Low-Temperature-Flux Syntheses for Ultraviolet-Transparent Borophosphates $Na_4MB_2P_3O_{13}$ (M = Rb, Cs) Exhibiting Second-Harmonic Generation Response

Chao Wu,[a,b,c] Longhua Li,[d] Junling Song,[a] Gang Yang,[a] Bing Yan,[b] Mark G. Humphrey,[b,e] Long Zhang,[c] Jianda Shao,[c] and Chi Zhang*[,a,b,c]

[a] China-Australia Joint Research Center for Functional Molecular Materials, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China

[b] China-Australia Joint Laboratory for Functional Molecules and Ordered Matter, School of Chemical Science and Engineering, Tongji University, 200092, P. R. China.

[c] Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, P. R. China. E-mail: czhang@siom.ac.cn

[d] China-Australia Joint Research Center for Functional Molecular Materials, Jiangsu University, Zhenjiang 212013, P. R. China

[e] Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

Table S1. Selected bond distances (Å) and angles (deg) for $Na_4RbB_2P_3O_{13}$[a].

P(1)-O(5)	1.483(8)	P(1)-O(14)	1.501(7)
P(1)-O(2)	1.570(5)	P(1)-O(15)	1.580(5)
P(2)-O(4)	1.500(7)	P(2)-O(16)	1.503(7)
P(2)-O(8)	1.566(5)	P(2)-O(11)	1.575(5)
P(3)-O(3)	1.494(6)	P(3)-O(6)	1.527(7)
P(3)-O(10)	1.570(5)	P(3)-O(9)	1.583(5)
P(4)-O(12)	1.497(7)	P(4)-O(26)	1.508(8)
P(4)-O(21)	1.575(5)	P(4)-O(19)	1.578(5)
P(5)-O(23)	1.497(7)	P(5)-O(17)	1.508(8)
P(5)-O(13)	1.570(5)	P(5)-O(24)	1.590(5)
P(6)-O(27)	1.480(7)	P(6)-O(22)	1.500(5)
P(6)-O(20)	1.567(5)	P(6)-O(25)	1.572(5)
B(1)-O(13)	1.501(9)	B(1)-O(18)	1.409(8)
B(1)-O(19)	1.521(10)	B(1)-O(20)	1.454(8)
B(2)-O(18)	1.432(8)	B(2)-O(21)	1.496(10)
B(2)-O(24)	1.507(10)	B(2)-O(25)#1	1.458(9)
B(3)-O(2)	1.501(9)	B(3)-O(7)	1.413(8)
B(3)-O(9)	1.435(8)	B(3)-O(11)	1.530(9)
B(4)-O(7)	1.421(9)	B(4)-O(8)	1.497(10)
B(4)-O(15)	1.514(10)	B(4)-O(10)#2	1.470(9)
O(5)-P(1)-O(14)	115.6(4)	O(5)-P(1)-O(2)	108.5(3)
O(14)-P(1)-O(2)	109.4(3)	O(5)-P(1)-O(15)	108.2(3)
O(14)-P(1)-O(15)	110.5(3)	O(2)-P(1)-O(15)	104.0(3)
O(4)-P(2)-O(16)	116.5(5)	O(4)-P(2)-O(8)	109.1(4)
O(16)-P(2)-O(8)	107.0(3)	O(4)-P(2)-O(11)	109.1(3)
O(16)-P(2)-O(11)	107.8(3)	O(8)-P(2)-O(11)	106.9(3)
O(3)-P(3)-O(6)	114.6(4)	O(3)-P(3)-O(10)	107.4(3)
O(6)-P(3)-O(10)	110.7(3)	O(3)-P(3)-O(9)	111.1(3)
O(6)-P(3)-O(9)	110.4(4)	O(10)-P(3)-O(9)	101.9(3)
O(12)-P(4)-O(26)	116.7(5)	O(12)-P(4)-O(21)	107.1(3)
O(26)-P(4)-O(21)	109.2(4)	O(12)-P(4)-O(19)	108.1(3)
O(26)-P(4)-O(19)	109.1(3)	O(21)-P(4)-O(19)	106.1(3)
O(23)-P(5)-O(17)	116.0(4)	O(23)-P(5)-O(13)	108.8(3)

O(17)-P(5)-O(13)	109.1(3)	O(23)-P(5)-O(24)	110.6(3)
O(17)-P(5)-O(24)	108.3(4)	O(13)-P(5)-O(24)	103.2(3)
O(27)-P(6)-O(22)	114.4(4)	O(27)-P(6)-O(20)	110.7(4)
O(22)-P(6)-O(20)	111.1(3)	O(27)-P(6)-O(25)	112.5(3)
O(22)-P(6)-O(25)	106.0(3)	O(20)-P(6)-O(25)	101.3(3)
O(18)-B(1)-O(20)	115.4(6)	O(18)-B(1)-O(13)	110.5(6)
O(20)-B(1)-O(13)	103.8(5)	O(18)-B(1)-O(19)	110.2(6)
O(20)-B(1)-O(19)	109.6(5)	O(13)-B(1)-O(19)	106.8(5)
O(18)-B(2)-O(25)#1	110.0(6)	O(18)-B(2)-O(21)	110.8(6)
O(25)#1-B(2)-O(21)	111.0(6)	O(18)-B(2)-O(24)	109.8(6)
O(25)#1-B(2)-O(24)	107.4(6)	O(21)-B(2)-O(24)	107.7(6)
O(7)-B(3)-O(9)	116.9(6)	O(7)-B(3)-O(2)	111.0(6)
O(9)-B(3)-O(2)	103.8(5)	O(7)-B(3)-O(11)	109.5(6)
O(9)-B(3)-O(11)	107.8(5)	O(2)-B(3)-O(11)	107.4(5)
O(7)-B(4)-O(10)#2	109.5(6)	O(7)-B(4)-O(8)	110.5(6)
O(10)#2-B(4)-O(8)	110.3(6)	O(7)-B(4)-O(15)	110.6(6)
O(10)#2-B(4)-O(15)	107.6(6)	O(8)-B(4)-O(15)	108.2(6)
Na(1)-O2#2	2.345(5)	Na(1)-O4#7	2.326(9)
Na(1)-O5#2	2.423(6)	Na(1)-O15	2.322(5)
Na(1)-O23#7	2.272(6)	Na(2)-O3	2.403(5)
Na(2)-O7	2.247(6)	Na(2)-O10#2	2.766(5)
Na(2)-O12	2.266(7)	Na(2)-O22#4	2.317(6)
Na(2)-O25#4	2.888(5)	Na(3)-O4#7	2.947(8)
Na(3)-O5#2	2.405(7)	Na(3)-O6#7	2.245(7)
Na(3)-O12#7	2.903(7)	Na(3)-O19#7	2.533(6)
Na(3)-O23#7	2.361(7)	Na(4)-O4#7	2.599(8)
Na(4)-O5	2.425(8)	Na(4)-O6#7	2.279(7)
Na(4)-O12#7	2.555(8)	Na(4)-O23#7	2.283(7)
Na(5)-O11#7	2.564(6)	Na(5)-O14#7	2.367(6)
Na(5)-O16#7	2.943(7)	Na(5)-O17#11	2.368(7)
Na(5)-O26#4	2.679(7)	Na(5)-O27#4	2.311(7)
Na(6)-O14	2.276(8)	Na(6)-O13#9	2.346(6)
Na(6)-O20#9	2.375(6)	Na(6)-O24#7	2.341(6)
Na(6)-O26#10	2.316(1)	Na(7)-O14#7	2.285(7)
Na(7)-O16#7	2.489(7)	Na(7)-O17#3	2.407(7)

Na(7)-O26#4	2.764(8)	Na(7)-O27#6	2.301(7)
Na(8)-O3#2	2.239(7)	Na(8)-O16#7	2.266(7)
Na(8)-O18#5	2.225(5)	Na(8)-O22#5	2.328(5)
Na(8)-O25#6	2.847(5)		
Rb(1)-O4#7	3.353(7)	Rb(1)-O5	2.945(7)
Rb(1)-O6#7	3.246(7)	Rb(1)-O8#9	3.055(5)
Rb(1)-O9#7	3.582(7)	Rb(1)-O11#7	2.947(5)
Rb(1)-O15	3.396(5)	Rb(1)-O16#9	3.318(6)
Rb(1)-O22#5	2.989(5)	Rb(1)-O27#5	3.439(7)
Rb(2)-O3#2	2.956(5)	Rb(2)-O6#2	3.393(7)
Rb(2)-O12#2	3.310(6)	Rb(2)-O17#4	2.967(7)
Rb(2)-O19	2.949(4)	Rb(2)-O21	3.065(5)
Rb(2)-O24#5	3.444(6)	Rb(2)-O26	3.325(6)
Rb(2)-O27	3.218(7)		

[a] Symmetry codes:
$Na_4RbB_2P_3O_{13}$: #1 x, y+1, z; #2 x, y–1, z; #3 x, y–1, z–1; #4 –x–1, –y–2, z–0.5; #5 –x–1, –y–2, z–0.5; #6 –x–1, –y–2, z–0.5; #7 –x–1.5, y–0.5, z–0.5; #8 –x–1.5, y–1.5, z–0.5; #9 –x–1.5, y+0.5, z–0.5; #10 x–0.5, –y–1.5, z; #11 x, y, z–1.

Table S2. Selected bond distances (Å) and angles (deg) for $Na_4CsB_2P_3O_{13}$[a].

P(1)-O(13)	1.500(5)	P(1)-O(5)	1.510(5)
P(1)-O(8)	1.562(4)	P(1)-O(12)	1.566(4)
P(2)-O(7)	1.498(6)	P(2)-O(14)	1.502(6)
P(2)-O(2)	1.573(4)	P(2)-O(4)	1.584(4)
P(3)-O(1)	1.481(6)	P(3)-O(9)	1.493(4)
P(3)-O(11)	1.569(4)	P(3)-O(10)	1.574(4)
P(4)-O(15)	1.482(6)	P(4)-O(16)	1.503(5)
P(4)-O(18)	1.569(4)	P(4)-O(17)	1.584(4)
P(5)-O(20)	1.496(6)	P(5)-O(19)	1.499(5)
P(5)-O(22)	1.567(4)	P(5)-O(21)	1.576(4)
P(6)-O(23)	1.490(6)	P(6)-O(26)	1.493(4)
P(6)-O(25)	1.564(4)	P(6)-O(24)	1.570(3)
B(1)-O(3)	1.428(7)	B(1)-O(4)	1.513(7)
B(1)-O(8)	1.499(7)	B(1)-O(11)	1.454(7)
B(2)-O(18)	1.478(7)	B(2)-O(21)	1.520(7)
B(2)-O(24)	1.461(7)	B(2)-O(27)	1.441(6)
B(3)-O(17)	1.507(7)	B(3)-O(22)	1.508(7)
B(3)-O(27)	1.416(6)	B(3)-O(25)#1	1.464(6)
B(4)-O(2)	1.506(7)	B(4)-O(3)	1.418(7)
B(4)-O(12)	1.508(7)	B(4)-O(10)#2	1.443(6)
O(13)-P(1)-O(5)	115.6(3)	O(13)-P(1)-O(8)	108.0(2)
O(5)-P(1)-O(8)	109.8(3)	O(13)-P(1)-O(12)	107.2(2)
O(5)-P(1)-O(12)	109.4(2)	O(8)-P(1)-O(12)	106.4(2)
O(7)-P(2)-O(14)	116.4(4)	O(7)-P(2)-O(2)	108.2(2)
O(14)-P(2)-O(2)	109.0(2)	O(7)-P(2)-O(4)	108.9(3)
O(14)-P(2)-O(4)	110.2(2)	O(2)-P(2)-O(4)	103.5(2)
O(1)-P(3)-O(9)	113.7(3)	O(1)-P(3)-O(11)	111.2(2)
O(9)-P(3)-O(11)	108.2(2)	O(1)-P(3)-O(10)	111.5(3)
O(9)-P(3)-O(10)	109.8(2)	O(11)-P(3)-O(10)	101.8(2)
O(15)-P(4)-O(16)	116.0(3)	O(15)-P(4)-O(18)	109.6(3)
O(16)-P(4)-O(18)	107.4(2)	O(15)-P(4)-O(17)	110.4(2)
O(16)-P(4)-O(17)	107.0(3)	O(18)-P(4)-O(17)	105.9(2)
O(20)-P(5)-O(19)	114.6(3)	O(20)-P(5)-O(22)	109.2(2)

O(19)-P(5)-O(22)	109.1(2)	O(20)-P(5)-O(21)	108.7(3)
O(19)-P(5)-O(21)	111.0(2)	O(22)-P(5)-O(21)	103.8(2)
O(23)-P(6)-O(26)	114.2(3)	O(23)-P(6)-O(25)	110.3(3)
O(26)-P(6)-O(25)	110.9(2)	O(23)-P(6)-O(24)	112.1(2)
O(26)-P(6)-O(24)	106.5(2)	O(25)-P(6)-O(24)	102.1(2)
O(3)-B(1)-O(11)	110.6(5)	O(3)-B(1)-O(8)	110.3(4)
O(11)-B(1)-O(8)	110.6(4)	O(3)-B(1)-O(4)	110.2(4)
O(11)-B(1)-O(4)	108.0(4)	O(8)-B(1)-O(4)	107.1(4)
O(27)-B(2)-O(24)	108.9(5)	O(27)-B(2)-O(18)	111.2(4)
O(24)-B(2)-O(18)	111.4(4)	O(27)-B(2)-O(21)	109.6(4)
O(24)-B(2)-O(21)	107.6(4)	O(18)-B(2)-O(21)	108.0(4)
O(27)-B(3)-O(25)#1	115.5(4)	O(27)-B(3)-O(17)	111.2(4)
O(25)#1-B(3)-O(17)	108.5(4)	O(27)-B(3)-O(22)	110.7(4)
O(25)#1-B(3)-O(22)	103.5(4)	O(17)-B(3)-O(22)	106.9(4)
Na(1)-O2#9	2.356(4)	Na(1)-O4#8	2.311(4)
Na(1)-O5	2.303(6)	Na(1)-O10#8	2.385(5)
Na(1)-O19	2.258(5)	Na(2)-O1	2.301(6)
Na(2)-O7#9	2.377(6)	Na(2)-O16	2.921(5)
Na(2)-O17	2.502(5)	Na(2)-O19	2.350(5)
Na(3)-O12#9	2.529(5)	Na(3)-O13#9	2.905(6)
Na(3)-O14#9	2.338(5)	Na(3)-O15#6	2.878(5)
Na(3)-O20	2.367(5)	Na(3)-O23#5	2.312(6)
Na(4)-O3	2.262(4)	Na(4)-O9#2	2.417(4)
Na(4)-O11	2.792(4)	Na(4)-O16	2.247(5)
Na(4)-O24#4	2.968(4)	Na(4)-O26#4	2.292(5)
Na(5)-O13	2.502(6)	Na(5)-O14	2.285(6)
Na(5)-O15#10	2.777(6)	Na(5)-O20#7	2.403(6)
Na(5)-O23#10	2.319(5)	Na(6)-O1	2.314(6)
Na(6)-O5#1	2.705(6)	Na(6)-O7#9	2.375(6)
Na(6)-O16#1	2.538(5)	Na(6)-O19#1	2.273(5)
Na(7)-O9#9	2.214(5)	Na(7)-O13	2.242(6)
Na(7)-O24#10	2.891(4)	Na(7)-O26#11	2.335(5)
Na(7)-O27#10	2.240(4)	Na(8)-O14#9	2.278(6)
Na(8)-O15#9	2.335(7)	Na(8)-O21#1	2.316(4)
Na(8)-O22	2.348(4)	Na(8)-O25#1	2.367(5)

Cs(1)-O1	3.419(6)	Cs(1)-O2#9	3.615(45)
Cs(1)-O3#9	3.763(6)	Cs(1)-O4#9	3.322(4)
Cs(1)-O5#1	3.388(5)	Cs(1)-O5	3.701(6)
Cs(1)-O7#9	3.123(4)	Cs(1)-O8	3.159(4)
Cs(1)-O10	3.746(6)	Cs(1)-O12#1	3.104(4)
Cs(1)-O13	3.347(4)	Cs(1)-O23#10	3.515(4)
Cs(1)-O26#10	3.125(6)	Cs(2)-O1	3.491(5)
Cs(2)-O9	3.075(4)	Cs(2)-O15#1	3.768(4)
Cs(2)-O15	3.349(4)	Cs(2)-O16#1	3.373(6)
Cs(2)-O17	3.079(4)	Cs(2)-O18#1	3.226(4)
Cs(2)-O20#3	3.150(5)	Cs(2)-O21#4	3.347(4)
Cs(2)-O22#3	3.567(4)	Cs(2)-O23#1	3.399(5)
Cs(2)-O25#1	3.784(4)	Cs(2)-O27#3	3.713(4)

[a] Symmetry codes:
$Na_4CsB_2P_3O_{13}$: #1 x, y–1, z; #2 x, y+1, z; #3 –x–1, –y–2, z–0.5; #4 –x–1, –y–1, z–0.5; #5 –x–1, –y–1, z+0.5; #6 –x–1, –y–2, z+0.5; #7 –x–0.5, y–0.5, z–0.5; #8 –x–1.5, y+0.5, z+0.5; #9 –x–1.5, y–0.5, z+0.5; #10 x–0.5, –y–1.5, z; #11 x–0.5, –y–0.5, z.

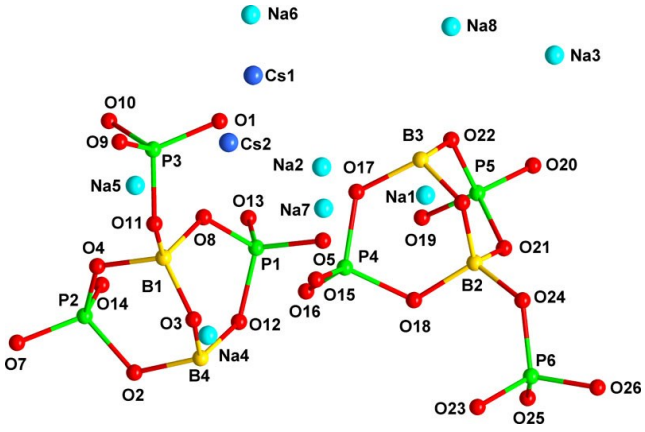

Figure S1. Asymmetric unit of $Na_4CsB_2P_3O_{13}$.

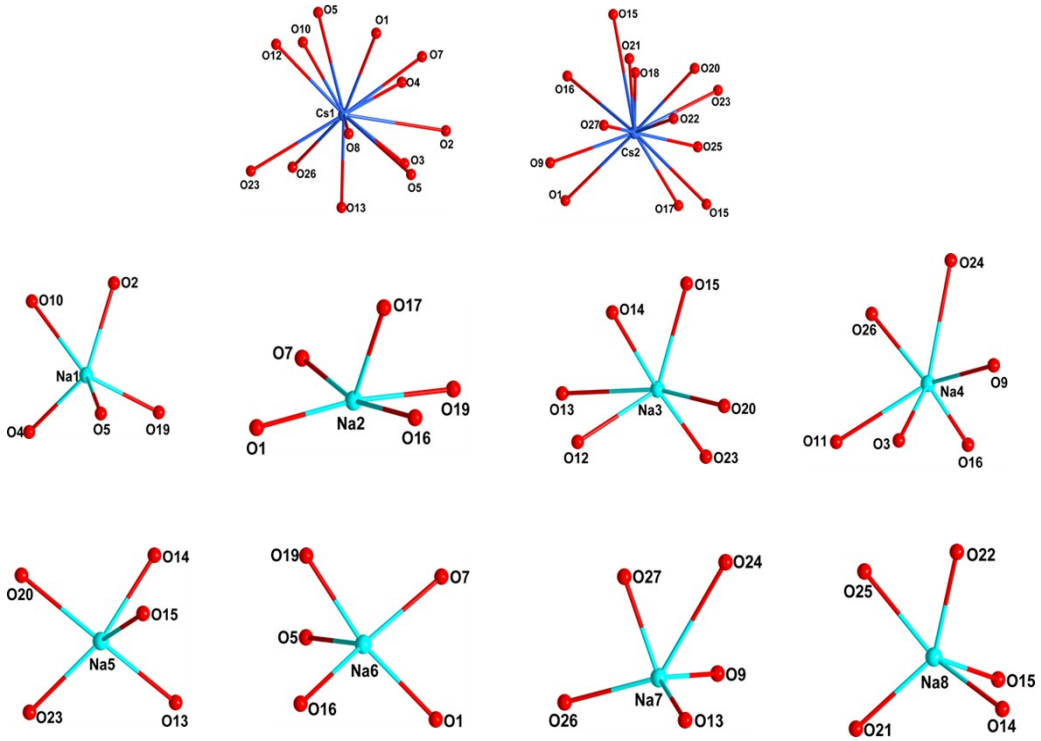

Figure S2. Coordination environment of the Na and Cs atoms in $Na_4CsB_2P_3O_{13}$.

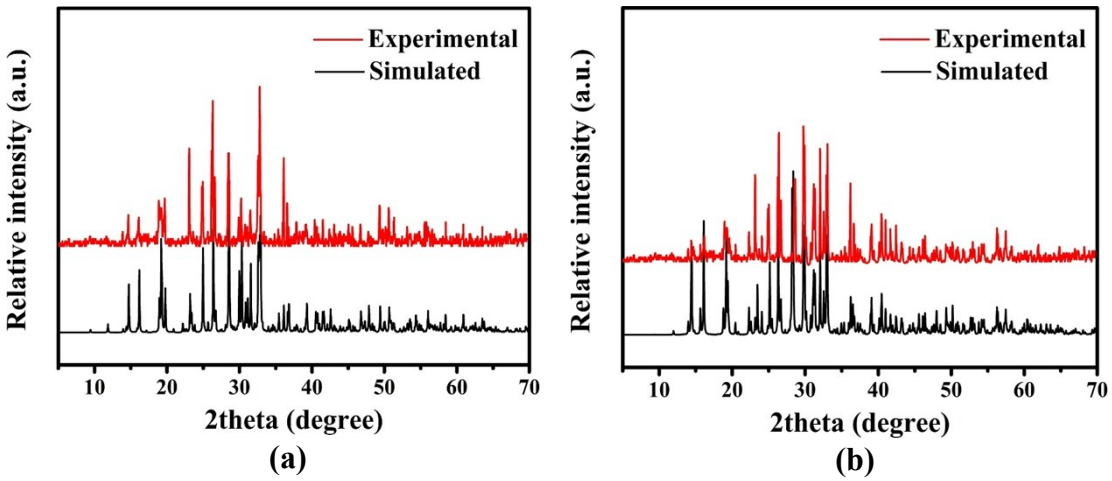

Figure S3. Experimental and simulated powder X-ray diffraction patterns of $Na_4RbB_2P_3O_{13}$ (a) and $Na_4CsB_2P_3O_{13}$ (b).

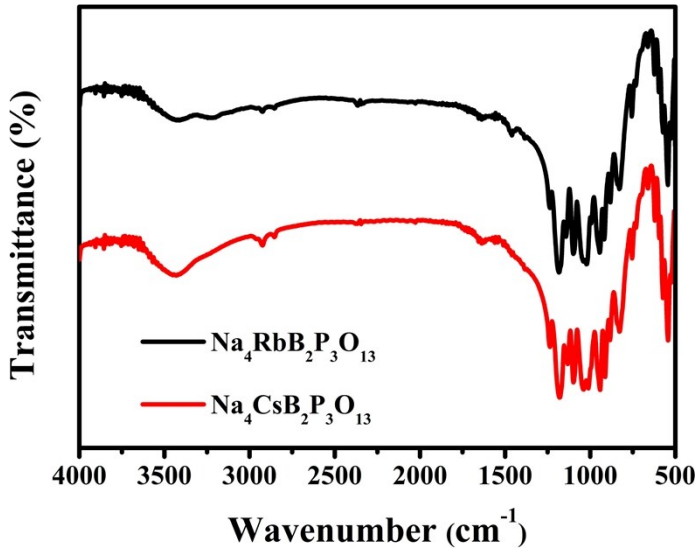

Figure S4. IR spectra of $Na_4RbB_2P_3O_{13}$ and $Na_4CsB_2P_3O_{13}$.

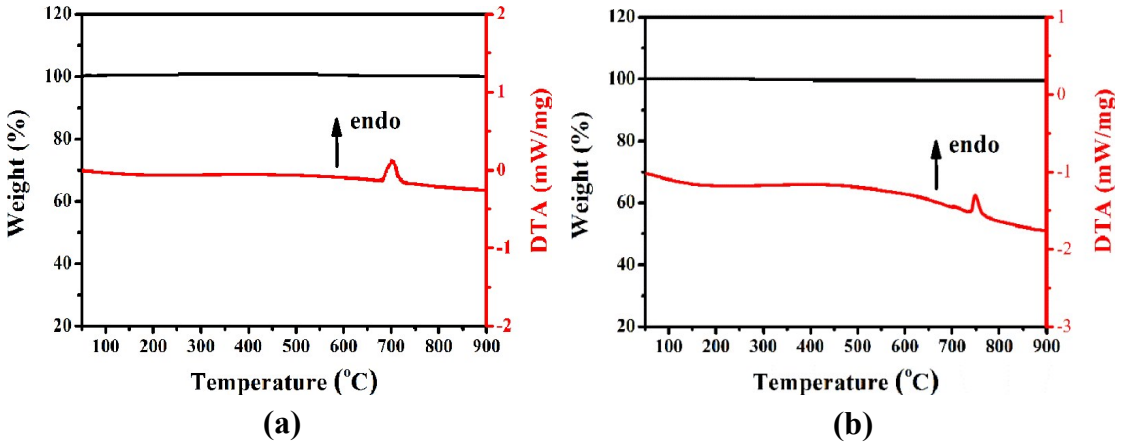

Figure S5. Thermogravimetric analyses of $Na_4RbB_2P_3O_{13}$ (a) and $Na_4CsB_2P_3O_{13}$ (b) under a N_2 atmosphere.

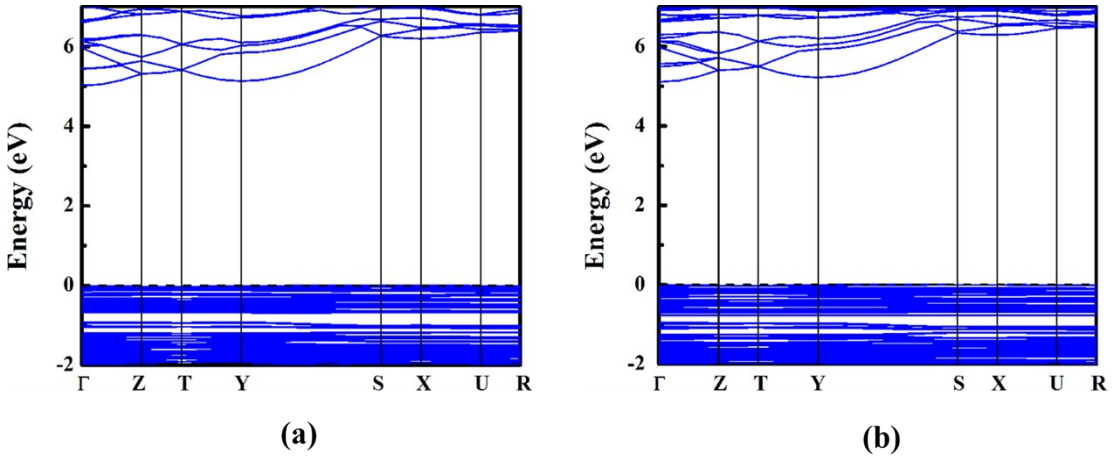

Figure S6. Band structures of $Na_4RbB_2P_3O_{13}$ (a) and $Na_4CsB_2P_3O_{13}$ (b).