Supporting Information

$A_3BBi(P_2O_7)_2$ (A = Rb, Cs; B = Pb, Ba): Isovalent Cation Substitution to Sustain Large Second Harmonic Generation Responses

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Table S1. Crystal data and structure refinements for **I** and **II**.

Empirical formula	$Rb_3BaBi(P_2O_7)_2$ (**I**)	$Cs_3BaBi(P_2O_7)_2$ (**II**)
Formula weight	950.61	1092.93
Temperature/K	273(2)	273(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
space group	$P2_1$	$P2_12_12_1$
a (Å)	8.9377(3)	9.4656(3)
b (Å)	9.8247(4)	9.9015(3)
c (Å)	9.1683(4)	17.6265(6)
β (°)	106.7460(10)	
Volume/ Å^3	770.93(5)	1652.02(9)
Z, Calculated density/ (g/cm^3)	2, 4.095	4, 4.394
Absorption coefficient (mm^{-1})	23.827	19.972
F(000)	844	1904
Crystal size/(mm^3)	0.162 × 0.096 × 0.085	0.109 × 0.087 × 0.052
Theta range for data collection/°	3.16 to 27.54	3.19 to 27.54
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 12$, $-11 \le l \le 11$	$-11 \le h \le 12$, $-12 \le k \le 12$, $-22 \le l \le 22$
Reflections collected / unique	11867 / 3476 [R(int) = 0.0360]	25550 / 3767 [R(int) = 0.0544]
Completeness / (%)	99.7	99.7
Refinement method	Full-matrix least-squares on F^2	
Data/restraint/parameters	3476 / 1 / 209	3767 / 6 / 209
Goodness-of-fit on F^2	0.981	0.907
Final R indices [I>2sigma(I)]$^\alpha$	R_1 = 0.0261, wR_2 = 0.0535	R_1 = 0.0211, wR_2 =0.0385
R indices (all data)$^\alpha$	R_1 = 0.0316, wR_2 = 0.0545	R_1 = 0.0258, wR_2 = 0.0394
Extinction coefficient	0.00101(13)	0.00381(6)
Largest diff. peak and hole/(e/Å^3)	1.015 and -0.881	0.732 and -0.763

$^\alpha R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ 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 ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sum (BVS) calculation for **I**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Rb(1)	4853(1)	3647(1)	12606(1)	26(1)	1.01
Rb(2)	11765(1)	228(1)	3092(1)	31(1)	0.91
Rb(3)	6823(1)	-997 (1)	2984(1)	38(1)	0.85
Ba(1)	7561(1)	1887(1)	9851(1)	16(1)	2.25
Bi(1)	10023(1)	50(1)	7274(1)	14(1)	2.84
P(1)	8812(2)	-2089(2)	10161(3)	18(1)	4.74
P(2)	8708(3)	2336(2)	14371(3)	19(1)	4.99
P(3)	6284(2)	1667(2)	5876(3)	20(1)	4.74
P(4)	6742(3)	5716(2)	10533(3)	20(1)	5.00
O(1)	7674(7)	4702(6)	9942(7)	32(2)	1.74
O(2)	5812(7)	2573(7)	6988(8)	36(2)	1.94
O(3)	10776(7)	2752(6)	11318(7)	27(2)	1.64
O(4)	7416(7)	5762(7)	12281(8)	31(2)	1.87
O(5)	5043(7)	5579(7)	10039(9)	37(2)	2.01
O(6)	10244(8)	-1419(7)	5393(9)	47(2)	1.97
O(7)	12530(7)	-2328(6)	4714(7)	23(2)	2.19
O(8)	10002(6)	-2840(6)	11451(6)	19(1)	1.96
O(9)	8537(8)	-648(6)	10559(8)	35(2)	1.91
O(10)	7119(7)	-2815(6)	9970(8)	34(2)	2.16
O(11)	7845(8)	2105(9)	12754(7)	49(2)	2.03
O(12)	9675(9)	1149(8)	15144(9)	52(2)	2.25
O(13)	7311(7)	465(6)	6664(8)	36(2)	1.99
O(14)	4990(8)	1257(7)	4515(8)	42(2)	1.73

Table S3. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sum (BVS) calculation for **II**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cs(1)	-2595(1)	-1550(1)	1607(1)	27(1)	0.99
Cs(2)	3890(1)	-13(1)	-12(1)	22(1)	0.98
Cs(3)	4179(1)	-5015(1)	886(1)	29(1)	0.83
Ba(1)	642(1)	1848(1)	1327(1)	11(1)	2.29
Bi(1)	2692(1)	-1475(1)	2403(1)	10(1)	2.90
P(1)	1323(2)	-2100(2)	810(1)	14(1)	4.91
P(2)	4753(2)	1364(2)	1920(1)	12(1)	4.93
P(3)	392(2)	5799(2)	1919(1)	12(1)	4.76
P(4)	-3057(2)	2093(2)	774(1)	14(1)	4.84
O(1)	1333(4)	-3468(4)	2496(2)	16(1)	1.97
O(2)	4568(5)	-31(5)	2257(3)	34(1)	2.00
O(3)	4571(4)	-2734(4)	2495(3)	26(1)	2.21
O(4)	-2718(5)	3284(4)	1287(2)	28(1)	1.97
O(5)	-1808(5)	1220(5)	618(3)	28(1)	1.95
O(6)	-3882(5)	2528(5)	84(3)	31(1)	1.95
O(7)	-1118(5)	5773(4)	2203(2)	22(1)	1.63
O(8)	950(5)	4442(4)	1685(3)	34(1)	1.85
O(9)	5910(4)	1106(4)	1267(2)	16(1)	2.23
O(10)	2790(5)	-2279(4)	1161(2)	20(1)	2.04
O(11)	337(5)	-3279(5)	1162(3)	30(1)	2.23
O(12)	3454(5)	1937(6)	1571(3)	36(1)	1.89
O(13)	716(6)	-821(5)	1128(4)	55(2)	1.81
O(14)	1278(5)	-2274(6)	-24(3)	47(2)	1.72

Table S4. Selected bond distances (Å) and angles (deg) for **I**.

Rb(1)-O(13)#1	2.851(6)	P(1)-O(9)	1.499(6)
Rb(1)-O(10)#1	2.889(6)	P(1)-O(3)#7	1.512(6)
Rb(1)-O(14)#2	2.910(7)	P(1)-O(8)	1.533(6)
Rb(1)-O(7)#3	3.019(6)	P(1)-O(10)	1.636(6)
Rb(1)-O(11)	3.042(7)	P(2)-O(11)	1.478(7)
Rb(1)-O(5)	3.066(7)	P(2)-O(12)	1.502(7)
Rb(1)-O(4)	3.170(6)	P(2)-O(6)#3	1.518(7)
Rb(2)-O(7)	2.898(6)	P(2)-O(7)#3	1.604(6)
Rb(2)-O(3)#4	2.958(6)	P(3)-O(14)	1.492(7)
Rb(2)-O(14)#5	2.978(7)	P(3)-O(2)	1.503(7)
Rb(2)-O(1)#6	3.009(7)	P(3)-O(13)	1.541(6)
Rb(2)-O(12)#4	3.142(7)	P(3)-O(7)#11	1.650(6)
Rb(2)-O(6)	3.251(8)	P(4)-O(5)	1.460(7)
Rb(2)-O(9)#4	3.255(7)	P(4)-O(1)	1.497(6)
Rb(2)-O(2)#6	3.404(7)	P(4)-O(4)	1.542(7)
Rb(2)-O(8)#4	3.530(6)	P(4)-O(10)#13	1.601(6)
Rb(3)-O(2)#8	2.748(6)	O(9)-P(1)-O(3)#7	114.5(4)
Rb(3)-O(9)#4	3.061(7)	O(9)-P(1)-O(8)	113.1(4)
Rb(3)-O(5)#8	3.194(8)	O(3)#7-P(1)-O(8)	110.4(3)
Rb(3)-O(11)#4	3.206(9)	O(9)-P(1)-O(10)	103.1(4)
Rb(3)-O(6)	3.241(7)	O(3)#7-P(1)-O(10)	108.4(4)
Rb(3)-O(14)	3.298(8)	O(8)-P(1)-O(10)	106.7(3)
Rb(3)-O(4)#9	3.321(7)	O(11)-P(2)-O(12)	114.7(5)
Rb(3)-O(10)#4	3.364(7)	O(11)-P(2)-O(6)#3	112.9(5)
Rb(3)-O(12)#4	3.458(10)	O(12)-P(2)-O(6)#3	108.1(5)
Rb(3)-O(13)	3.576(8)	O(11)-P(2)-O(7)#3	108.4(4)
Ba(1)-O(11)	2.609(6)	O(12)-P(2)-O(7)#3	107.6(4)
Ba(1)-O(9)	2.657(6)	O(6)#3-P(2)-O(7)#3	104.5(4)
Ba(1)-O(5)#10	2.686(7)	O(14)-P(3)-O(2)	115.2(4)
Ba(1)-O(2)	2.724(7)	O(14)-P(3)-O(13)	113.5(4)
Ba(1)-O(1)	2.768(6)	O(2)-P(3)-O(13)	112.5(4)
Ba(1)-O(8)#3	2.782(5)	O(14)-P(3)-O(7)#11	107.6(4)
Ba(1)-O(3)	2.926(6)	O(2)-P(3)-O(7)#11	101.6(4)
Ba(1)-O(13)	3.188(8)	O(13)-P(3)-O(7)#11	105.1(3)
Bi(1)-O(12)#4	2.175(7)	O(5)-P(4)-O(1)	117.6(4)
Bi(1)-O(6)	2.301(7)	O(5)-P(4)-O(4)	112.7(4)
Bi(1)-O(4)#7	2.315(6)	O(1)-P(4)-O(4)	107.7(4)
Bi(1)-O(13)	2.361(6)	O(5)-P(4)-O(10)#13	106.2(4)
Bi(1)-O(8)#3	2.383(5)	O(1)-P(4)-O(10)#13	107.0(4)
		O(4)-P(4)-O(10)#13	104.6(4)

Symmetry transformations used to generate equivalent atoms:

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

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

#7 -x+2,y-1/2,-z+2 #8 -x+1,y-1/2,-z+1 #9 x,y-1,z-1
#10 -x+1,y-1/2,-z+2 #11 -x+2,y+1/2,-z+1 #12 -x+1,y+1/2,-z+1
#13 x,y+1,z #14 x,y+1,z+1 #15 x,y-1,z
#16 x-1,y,z

Table S5 Selected bond distances (Å) and angles (deg) for **II**.

Cs(1)-O(9)#1	3.047(4)	P(1)-O(14)	1.482(5)
Cs(1)-O(7)#2	3.175(4)	P(1)-O(13)	1.499(5)
Cs(1)-O(14)#3	3.206(6)	P(1)-O(10)	1.530(5)
Cs(1)-O(2)#1	3.284(5)	P(1)-O(11)	1.618(5)
Cs(1)-O(3)#1	3.319(4)	P(2)-O(12)	1.488(5)
Cs(1)-O(13)	3.326(6)	P(2)-O(3)#12	1.508(4)
Cs(1)-O(5)	3.335(5)	P(2)-O(2)	1.514(5)
Cs(1)-O(11)	3.354(5)	P(2)-O(9)	1.608(4)
Cs(1)-O(8)#4	3.528(5)	P(3)-O(8)	1.502(4)
Cs(1)-O(12)#4	3.636(5)	P(3)-O(7)	1.515(5)
Cs(1)-O(1)#5	3.639(4)	P(3)-O(1)#13	1.534(4)
Cs(2)-O(11)#6	2.974(4)	P(3)-O(11)#13	1.617(5)
Cs(2)-O(9)	3.157(4)	P(4)-O(5)	1.490(5)
Cs(2)-O(4)#7	3.209(4)	P(4)-O(6)	1.507(5)
Cs(2)-O(10)	3.224(4)	P(4)-O(4)	1.521(4)
Cs(2)-O(6)#8	3.287(5)	P(4)-O(9)#1	1.633(4)
Cs(2)-O(14)	3.336(5)	O(14)-P(1)-O(13)	117.2(4)
Cs(2)-O(12)	3.418(5)	O(14)-P(1)-O(10)	114.5(3)
Cs(2)-O(14)#6	3.511(6)	O(13)-P(1)-O(10)	107.1(3)
Cs(2)-O(8)#7	3.580(5)	O(14)-P(1)-O(11)	106.3(3)
Cs(2)-O(6)#7	3.600(5)	O(13)-P(1)-O(11)	104.2(3)
Cs(3)-O(10)	3.050(4)	O(10)-P(1)-O(11)	106.6(2)
Cs(3)-O(5)#6	3.054(5)	O(12)-P(2)-O(3)#12	114.1(3)
Cs(3)-O(12)#2	3.322(5)	O(12)-P(2)-O(2)	114.5(3)
Cs(3)-O(6)#9	3.359(5)	O(3)#12-P(2)-O(2)	108.7(3)
Cs(3)-O(14)#6	3.375(6)	O(12)-P(2)-O(9)	109.1(3)
Cs(3)-O(8)#2	3.408(5)	O(3)#12-P(2)-O(9)	107.1(2)
Cs(3)-O(4)#9	3.458(5)	O(2)-P(2)-O(9)	102.4(2)
Cs(3)-O(2)#10	3.481(5)	O(8)-P(3)-O(7)	114.0(3)
Cs(3)-O(3)	3.644(5)	O(8)-P(3)-O(1)#13	113.7(3)
Ba(1)-O(6)#7	2.603(5)	O(7)-P(3)-O(1)#13	109.7(2)
Ba(1)-O(8)	2.660(4)	O(8)-P(3)-O(11)#13	106.9(3)
Ba(1)-O(13)	2.667(5)	O(7)-P(3)-O(11)#13	104.6(3)
Ba(1)-O(12)	2.698(5)	O(1)#13-P(3)-O(11)#13	107.3(2)
Ba(1)-O(5)	2.707(5)	O(5)-P(4)-O(6)	115.3(3)
Ba(1)-O(1)#5	2.810(4)	O(5)-P(4)-O(4)	113.1(3)
Ba(1)-O(7)#4	2.838(4)	O(6)-P(4)-O(4)	111.6(3)
Bi(1)-O(3)	2.177(4)	O(5)-P(4)-O(9)#1	103.1(2)
Bi(1)-O(2)	2.295(5)	O(6)-P(4)-O(9)#1	106.9(3)
Bi(1)-O(4)#4	2.321(4)	O(4)-P(4)-O(9)#1	105.9(2)
Bi(1)-O(10)	2.332(4)		
Bi(1)-O(1)	2.361(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z
#2 x,y-1,z
#3 x-1/2,-y-1/2,-z
#4 -x,y-1/2,-z+1/2
#5 -x,y+1/2,-z+1/2
#6 x+1/2,-y-1/2,-z
#7 x+1/2,-y+1/2,-z
#8 x+1,y,z
#9 x+1,y-1,z
#10 -x+1,y-1/2,-z+1/2
#11 x-1/2,-y+1/2,-z
#12 -x+1,y+1/2,-z+1/2
#13 x,y+1,z
#14 x-1,y+1,z

Table S6. Anisotropic displacement parameters ($A^2 \times 10^3$) for **I**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^2\ U11 + ... + 2\ h\ k\ a\times b\times U12\ ]$.

	U11	U22	U33	U23	U13	U12
Rb(1)	24(1)	27(1)	24(1)	3(1)	3(1)	7(1)
Rb(2)	33(1)	28(1)	32(1)	9(1)	11(1)	4(1)
Rb(3)	38(1)	46(1)	35(1)	-8(1)	20(1)	-13(1)
Ba(1)	18(1)	14(1)	14(1)	-1(1)	4(1)	-1(1)
Bi(1)	13(1)	15(1)	14(1)	2(1)	3(1)	1(1)
P(1)	11(1)	14(1)	25(1)	5(1)	2(1)	2(1)
P(2)	21(1)	24(1)	14(1)	9(1)	9(1)	5(1)
P(3)	14(1)	29(1)	14(1)	9(1)	1(1)	0(1)
P(4)	14(1)	17(1)	29(1)	1(1)	7(1)	-3(1)
O(1)	36(4)	19(4)	43(4)	-6(3)	17(4)	3(3)
O(2)	34(4)	50(5)	28(4)	-3(3)	16(3)	3(3)
O(3)	33(4)	30(4)	14(3)	2(3)	1(3)	0(3)
O(4)	21(3)	41(4)	33(4)	-6(3)	11(3)	0(3)
O(5)	10(3)	46(4)	52(4)	5(3)	1(3)	-3(3)
O(6)	50(5)	45(5)	52(5)	-8(4)	26(4)	18(4)
O(7)	25(3)	27(4)	20(3)	0(3)	9(3)	0(2)
O(8)	17(3)	17(3)	21(3)	10(3)	1(3)	-1(2)
O(9)	42(4)	15(3)	54(5)	-1(3)	24(4)	6(3)
O(10)	18(3)	18(4)	58(5)	17(3)	1(3)	-1(2)
O(11)	49(5)	82(6)	20(4)	1(4)	15(4)	0(4)
O(12)	59(5)	63(6)	48(5)	42(4)	39(4)	43(4)
O(13)	21(3)	24(4)	60(5)	21(3)	5(3)	-4(3)
O(14)	36(4)	47(5)	32(4)	3(3)	-8(4)	-16(3)

Table S7. Anisotropic displacement parameters ($A^2 \times 10^3$) for **II**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^2\ U11 + ... + 2\ h\ k\ a\times b\times U12\ ]$.

	U11	U22	U33	U23	U13	U12
Cs(1)	23(1)	25(1)	34(1)	8(1)	4(1)	7(1)
Cs(2)	24(1)	23(1)	19(1)	-2(1)	3(1)	-3(1)
Cs(3)	30(1)	24(1)	34(1)	-4(1)	0(1)	7(1)
Ba(1)	12(1)	12(1)	11(1)	1(1)	1(1)	0(1)
Bi(1)	10(1)	9(1)	11(1)	1(1)	-1(1)	1(1)
P(1)	17(1)	12(1)	15(1)	3(1)	-1(1)	-2(1)
P(2)	9(1)	13(1)	16(1)	-4(1)	2(1)	-3(1)
P(3)	17(1)	10(1)	11(1)	0(1)	1(1)	-2(1)
P(4)	11(1)	20(1)	10(1)	2(1)	-1(1)	-4(1)
O(1)	19(2)	20(2)	9(2)	1(2)	2(2)	-9(2)
O(2)	37(3)	19(2)	47(3)	0(2)	16(3)	-4(2)
O(3)	18(2)	37(3)	23(3)	17(2)	9(2)	13(2)
O(4)	51(3)	22(3)	12(2)	2(2)	-2(2)	-22(2)
O(5)	12(2)	46(3)	26(3)	2(2)	2(2)	6(2)
O(6)	38(3)	40(3)	15(2)	6(2)	-8(2)	7(2)
O(7)	20(3)	28(3)	20(3)	0(2)	3(2)	-6(2)
O(8)	35(3)	17(2)	49(3)	-11(2)	3(3)	7(2)
O(9)	13(2)	18(2)	16(2)	-4(2)	6(2)	-4(2)
O(10)	18(3)	28(3)	14(2)	-1(2)	3(2)	3(2)
O(11)	32(2)	31(2)	27(2)	10(2)	-4(2)	-11(2)
O(12)	13(3)	60(4)	35(3)	10(3)	-1(2)	3(3)
O(13)	34(3)	19(3)	112(5)	-23(3)	-21(4)	14(3)
O(14)	39(3)	89(5)	12(3)	12(3)	-4(3)	-18(3)

Table S8. Dipole moments for **I**

Species			Dipole moments			
			x **(a)**	***y*** **(b)**	***z*** **(c)**	**Magnitude**
						Debye
Bi	$Bi(1)O_5$		-0.15	2.58	-3.07	3.98
			-0.15	2.58	-3.07	3.98
			-0.15	2.58	-3.07	3.98
			-0.15	2.58	-3.07	3.98
			0.30	5.16	6.14	7.96
			0.30	5.16	6.14	7.96
	Sum		**0**	**20.64**	**0**	**20.64**
P	P_2O_7	$P(1)O_4$	2.45	-1.11	-0.19	2.75
		$P(4)O_4$	-1.89	2.92	-0.72	3.44
	P_2O_7	$P(2)O_4$	-0.23	1.41	2.23	2.70
		$P(3)O_4$	2.85	2.64	-0.28	3.95
	P_2O_7	$P(1)O_4$	-2.45	-1.11	0.19	2.75
		$P(4)O_4$	1.89	2.92	0.72	3.44
	P_2O_7	$P(2)O_4$	0.23	1.41	-2.23	2.70
		$P(3)O_4$	-2.85	2.64	0.28	3.95
	Sum		**0**	**11.72**	**0**	**11.72**
Unit cell			**0**	**32.36**	**0**	**32.36**

Table S9. Dipole moments for **II**

Species			Dipole moments			
			x **(a)**	***y*** **(b)**	***z*** **(c)**	**Magnitude**
						Debye
Bi	$Bi(1)O_5$		11.22	-10.80	0.92	15.59
			-11.22	10.80	0.92	15.59
			11.22	10.80	-0.92	15.59
			-11.22	-10.80	-0.92	15.59
	Sum		**0**	**0**	**0**	**0**
P	P_2O_7	$P(1)O_4$	-1.41	-1.73	2.82	3.60
		$P(3)O_4$	-0.80	1.99	-1.71	2.74
	P_2O_7	$P(2)O_4$	2.72	-1.68	-0.76	3.28
		$P(4)O_4$	-1.76	-2.02	2.25	3.50
	P_2O_7	$P(1)O_4$	1.41	-1.73	-2.82	3.60
		$P(3)O_4$	0.80	1.99	1.71	2.74
	P_2O_7	$P(2)O_4$	-2.72	-1.68	0.76	3.28
		$P(4)O_4$	1.76	-2.02	-2.25	3.50
	P_2O_7	$P(1)O_4$	1.41	1.73	2.82	3.60
		$P(3)O_4$	0.80	-1.99	-1.71	2.74
	P_2O_7	$P(2)O_4$	-2.72	1.68	-0.76	3.28
		$P(4)O_4$	1.76	2.02	2.25	3.50
	P_2O_7	$P(1)O_4$	-1.41	1.73	-2.82	3.60
		$P(3)O_4$	-0.80	-1.99	1.71	2.74
	P_2O_7	$P(2)O_4$	2.72	1.68	0.76	3.28
		$P(4)O_4$	-1.76	2.02	-2.25	3.50
	Sum		**0**	**0**	**0**	**0**
Unit cell			**0**	**0**	**0**	**0**

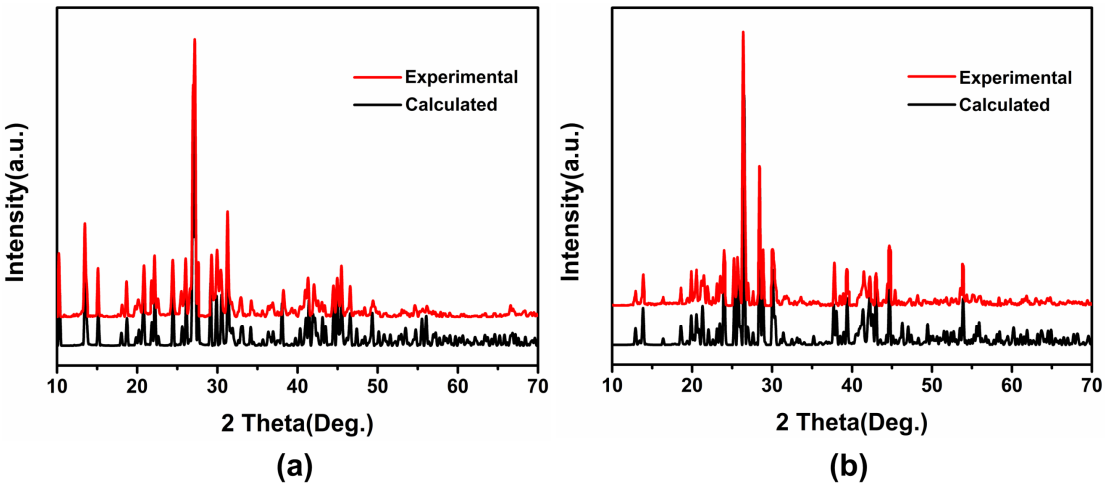

Figure S1. Calculated and experimental PXRD patterns of (a) **I** and (b) **II**.

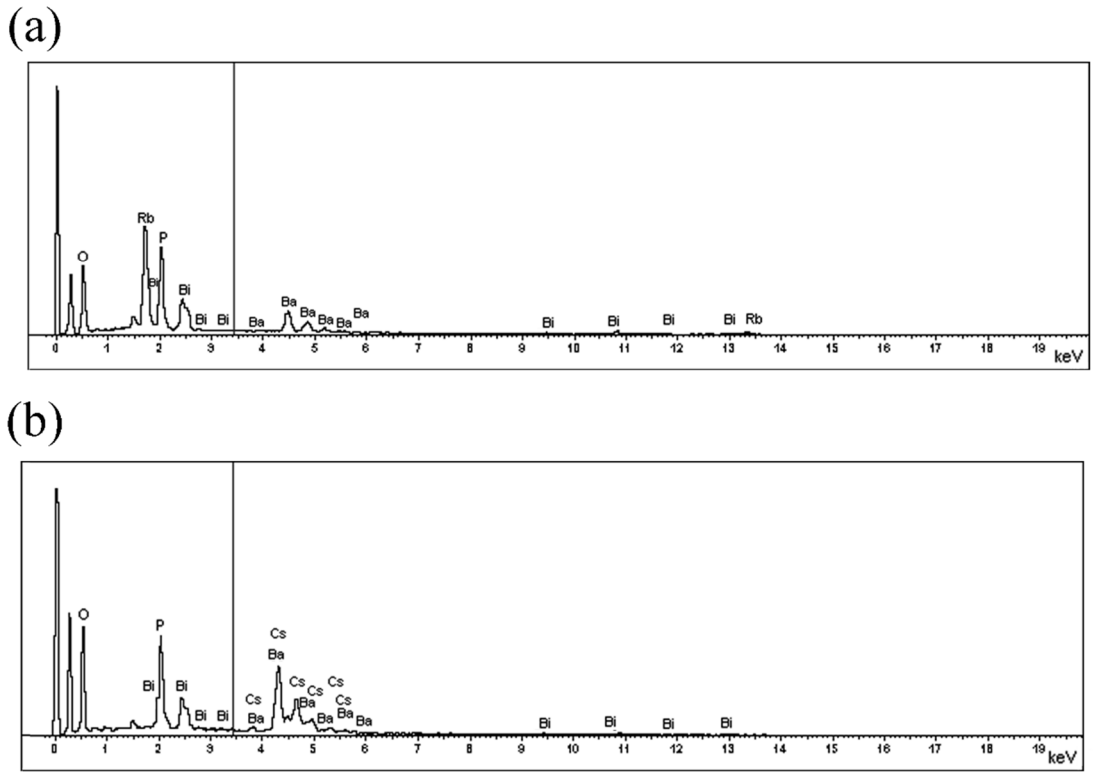

Figure S2. The energy-dispersive spectroscopy of (a) **I** and (b) **II**.

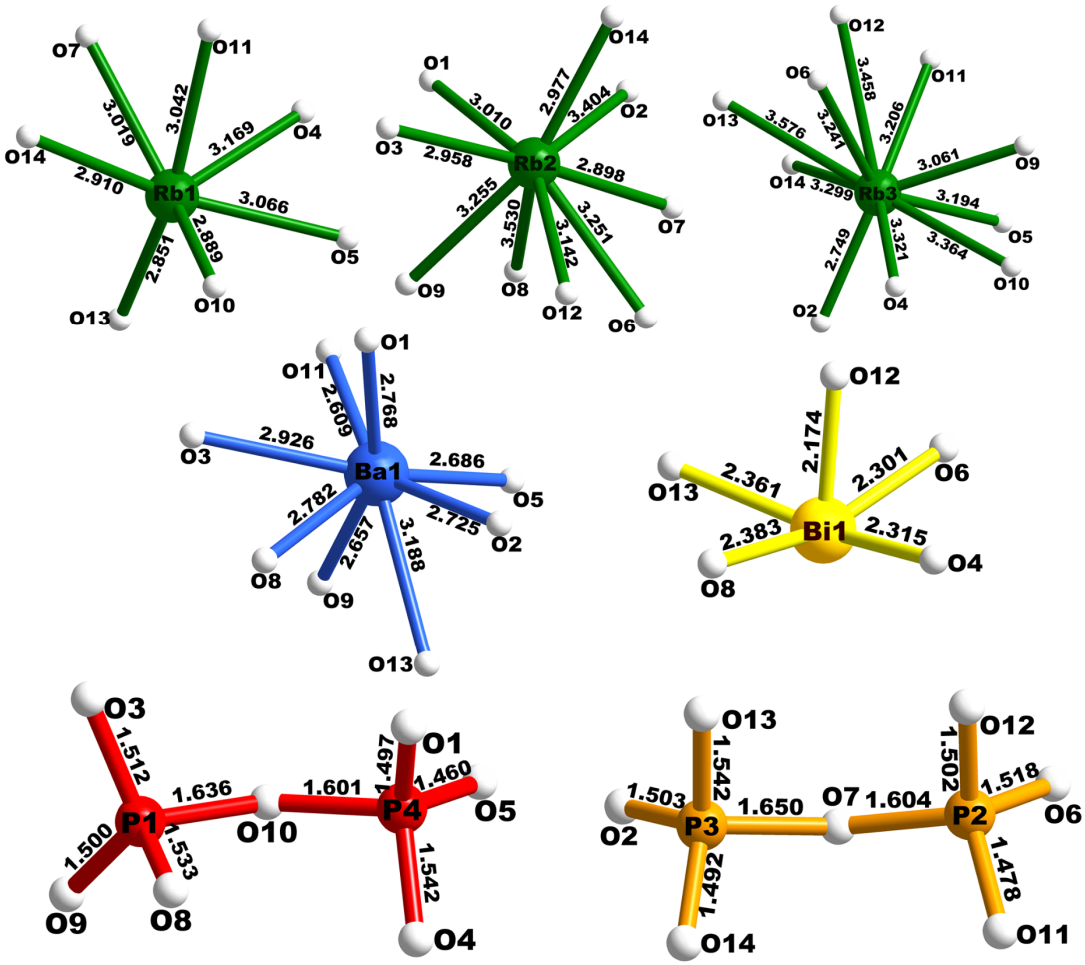

Figure S3. Atomic coordination environments of **I**.

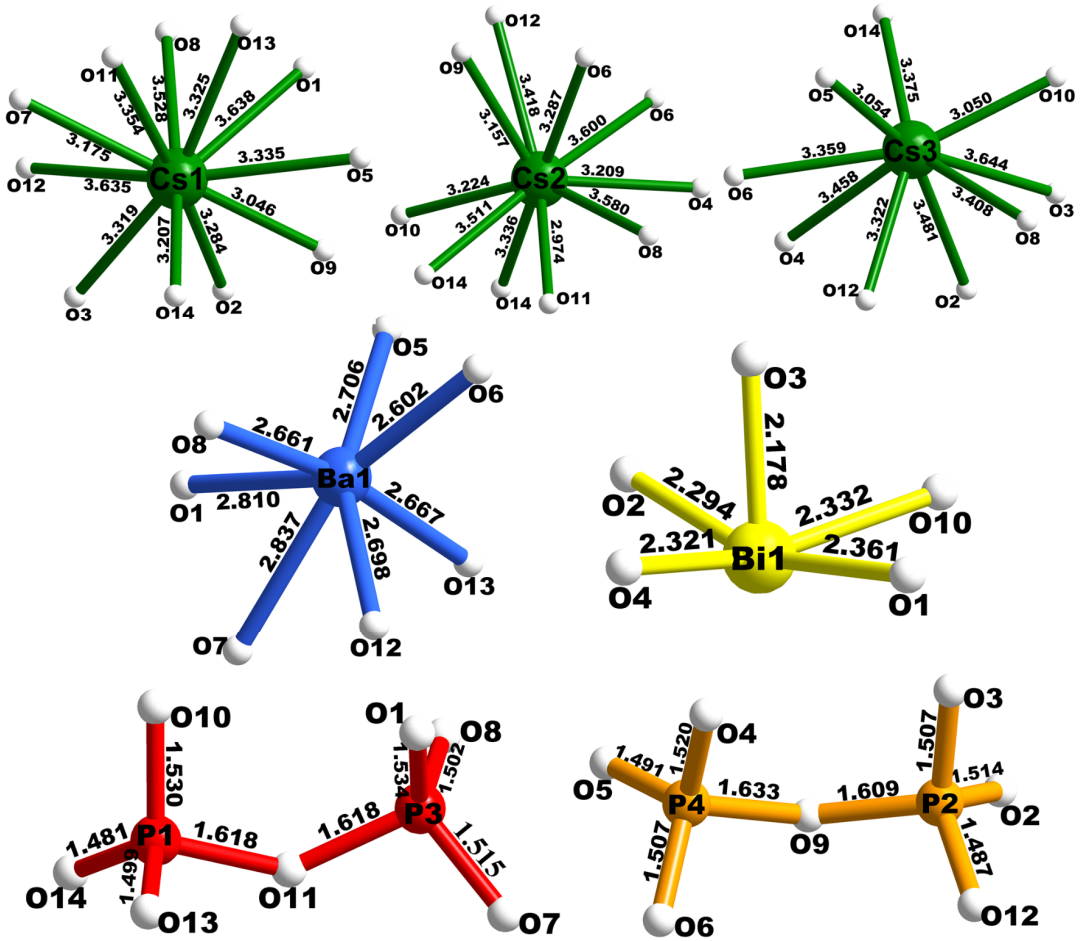

Figure S4. Atomic coordination environments of **II**.

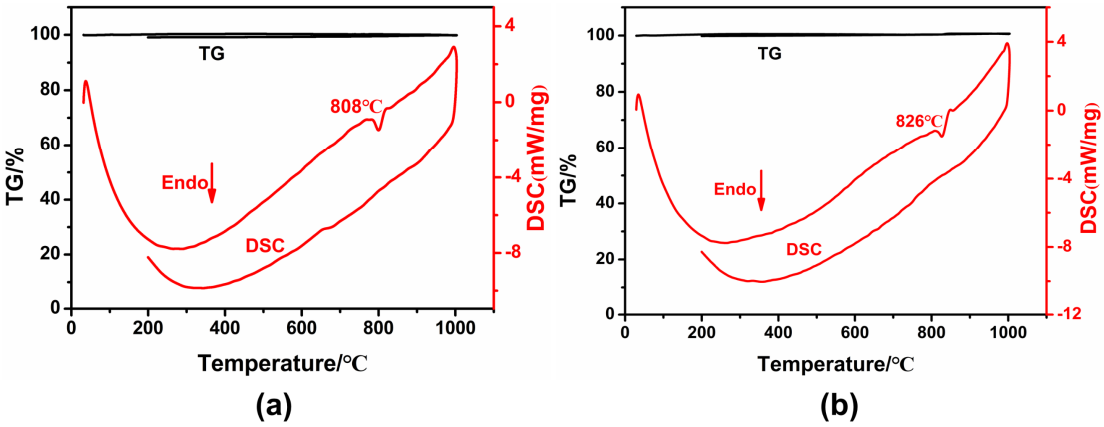

Figure S5. TG-DSC curves of **I** (a) and **II** (b).

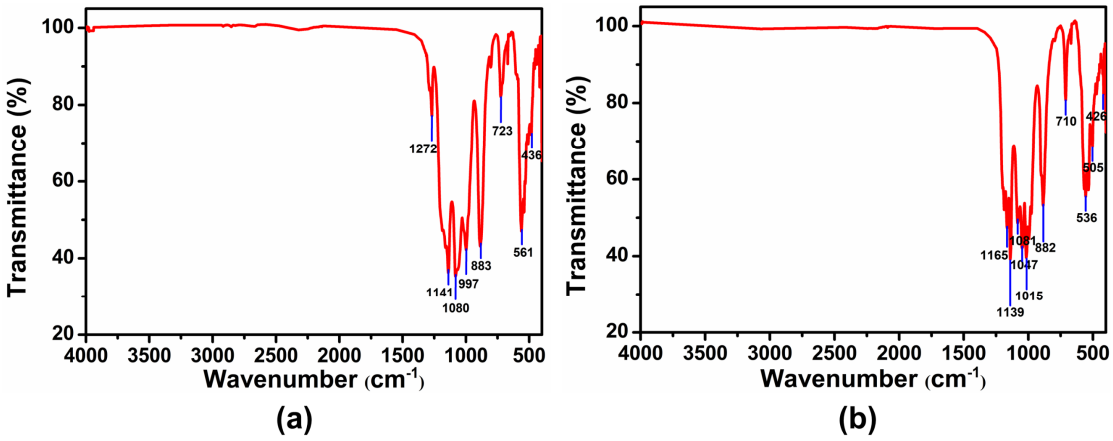

Figure S6. Infrared spectra of **I** (a) and **II** (b).

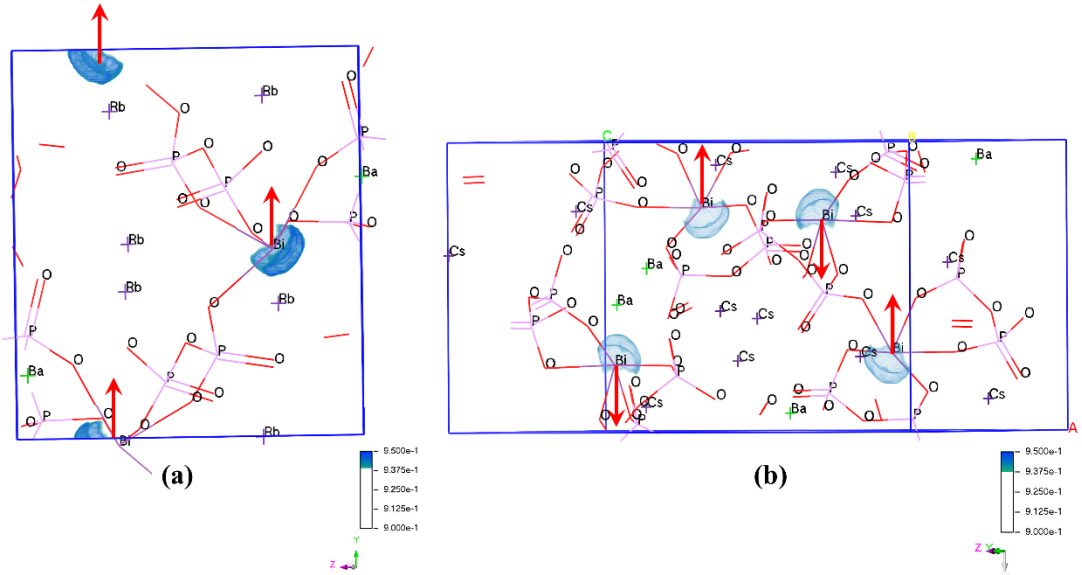

Figure S7. The ELF of **I** (a) and **II** (b).

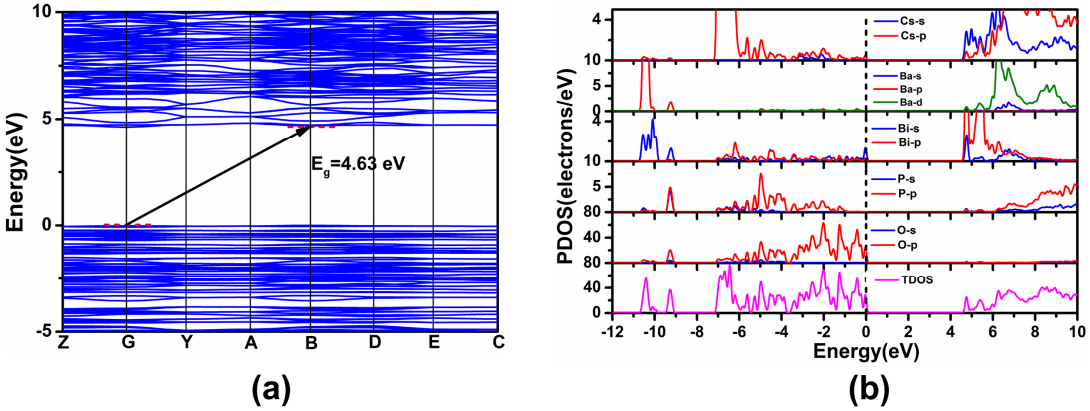

Figure S8. Band structure and projected density of states (PDOS) of suppositional crystal *v*-$Cs_3BaBi(P_2O_7)_2$.