7)	O(11)#12-Rb(3)-O(3)	106.0(5)
O(4)#9-Rb(1)-O(14)#7	77.6(7)	O(11)#12-Rb(3)-O(12)#11	124.7(5)
O(7)#1-Rb(1)-O(14)#7	172.2(7)	O(3)-Rb(3)-O(12)#11	75.0(6)
O(4)#9-Rb(1)-O(9)#1	86.1(6)	O(11)#12-Rb(3)-O(6)#12	68.3(5)
O(7)#1-Rb(1)-O(9)#1	48.2(5)	O(3)-Rb(3)-O(6)#12	156.1(7)
O(14)#7-Rb(1)-O(9)#1	138.8(7)	O(12)#11-Rb(3)-O(6)#12	127.9(7)
O(4)#9-Rb(1)-O(1)#7	99.7(6)	O(11)#12-Rb(3)-O(13)#13	124.9(7)
O(7)#1-Rb(1)-O(1)#7	127.3(6)	O(3)-Rb(3)-O(13)#13	64.2(7)
O(14)#7-Rb(1)-O(1)#7	46.1(7)	O(12)#11-Rb(3)-O(13)#13	105.6(7)
O(9)#1-Rb(1)-O(1)#7	173.6(6)	O(6)#12-Rb(3)-O(13)#13	99.2(7)
O(4)#9-Rb(1)-O(5)#5	100.8(7)	O(11)#12-Rb(3)-O(4)#12	46.9(5)
O(7)#1-Rb(1)-O(5)#5	51.5(6)	O(3)-Rb(3)-O(4)#12	91.1(6)
O(14)#7-Rb(1)-O(5)#5	120.9(7)	O(12)#11-Rb(3)-O(4)#12	161.5(6)
O(9)#1-Rb(1)-O(5)#5	99.1(5)	O(6)#12-Rb(3)-O(4)#12	67.9(6)
O(1)#7-Rb(1)-O(5)#5	77.4(6)	O(13)#13-Rb(3)-O(4)#12	78.2(7)
O(4)#9-Rb(1)-O(10)	134.2(6)	O(11)#12-Rb(3)-O(2)#11	162.4(6)
O(7)#1-Rb(1)-O(10)	86.5(6)	O(3)-Rb(3)-O(2)#11	59.6(5)
O(14)#7-Rb(1)-O(10)	99.8(7)	O(12)#11-Rb(3)-O(2)#11	45.2(6)
O(9)#1-Rb(1)-O(10)	65.8(5)	O(6)#12-Rb(3)-O(2)#11	129.0(5)
O(1)#7-Rb(1)-O(10)	111.0(4)	O(13)#13-Rb(3)-O(2)#11	60.6(7)
O(5)#5-Rb(1)-O(10)	118.1(6)	O(4)#12-Rb(3)-O(2)#11	136.4(5)
O(4)#9-Rb(1)-O(13)#7	82.0(8)	O(11)#12-Rb(3)-O(8)#11	123.9(6)

O(7)#1-Rb(1)-O(13)#7	141.6(6)	O(3)-Rb(3)-O(8)#11	129.8(6)
O(14)#7-Rb(1)-O(13)#7	46.1(7)	O(12)#11-Rb(3)-O(8)#11	72.9(5)
O(9)#1-Rb(1)-O(13)#7	94.6(6)	O(6)#12-Rb(3)-O(8)#11	62.5(5)
O(1)#7-Rb(1)-O(13)#7	88.8(6)	O(13)#13-Rb(3)-O(8)#11	88.8(8)
O(5)#5-Rb(1)-O(13)#7	166.2(7)	O(4)#12-Rb(3)-O(8)#11	125.6(6)
O(10)-Rb(1)-O(13)#7	66.1(7)	O(2)#11-Rb(3)-O(8)#11	70.3(5)
O(4)#9-Rb(1)-O(6)#5	134.8(7)	O(11)#12-Rb(3)-O(2)#13	109.5(5)
O(7)#1-Rb(1)-O(6)#5	78.2(6)	O(3)-Rb(3)-O(2)#13	108.8(6)
O(14)#7-Rb(1)-O(6)#5	97.0(7)	O(12)#11-Rb(3)-O(2)#13	122.6(6)
O(9)#1-Rb(1)-O(6)#5	120.5(5)	O(6)#12-Rb(3)-O(2)#13	55.6(6)
O(1)#7-Rb(1)-O(6)#5	53.3(6)	O(13)#13-Rb(3)-O(2)#13	44.8(6)
O(5)#5-Rb(1)-O(6)#5	43.7(5)	O(4)#12-Rb(3)-O(2)#13	73.1(6)
O(10)-Rb(1)-O(6)#5	91.0(5)	O(2)#11-Rb(3)-O(2)#13	86.01(11)
O(13)#7-Rb(1)-O(6)#5	126.0(7)	O(8)#11-Rb(3)-O(2)#13	61.5(5)
O(6)-P(1)-O(5)	116.1(15)	O(2)-P(3)-O(13)	117(2)
O(6)-P(1)-O(7)	114.9(15)	O(2)-P(3)-O(12)	111.5(14)
O(5)-P(1)-O(7)	107.2(15)	O(13)-P(3)-O(12)	110.1(15)
O(6)-P(1)-O(9)	109.9(12)	O(2)-P(3)-O(14)	105.8(16)
O(5)-P(1)-O(9)	105.8(11)	O(13)-P(3)-O(14)	103(2)
O(7)-P(1)-O(9)	101.4(12)	O(12)-P(3)-O(14)	108.2(13)
O(4)-P(2)-O(3)	116.4(13)	O(1)-P(4)-O(8)	114.0(13)
O(4)-P(2)-O(11)	113.8(13)	O(1)-P(4)-O(10)	111.0(12)
O(3)-P(2)-O(11)	111.8(13)	O(8)-P(4)-O(10)	115.5(14)
O(4)-P(2)-O(9)	106.7(12)	O(1)-P(4)-O(14)	99.5(13)
O(3)-P(2)-O(9)	104.6(13)	O(8)-P(4)-O(14)	107.5(17)
O(11)-P(2)-O(9)	101.9(11)	O(10)-P(4)-O(14)	107.7(13)

Symmetry transformations used to generate equivalent atoms:

#1 -*x*+1, *y*+1/2, -*z*+1 #2 -*x*+1, *y*-1/2, -*z*+2

#3 -*x*+1, *y*-1/2, -*z*+1 #4 -*x*+2, *y*+1/2, -*z*+2

#5 *x*, *y*+1, *z* #6 *x*, *y*+1, *z*+1 #7 -*x*+1, *y*+1/2, -*z*+2

#8 -*x*+2, *y*+3/2, -*z*+1 #9 *x*-1, *y*+1, *z* #10 *x*, *y*-1, *z*-1

#11 -*x*+2, *y*-1/2, -*z*+1 #12 -*x*+2, *y*+1/2, -*z*+1

#13 *x*, *y*, *z*-1 #14 *x*, *y*-1, *z* #15 *x*, *y*, *z*+1

#16 -*x*+2, *y*-1/2, -*z*+2 #17 *x*+1, *y*-1, *z*

Table S6. The dipole moments of single P–O and Bi–O units in $K_3SrBi(P_2O_7)_2$ and $Rb_3SrBi(P_2O_7)_2$.

		a	b	c	Magnitude
$K_3SrBi(P_2O_7)_2$	$Bi(1)O_6$	4.14	-0.83	-2.10	4.16
	$P(1)O_4$	1.56	2.32	0.34	2.76
	$P(2)O_4$	4.21	2.43	-0.14	4.83
	$P(3)O_4$	-2.67	-1.25	0.13	2.92
	$P(4)O_4$	-0.73	0.67	1.39	1.53
	$P(1)P(3)O_7$	-1.11	1.06	0.47	1.51
	$P(2)P(4)O_7$	3.48	3.10	1.25	4.56
	Average(P_2O_7)	—	—	—	3.04
$Rb_3SrBi(P_2O_7)_2$	$Bi(1)O_6$	1.52	-1.79	-0.89	2.36
	$P(1)O_4$	-0.81	2.13	3.19	3.74
	$P(2)O_4$	3.69	2.36	-0.81	4.26
	$P(3)O_4$	-2.26	1.46	1.06	2.65
	$P(4)O_4$	2.27	-3.45	2.74	4.60
	$P(1)P(2)O_7$	2.88	4.49	2.38	5.51
	$P(3)P(4)O_4$	0.01	-1.99	3.80	4.29
	Average(P_2O_7)	—	—	—	4.90

Table S7. ϕ and Θ angles of $K_3SrBi(P_2O_7)_2$ and $Rb_3SrBi(P_2O_7)_2$.

		$K_3SrBi(P_2O_7)_2$	$Rb_3SrBi(P_2O_7)_2$
P_2O_7	ϕ_1	24.6	85.1
	ϕ_2	115.1	45.5
	ϕ_3	73.7	132.0
	ϕ_4	57.4	54.6
	ϕ	67.7	79.3
BiO_6	Θ_1	66.9	54.2
	Θ_2	26.5	149.6
	Θ_3	133.7	125.6
	Θ_4	71.6	32.9
	Θ_5	145.5	95.5
	Θ_6	76.4	72.1
	Θ	86.8	88.3

Table S8. SHG and UV cut-off edges of compounds in the family of $A_3BBi(P_2O_7)_2$.

Compound	SHG (× KDP)	UV cut-off edge (nm)
$Rb_3PbBi(P_2O_7)_2$[1]	2.8	285
$Cs_3PbBi(P_2O_7)_2$[1]	1.1	276
$Rb_3BaBi(P_2O_7)_2$[2]	2.5	241
$Cs_3BaBi(P_2O_7)_2$[2]	0.8	244
$Cs_3CaBi(P_2O_7)_2$[3]	——	285
$Cs_3SrBi(P_2O_7)_2$[3]	——	288
$K_3SrBi(P_2O_7)_2$	4.0	~240
$Rb_3SrBi(P_2O_7)_2$	2.1	~240

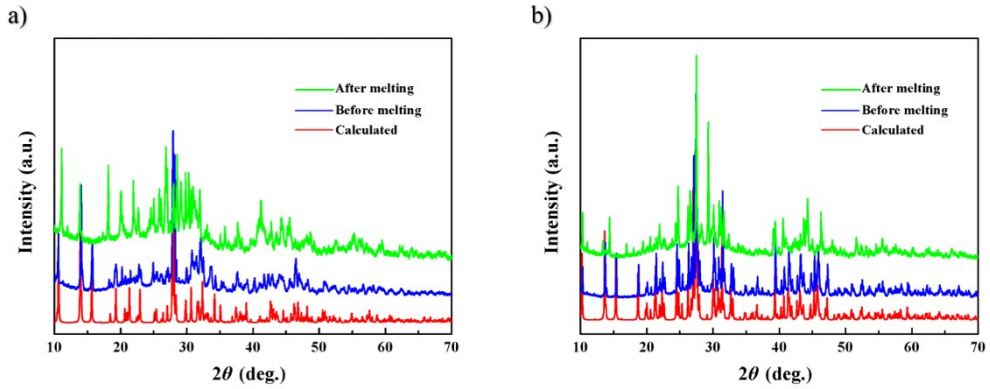


Figure S1. PXRD patterns of a) $K_3SrBi(P_2O_7)_2$ and b) $Rb_3SrBi(P_2O_7)_2$.

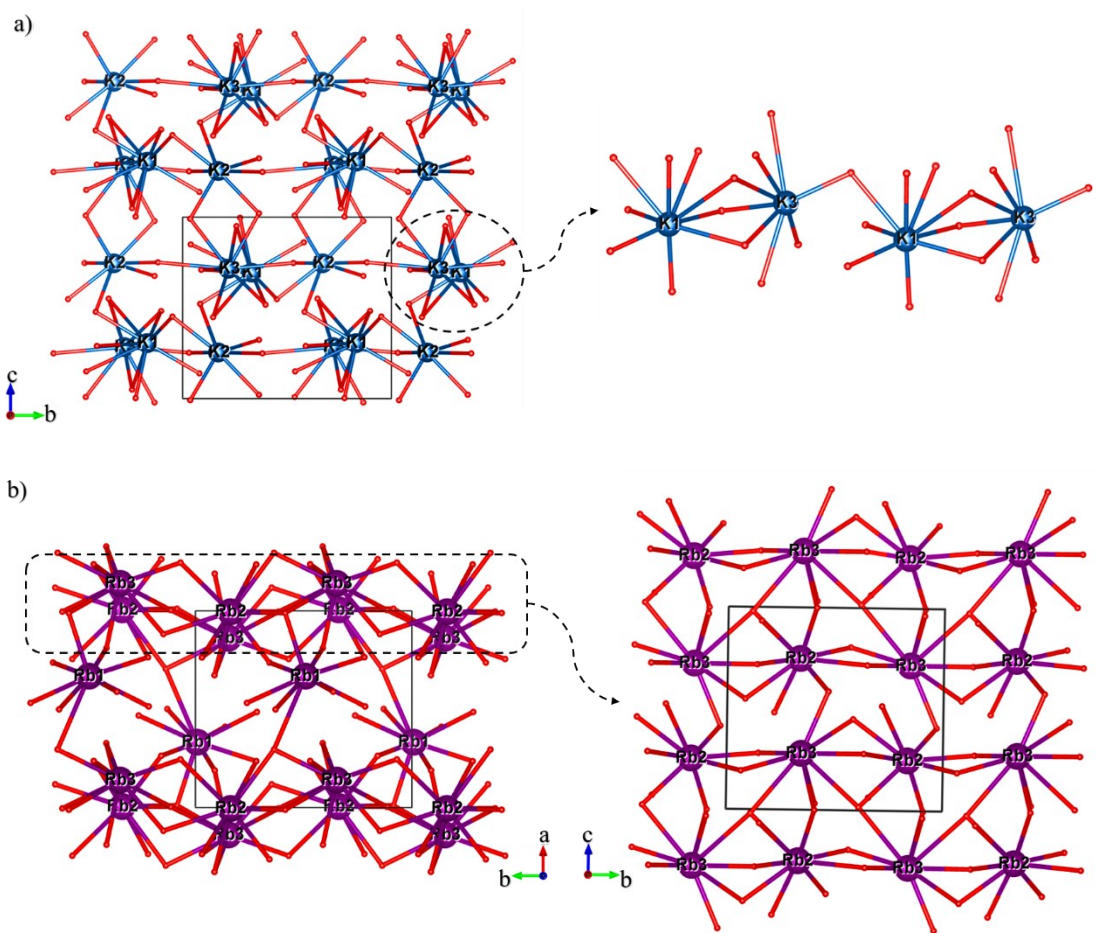


Figure S2. a) K–O framework of $K_3SrBi(P_2O_7)_2$ and b) Rb–O framework of $Rb_3SrBi(P_2O_7)_2$.

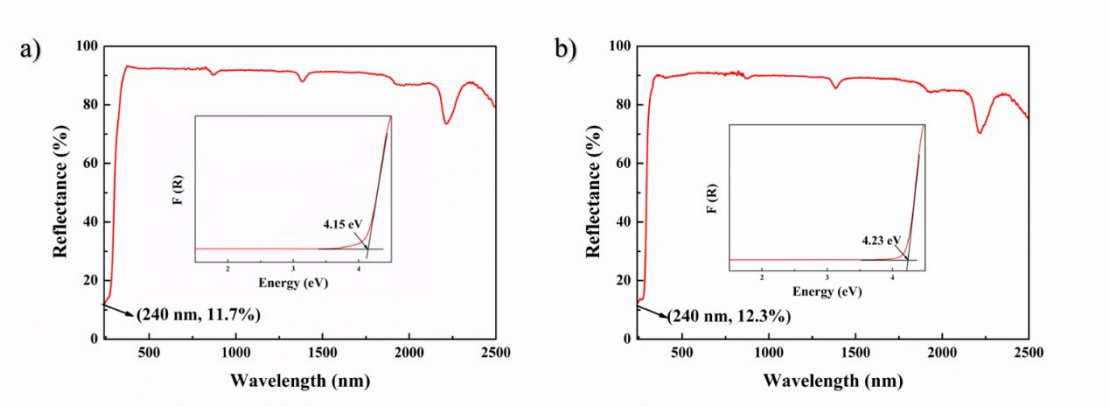


Figure S3. UV-Vis-NIR diffuse reflectance and absorption spectra of a) $K_3SrBi(P_2O_7)_2$ and b) $Rb_3SrBi(P_2O_7)_2$.

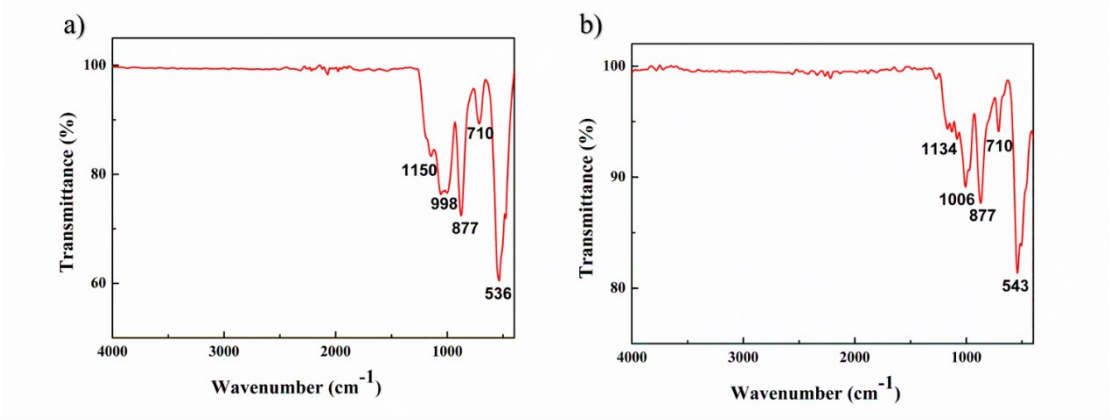


Figure S4. IR spectra of a) $K_3SrBi(P_2O_7)_2$ and b) $Rb_3SrBi(P_2O_7)_2$.

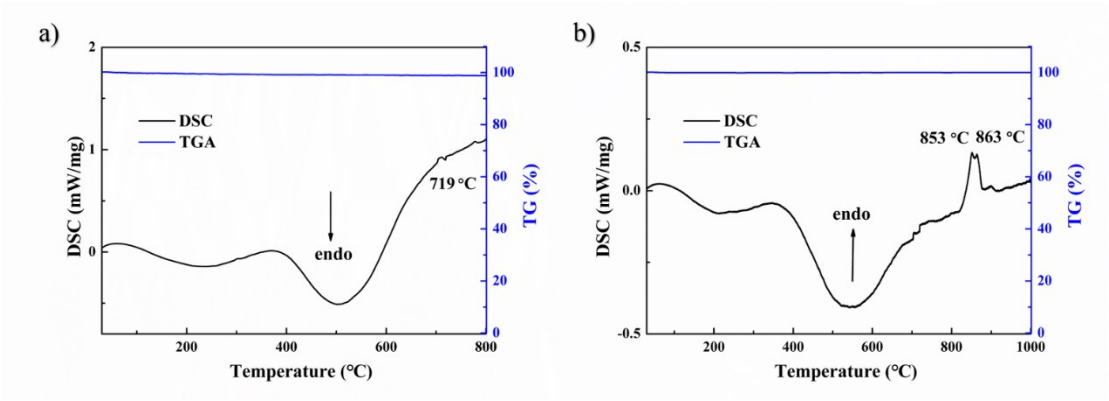
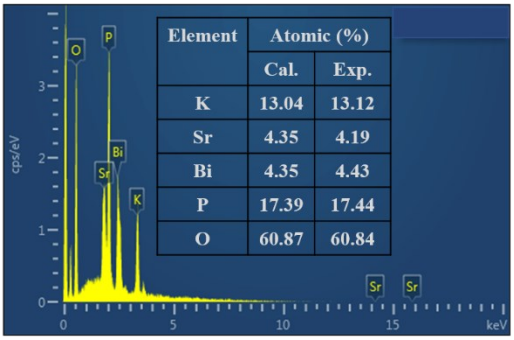


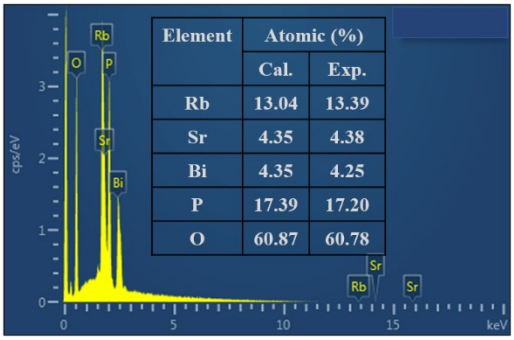
Figure S5. TG and DSC curves of a) $K_3SrBi(P_2O_7)_2$ and b) $Rb_3SrBi(P_2O_7)_2$.

a)



Element	Atomic (%)	
	Cal.	Exp.
K	13.04	13.12
Sr	4.35	4.19
Bi	4.35	4.43
P	17.39	17.44
O	60.87	60.84

b)



Element	Atomic (%)	
	Cal.	Exp.
Rb	13.04	13.39
Sr	4.35	4.38
Bi	4.35	4.25
P	17.39	17.20
O	60.87	60.78

Figure S6. EDS spectra of a) $K_3SrBi(P_2O_7)_2$ and b) $Rb_3SrBi(P_2O_7)_2$.

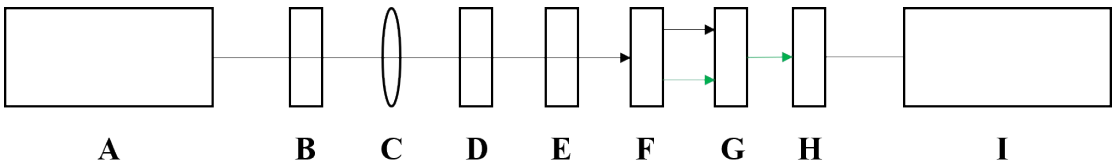


Figure S7. Experimental optical path diagram of SHG measurement (A: Nd^{3+} laser, B: filter, C: lens, D: attenuator, E: 1064 nm filter, F: sample, G: 532 nm filter, H: photomultiplier tube, I: oscilloscope).

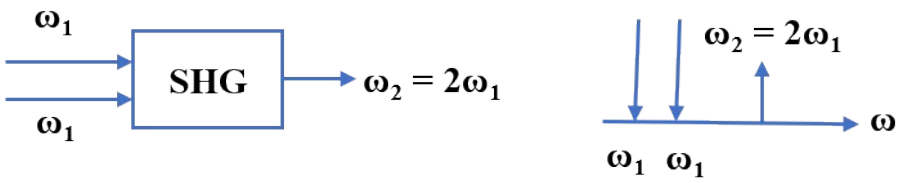


Figure S8. The schematic diagram of the second harmonic generation (SHG).

REFERENCES

[1] X.F. Lu, Z. H. Chen, X. R. Shi, Q. Jing and M. H. Lee, Two pyrophosphates with large birefringences and second-harmonic responses as ultraviolet nonlinear optical materials, *Angew. Chem. It. Ed.*, 2020, **59**, 17648–17654.

[2] L. Qi, Z. H. Chen, X. R. Shi, X. D. Zhang, Q. Jing, N. Li, Z. Q. Jiang, B. B. Zhang and M. H. Lee, $A_3BBi(P_2O_7)_2$ (A = Rb, Cs; B = Pb, Ba): isovalent cation substitution to sustain large second-harmonic generation responses, *Chem. Mater.*, 2020, **32**, 8713–8723.

[3] I. Zatovsky, N. Strutynska, Y. Hizhnyi, V. N. Baumer, I. V. Ogorodnyk, N. S. Slobodyanik, I. V. Odynets and K. Nickolai, New complex phosphates $Cs_3M^{II}Bi(P_2O_7)_2$ (M^{II} = Ca, Sr, Pb): synthesis, characterization, crystal and electronic structure, *Dalton Trans.*, 2018, **47**, 2274–2283.