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Supporting Information

$ACaBO_3$ (A=Cs, Rb): Two new cubic borates with isolated BO_3 groups

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Table S1a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $CsCaBO_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Cs(1)	6399(1)	3601(1)	8601(1)	25(1)
Ca(1)	8568(1)	8568(1)	8568(1)	15(1)
B(1)	10960(8)	5960(8)	9040(8)	17(2)
O(1)	10869(6)	7337(5)	10242(5)	20(1)

Table S1b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $RbCaBO_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Rb(1)	6210(1)	8790(1)	1210(1)	26(1)
Ca(1)	11007(1)	11007(1)	1007(1)	14(1)
B(1)	11705(7)	8295(7)	3295(7)	17(2)
O(1)	10280(4)	8160(4)	2094(4)	18(1)

Table S2a. Selected bond distances (Å) and angles (deg) for $CsCaBO_3$.

Cs(1)-O(1)#1	3.150(4)	O(1)#2-Cs(1)-O(1)#8	95.40(9)
Cs(1)-O(1)#2	3.150(4)	O(1)#3-Cs(1)-O(1)#8	67.118(15)
Cs(1)-O(1)#3	3.150(4)	O(1)#4-Cs(1)-O(1)#8	159.33(5)
Cs(1)-O(1)#4	3.223(4)	O(1)#5-Cs(1)-O(1)#8	134.62(14)
Cs(1)-O(1)#5	3.223(4)	O(1)#6-Cs(1)-O(1)#8	122.06(8)
Cs(1)-O(1)#6	3.223(4)	O(1)#1-Cs(1)-O(1)#7	67.118(16)
Cs(1)-O(1)#8	3.696(4)	O(1)#2-Cs(1)-O(1)#7	60.79(15)
Cs(1)-O(1)#7	3.696(4)	O(1)#3-Cs(1)-O(1)#7	95.40(9)
Cs(1)-O(1)#9	3.696(4)	O(1)#4-Cs(1)-O(1)#7	122.06(8)
Ca(1)-O(1)#10	2.336(5)	O(1)#5-Cs(1)-O(1)#7	159.33(5)
Ca(1)-O(1)#2	2.336(5)	O(1)#6-Cs(1)-O(1)#7	134.62(14)
Ca(1)-O(1)#4	2.336(5)	O(1)#8-Cs(1)-O(1)#7	37.88(11)
Ca(1)-O(1)#11	2.347(5)	O(1)#1-Cs(1)-O(1)#9	95.40(9)
Ca(1)-O(1)	2.347(5)	O(1)#2-Cs(1)-O(1)#9	67.118(15)
Ca(1)-O(1)#12	2.347(5)	O(1)#3-Cs(1)-O(1)#9	60.79(15)
B(1)-O(1)#2	1.386(4)	O(1)#4-Cs(1)-O(1)#9	134.62(14)
B(1)-O(1)	1.386(4)	O(1)#5-Cs(1)-O(1)#9	122.06(8)
B(1)-O(1)#16	1.386(4)	O(1)#6-Cs(1)-O(1)#9	159.33(5)
O(1)-Ca(1)#14	2.336(5)	O(1)#8-Cs(1)-O(1)#9	37.88(11)
O(1)-Cs(1)#17	3.150(4)	O(1)#7-Cs(1)-O(1)#9	37.88(11)
O(1)-Cs(1)#14	3.223(4)	O(1)#10-Ca(1)-O(1)#2	101.18(13)
O(1)-Cs(1)#13	3.696(4)	O(1)#10-Ca(1)-O(1)#4	101.18(13)
O(1)#1-Cs(1)-O(1)#2	112.41(7)	O(1)#2-Ca(1)-O(1)#4	101.18(13)
O(1)#1-Cs(1)-O(1)#3	112.41(7)	O(1)#10-Ca(1)-O(1)#11	61.62(19)
O(1)#2-Cs(1)-O(1)#3	112.41(7)	O(1)#2-Ca(1)-O(1)#11	108.94(2)
O(1)#1-Cs(1)-O(1)#4	111.51(10)	O(1)#4-Ca(1)-O(1)#11	147.47(11)
O(1)#2-Cs(1)-O(1)#4	68.99(16)	O(1)#10-Ca(1)-O(1)	147.47(11)
O(1)#3-Cs(1)-O(1)#4	130.56(8)	O(1)#2-Ca(1)-O(1)	61.62(19)
O(1)#1-Cs(1)-O(1)#5	130.56(8)	O(1)#4-Ca(1)-O(1)	108.94(2)
O(1)#2-Cs(1)-O(1)#5	111.51(10)	O(1)#11-Ca(1)-O(1)	96.23(14)
O(1)#3-Cs(1)-O(1)#5	68.99(16)	O(1)#10-Ca(1)-O(1)#12	108.94(2)
O(1)#4-Cs(1)-O(1)#5	65.66(12)	O(1)#2-Ca(1)-O(1)#12	147.47(11)
O(1)#1-Cs(1)-O(1)#6	68.99(16)	O(1)#4-Ca(1)-O(1)#12	61.62(19)
O(1)#2-Cs(1)-O(1)#6	130.56(8)	O(1)#11-Ca(1)-O(1)#12	96.23(14)
O(1)#3-Cs(1)-O(1)#6	111.51(10)	O(1)-Ca(1)-O(1)#12	96.23(14)
O(1)#4-Cs(1)-O(1)#6	65.66(12)	O(1)#2-B(1)-O(1)	119.93(4)
O(1)#5-Cs(1)-O(1)#6	65.66(12)	O(1)#2-B(1)-O(1)#16	119.93(4)
O(1)#1-Cs(1)-O(1)#8	60.79(15)	O(1)-B(1)-O(1)#16	119.93(4)

#1 -x+3/2,-y+1,z-1/2 #2 -z+2,x-1/2,-y+3/2
#3 y,z-1,x #4 x-1/2,-y+3/2,-z+2 #5 z-1/2,-x+3/2,-y+2
#6 y-1/2,-z+3/2,-x+2 #7 -x+2,y-1/2,-z+3/2

#8 -y+3/2,-z+1,x-1/2 #9 z,x-1,y #10 -y+3/2,-z+2,x-1/2
#11 z,x,y #12 y,z,x #13 -x+2,y+1/2,-z+3/2
#14 x+1/2,-y+3/2,-z+2 #15 -x+1,y+1/2,-z+3/2
#16 y+1/2,-z+3/2,-x+2 #17 -x+3/2,-y+1,z+1/2

Table S2b. Selected bond distances (Å) and angles (deg) for $RbCaBO_3$.

Rb(1)-O(1)#1	2.933(4)	O(1)#3-Rb(1)-O(1)	137.76(6)
Rb(1)-O(1)#2	2.933(4)	O(1)#4-Rb(1)-O(1)	67.76(9)
Rb(1)-O(1)#3	2.933(4)	O(1)#1-Rb(1)-O(1)#5	137.76(6)
Rb(1)-O(1)#4	3.129(4)	O(1)#2-Rb(1)-O(1)#5	72.38(11)
Rb(1)-O(1)	3.129(4)	O(1)#3-Rb(1)-O(1)#5	109.24(7)
Rb(1)-O(1)#5	3.129(4)	O(1)#4-Rb(1)-O(1)#5	67.76(9)
Ca(1)-O(1)	2.327(3)	O(1)-Rb(1)-O(1)#5	67.76(9)
Ca(1)-O(1)#1	2.327(4)	O(1)-Ca(1)-O(1)#1	100.66(10)
Ca(1)-O(1)#10	2.327(3)	O(1)-Ca(1)-O(1)#10	100.66(10)
Ca(1)-O(1)#11	2.338(4)	O(1)#1-Ca(1)-O(1)#10	100.66(10)
Ca(1)-O(1)#7	2.338(4)	O(1)-Ca(1)-O(1)#11	62.03(14)
Ca(1)-O(1)#12	2.338(4)	O(1)#1-Ca(1)-O(1)#11	148.13(8)
B(1)-O(1)#11	1.388(3)	O(1)#10-Ca(1)-O(1)#11	108.51(3)
B(1)-O(1)	1.388(3)	O(1)-Ca(1)-O(1)#7	108.51(3)
B(1)-O(1)#14	1.388(3)	O(1)#1-Ca(1)-O(1)#7	62.03(14)
O(1)-Ca(1)#6	2.338(4)	O(1)#10-Ca(1)-O(1)#7	148.13(8)
O(1)-Rb(1)#16	2.933(4)	O(1)#11-Ca(1)-O(1)#7	96.53(10)
O(1)#1-Rb(1)-O(1)#2	109.42(6)	O(1)-Ca(1)-O(1)#12	148.13(8)
O(1)#1-Rb(1)-O(1)#3	109.42(6)	O(1)#1-Ca(1)-O(1)#12	108.51(3)
O(1)#2-Rb(1)-O(1)#3	109.42(6)	O(1)#10-Ca(1)-O(1)#12	62.03(14)
O(1)#1-Rb(1)-O(1)#4	109.24(7)	O(1)#11-Ca(1)-O(1)#12	96.53(10)
O(1)#2-Rb(1)-O(1)#4	137.76(6)	O(1)#7-Ca(1)-O(1)#12	96.53(10)
O(1)#3-Rb(1)-O(1)#4	72.38(11)	O(1)#11-B(1)-O(1)	119.92(4)
O(1)#1-Rb(1)-O(1)	72.38(11)	O(1)#11-B(1)-O(1)#14	119.92(4)
O(1)#2-Rb(1)-O(1)	109.24(7)	O(1)-B(1)-O(1)#14	119.92(4)

#1 -x+1/2,-y+1,z+1/2 #2 -z,x+1/2,-y+1/2
#3 y,z+1,x #4 z+1/2,-x+1/2,-y #5 x+1/2,-y+1/2,-z
#6 y+1/2,-z+1/2,-x #7 -x,y+1/2,-z+1/2
#8 -y+1/2,-z+1,x+1/2 #9 z,x+1,y #10 -y+1/2,-z,x+1/2
#11 y,z,x #12 z,x,y #13 -x,y-1/2,-z+1/2
#14 x-1/2,-y+1/2,-z #15 y-1/2,-z+1/2,-x
#16 x-1/2,-y+3/2,-z #17 -x+1/2,-y+1,z-1/2

Discussion on the structure symmetry of $ACaBO_3$ (A= Cs, Rb)

$ACaBO_3$ (A= Cs, Rb) crystalize in the space group $P2_13$, which contains a 3 axis along <1 1 1> direction and a 2_1 axis along the *c* direction. We have discussed the structure symmetry in $ACaBO_3$ (A= Cs, Rb). The CaO_6 octahedra are connected with three BO_3 units through edge sharing, which is favorable for the symmetry of 3 axis along the diagonal direction. As shown in Fig. S1†, $B(a)O_3$ rotates 120° along the <-1 -1 -1> axis to overlap $B(b)O_3$ and then rotates 120° along the <-1 -1 1> axis to overlap $B(c)O_3$. There is a 2_1 symmetry along the *c* axis between $B(a)O_3$ and $B(c)O_3$: $B(a)O_3$ can rotate 180° along the *c* axis to overlap $B(ac)O_3$ and then translates 1/2c along the *c* axis to overlap $B(c)O_3$. In addition besides the Ca cation, the compensation effect of the Cs/Rb cation on $[CaBO_3]^-$ framework is also responsible for the alignment of the BO_3 triangles. Therefore, it may be the synergistic effect of the Ca and Cs/Rb cations that makes BO_3 triangles arranged in the 2_1 symmetry along the *c* direction and the 3 axis symmetry along the <1 1 1> direction, which allows $ACaBO_3$ (A= Cs, Rb) to crystallize in the cubic space group $P2_13$.

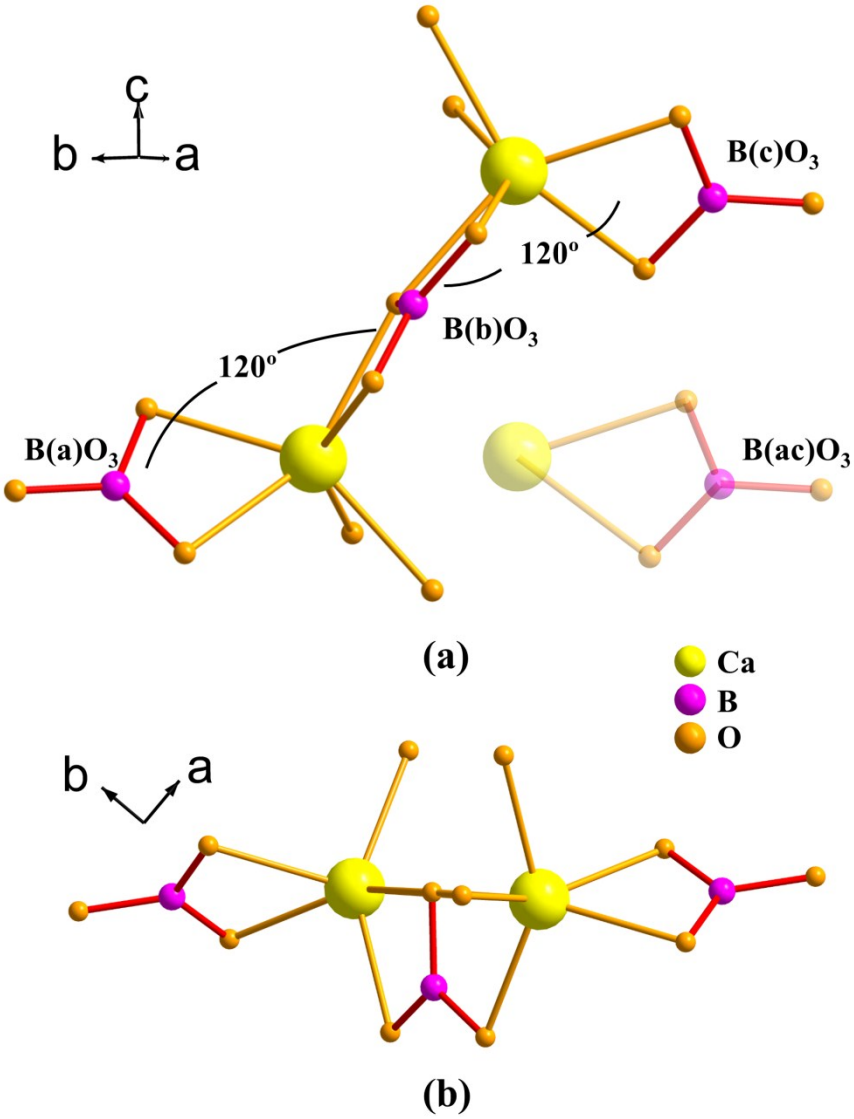

Fig. S1 The symmetry analysis of the BO_3 triangles in $ACaBO_3$ (A= Cs, Rb)

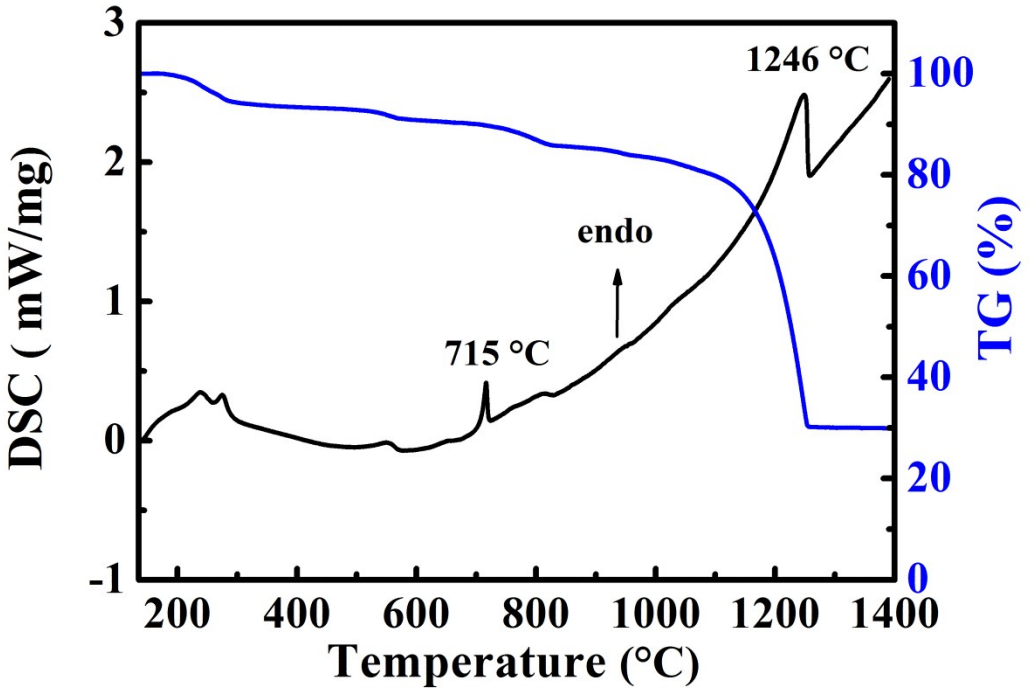

Fig. S2. TG-DSC curves of $CsCaBO_3$

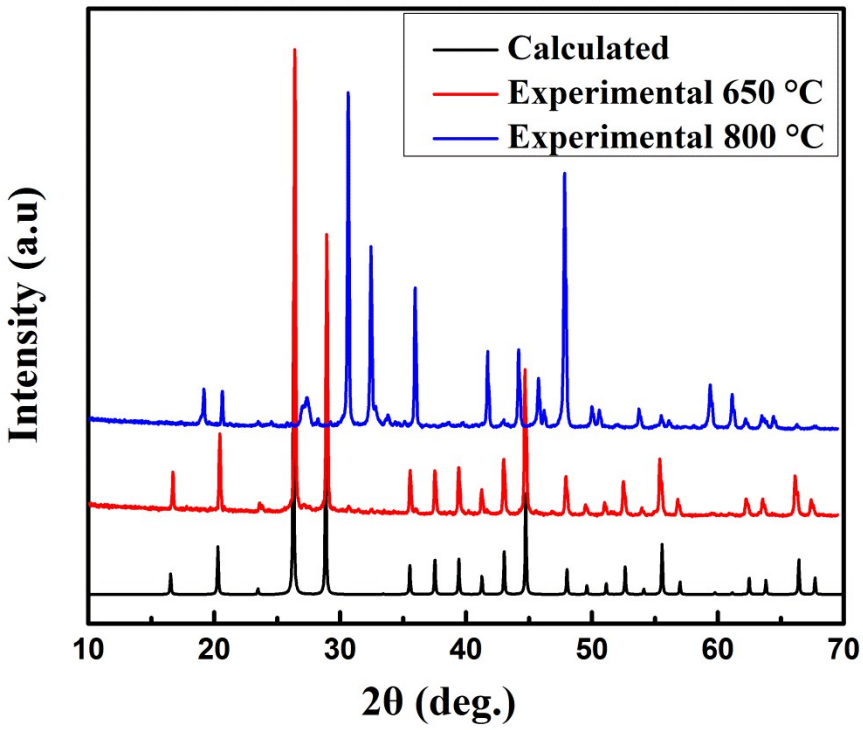

Fig. S3. Experimental and calculated XRD patterns of $CsCaBO_3$

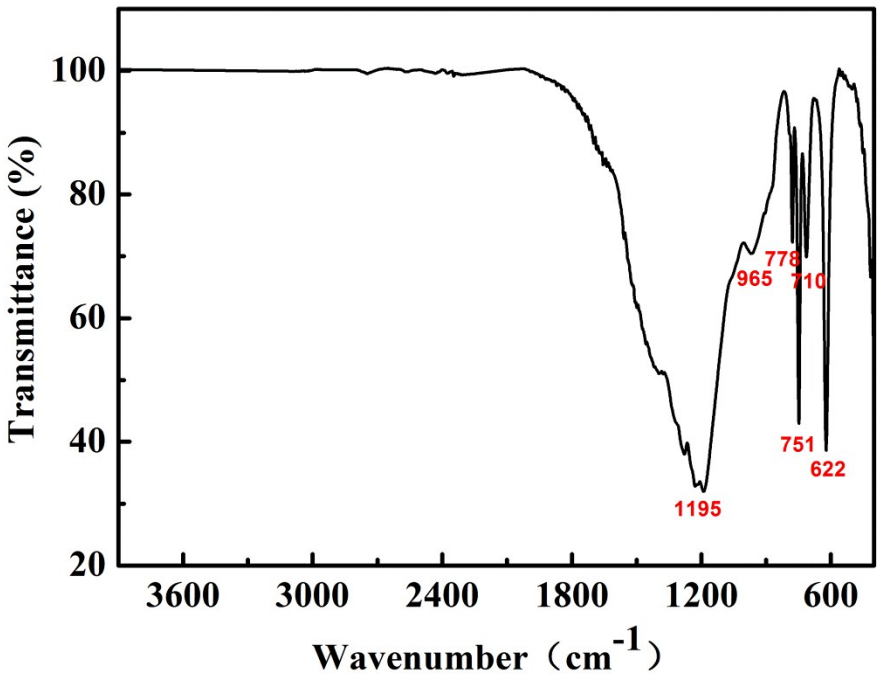

Fig. S4. IR spectra of $CsCaBO_3$

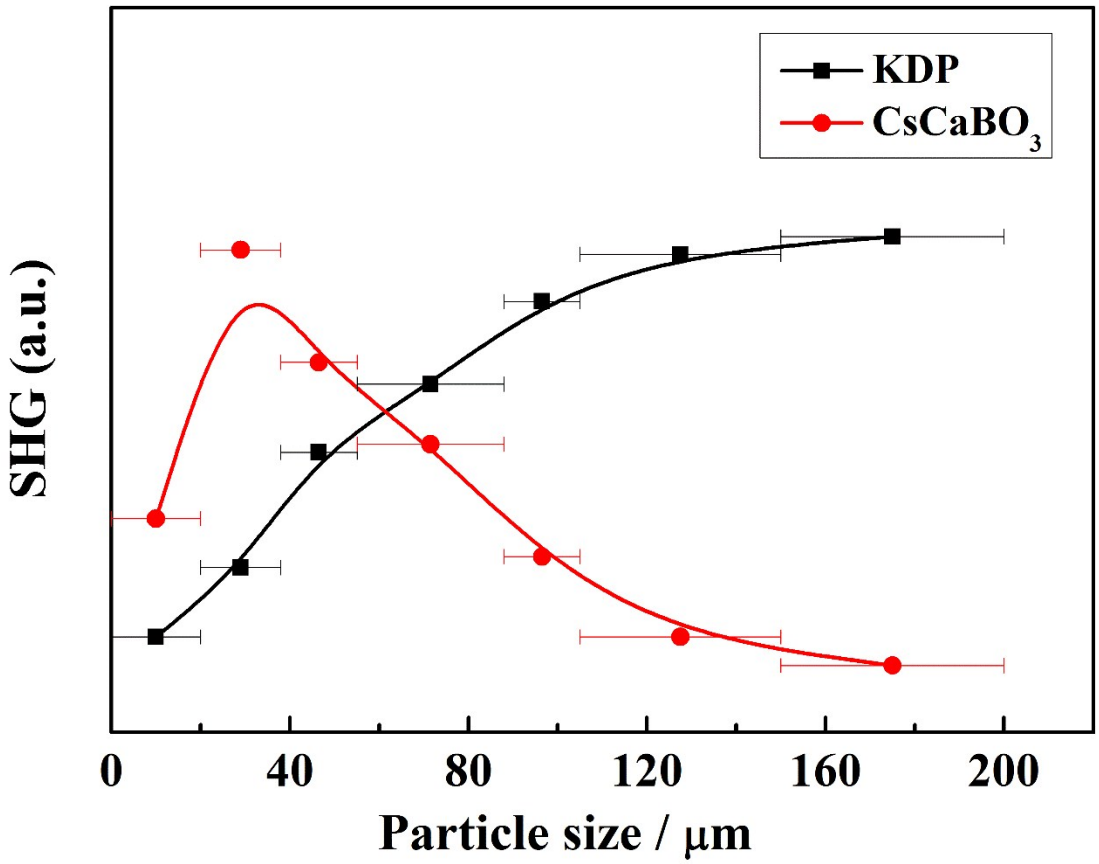

Fig. S5. Phase-matching curves of $CsCaBO_3$.

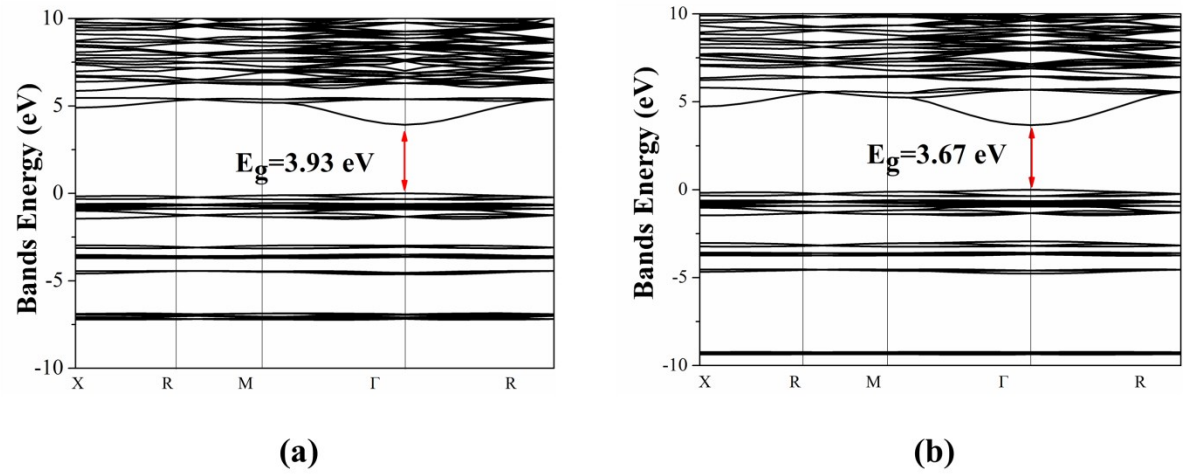

Fig. S6. Band structures of $CsCaBO_3$ (a) and $RbCaBO_3$ (b).