Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs): a structure analogous to SBBO with three-dimensional open-framework layers

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Table S1a. Atomic coordinates ($\times 10^4$)，equivalent isotropic displacement parameters ($Å^2\times 10^3$) and BVS for $Rb_2Ca_3B_{16}O_{28}$.

Atom	x	y	z	U (eq)	BVS
Rb(1)	2497(1)	10300(1)	4039(1)	37(1)	0.726
Ca(1)	-7(1)	2635(1)	6025(1)	5(1)	2.295
Ca(2)	0	7670(1)	7500	7(1)	2.096
B(1)	3114(2)	10447(6)	6485(4)	12(1)	3.129
B(2)	1902(2)	9730(6)	1557(4)	13(1)	3.096
B(3)	797(2)	5800(6)	5884(3)	9(1)	3.107
B(4)	710(2)	9216(6)	9239(3)	8(1)	3.017
B(5)	-985(2)	4233(6)	7400(3)	10(1)	2.992
B(6)	926(2)	9187(6)	5879(3)	10(1)	3.076
B(7)	871(2)	5923(6)	9211(3)	10(1)	3.025
B(8)	980(2)	9196(6)	2518(3)	9(1)	3.026
O(1)	793(1)	7427(3)	6257(2)	15(1)	2.095
O(2)	1595(1)	9437(4)	5805(2)	18(1)	1.904
O(3)	-780(1)	2489(3)	7143(2)	10(1)	2.016
O(4)	1651(1)	9293(4)	2428(2)	14(1)	2.032
O(5)	628(1)	5451(3)	8215(2)	8(1)	1.963
O(6)	650(1)	382(3)	6564(2)	9(1)	2.015
O(7)	591(1)	2435(3)	4573(2)	10(1)	2.027
O(8)	2504(1)	14200(4)	3631(3)	24(1)	2.191
O(9)	3345(1)	10465(3)	2255(2)	13(1)	1.970
O(10)	783(1)	9434(3)	8240(2)	12(1)	2.056
O(11)	-659(1)	610(3)	5145(2)	11(1)	2.077
O(12)	3461(1)	11138(4)	5750(2)	15(1)	1.855
O(13)	-694(1)	4499(3)	5111(2)	13(1)	2.080
O(14)	828(1)	4431(3)	6516(2)	12(1)	2.115

Table S1b. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters ($Å^2$ × 10^3) and BVS for $Cs_2Ca_3B_{16}O_{28}$.

Atom	x	y	z	U (eq)	BVS
Rb(1)	2514(1)	10111(1)	4050(1)	43(1)	0.930
Ca(1)	-7(1)	2628(1)	6011(1)	7(1)	2.309
Ca(2)	0	7665(2)	7500	7(1)	2.158
B(1)	3125(3)	10371(8)	6518(5)	10(1)	3.151
B(2)	1893(3)	9825(9)	1555(5)	14(1)	3.105
B(3)	789(3)	5805(8)	5872(4)	8(1)	3.083
B(4)	712(3)	9225(8)	9219(4)	7(1)	3.021
B(5)	-970(3)	4227(8)	7422(4)	9(1)	3.038
B(6)	921(3)	9181(8)	5865(5)	10(1)	3.101
B(7)	872(3)	5923(8)	9183(5)	9(1)	3.045
B(8)	964(3)	9190(8)	2490(5)	9(1)	3.047
O(1)	773(2)	7439(5)	6239(3)	14(1)	2.101
O(2)	1590(2)	9380(6)	5804(3)	17(1)	1.981
O(3)	-759(2)	2488(5)	7166(3)	9(1)	2.028
O(4)	1631(2)	9271(5)	2399(3)	13(1)	2.078
O(5)	623(2)	5452(5)	8209(3)	8(1)	1.984
O(6)	645(2)	381(5)	6546(3)	9(1)	2.044
O(7)	600(2)	2438(5)	4561(3)	11(1)	2.011
O(8)	2496(2)	14404(7)	3598(4)	28(1)	2.098
O(9)	3368(2)	10515(5)	2284(3)	14(1)	2.063
O(10)	771(2)	9440(5)	8224(3)	12(1)	2.066
O(11)	-667(2)	608(5)	5160(3)	11(1)	2.080
O(12)	3463(2)	11119(6)	5795(3)	15(1)	1.883
O(13)	-689(2)	4505(5)	5124(3)	13(1)	2.036
O(14)	815(2)	4443(5)	6505(3)	12(1)	2.133

Table S2a. Selected bond distances (Å) and angles (deg) for $Rb_2Ca_3B_{16}O_{28}$.

Rb(1)-O(4)	2.894(4)	B(6)-O(6)#7	1.444(5)
Rb(1)-O(9)	3.058(4)	B(6)-O(2)	1.466(5)
Rb(1)-O(8)	3.064(5)	B(6)-O(11)#6	1.481(5)
Rb(1)-O(12)	3.122(4)	B(6)-O(1)	1.483(5)
Rb(1)-O(8)#1	3.146(5)	B(7)-O(12)#13	1.455(5)
Rb(1)-O(2)	3.182(4)	B(7)-O(5)	1.465(5)
Rb(1)-O(12)#1	3.462(4)	B(7)-O(13)#4	1.485(5)
Ca(1)-O(3)	2.279(3)	B(7)-O(7)#9	1.494(5)
Ca(1)-O(6)	2.349(3)	B(8)-O(3)#6	1.450(5)
Ca(1)-O(14)	2.357(3)	B(8)-O(4)	1.464(5)
Ca(1)-O(7)	2.373(3)	B(8)-O(6)#14	1.481(5)
Ca(1)-O(13)	2.382(3)	B(8)-O(10)#3	1.504(5)
Ca(1)-O(11)	2.394(3)	O(4)-Rb(1)-O(9)	79.00(11)
Ca(1)-O(5)#4	2.768(3)	O(4)-Rb(1)-O(8)	97.95(9)
Ca(1)-O(3)#4	2.948(4)	O(9)-Rb(1)-O(8)	79.24(8)
Ca(1)-O(13)#6	3.109(3)	O(4)-Rb(1)-O(12)	175.86(8)
Ca(2)-O(10)	2.370(3)	O(9)-Rb(1)-O(12)	99.31(11)
Ca(2)-O(10)#4	2.370(3)	O(8)-Rb(1)-O(12)	85.40(9)
Ca(2)-O(5)#4	2.373(3)	O(4)-Rb(1)-O(8)#1	138.97(9)
Ca(2)-O(5)	2.373(3)	O(9)-Rb(1)-O(8)#1	142.00(9)
Ca(2)-O(1)	2.434(3)	O(8)-Rb(1)-O(8)#1	93.21(9)
Ca(2)-O(1)#4	2.434(3)	O(12)-Rb(1)-O(8)#1	42.73(8)
Ca(2)-O(6)#7	2.838(3)	O(4)-Rb(1)-O(2)	96.33(11)
Ca(2)-O(6)#8	2.838(3)	O(9)-Rb(1)-O(2)	170.11(7)
Ca(2)-O(7)#9	3.025(4)	O(8)-Rb(1)-O(2)	110.20(8)
Ca(2)-O(7)#6	3.025(4)	O(12)-Rb(1)-O(2)	84.75(11)
B(1)-O(9)#2	1.335(6)	O(8)#1-Rb(1)-O(2)	43.08(8)
B(1)-O(12)	1.364(5)	O(4)-Rb(1)-O(12)#1	84.76(9)
B(1)-O(8)#1	1.368(5)	O(9)-Rb(1)-O(12)#1	113.89(8)
B(2)-O(4)	1.345(6)	O(8)-Rb(1)-O(12)#1	40.38(8)
B(2)-O(2)#3	1.354(6)	O(12)-Rb(1)-O(12)#1	99.38(8)
B(2)-O(8)#10	1.380(5)	O(8)#1-Rb(1)-O(12)#1	78.65(8)
B(3)-O(1)	1.354(5)	O(2)-Rb(1)-O(12)#1	74.00(9)
B(3)-O(14)	1.356(5)	O(3)-Ca(1)-O(6)	102.13(11)
B(3)-O(13)#6	1.364(5)	O(3)-Ca(1)-O(14)	114.61(12)
B(4)-O(10)	1.363(5)	O(6)-Ca(1)-O(14)	84.19(13)
B(4)-O(11)#8	1.364(5)	O(3)-Ca(1)-O(7)	164.49(10)
B(4)-O(7)#9	1.380(5)	O(6)-Ca(1)-O(7)	82.18(11)
B(5)-O(3)	1.464(5)	O(14)-Ca(1)-O(7)	80.48(11)
B(5)-O(9)#12	1.477(5)	O(3)-Ca(1)-O(13)	84.83(12)
B(5)-O(5)#4	1.483(5)	O(6)-Ca(1)-O(13)	165.77(9)
B(5)-O(14)#4	1.490(5)	O(14)-Ca(1)-O(13)	104.36(12)

O(7)-Ca(1)-O(13)	87.98(12)	O(5)#4-Ca(2)-O(6)#7	129.88(10)
O(3)-Ca(1)-O(11)	81.88(12)	O(5)-Ca(2)-O(6)#7	115.30(11)
O(6)-Ca(1)-O(11)	90.54(12)	O(1)-Ca(2)-O(6)#7	52.10(9)
O(14)-Ca(1)-O(11)	163.39(10)	O(1)#4-Ca(2)-O(6)#7	136.73(9)
O(7)-Ca(1)-O(11)	83.20(11)	O(10)-Ca(2)-O(6)#8	75.37(11)
O(13)-Ca(1)-O(11)	78.06(12)	O(10)#4-Ca(2)-O(6)#8	53.27(10)
O(3)-Ca(1)-O(5)#4	54.84(9)	O(5)#4-Ca(2)-O(6)#8	115.30(11)
O(6)-Ca(1)-O(5)#4	139.99(10)	O(5)-Ca(2)-O(6)#8	129.88(10)
O(14)-Ca(1)-O(5)#4	79.05(11)	O(1)-Ca(2)-O(6)#8	136.73(9)
O(7)-Ca(1)-O(5)#4	129.41(9)	O(1)#4-Ca(2)-O(6)#8	52.10(9)
O(13)-Ca(1)-O(5)#4	53.95(10)	O(6)#7-Ca(2)-O(6)#8	84.71(13)
O(11)-Ca(1)-O(5)#4	114.23(12)	O(10)-Ca(2)-O(7)#9	49.72(8)
O(3)-Ca(1)-O(3)#4	82.37(13)	O(10)#4-Ca(2)-O(7)#9	132.64(9)
O(6)-Ca(1)-O(3)#4	52.12(9)	O(5)#4-Ca(2)-O(7)#9	124.95(9)
O(14)-Ca(1)-O(3)#4	51.04(9)	O(5)-Ca(2)-O(7)#9	52.29(8)
O(7)-Ca(1)-O(3)#4	111.38(12)	O(1)-Ca(2)-O(7)#9	109.83(12)
O(13)-Ca(1)-O(3)#4	141.92(9)	O(1)#4-Ca(2)-O(7)#9	69.92(12)
O(11)-Ca(1)-O(3)#4	134.63(9)	O(6)#7-Ca(2)-O(7)#9	102.96(9)
O(5)#4-Ca(1)-O(3)#4	89.89(9)	O(6)#8-Ca(2)-O(7)#9	79.37(9)
O(3)-Ca(1)-O(13)#6	137.28(9)	O(10)-Ca(2)-O(7)#6	132.64(9)
O(6)-Ca(1)-O(13)#6	112.29(11)	O(10)#4-Ca(2)-O(7)#6	49.72(8)
O(14)-Ca(1)-O(13)#6	48.35(10)	O(5)#4-Ca(2)-O(7)#6	52.29(8)
O(7)-Ca(1)-O(13)#6	50.15(9)	O(5)-Ca(2)-O(7)#6	124.95(9)
O(13)-Ca(1)-O(13)#6	67.84(12)	O(1)-Ca(2)-O(7)#6	69.92(12)
O(11)-Ca(1)-O(13)#6	120.92(11)	O(1)#4-Ca(2)-O(7)#6	109.83(12)
O(5)#4-Ca(1)-O(13)#6	82.44(11)	O(6)#7-Ca(2)-O(7)#6	79.37(9)
O(3)#4-Ca(1)-O(13)#6	99.02(10)	O(6)#8-Ca(2)-O(7)#6	102.96(9)
O(10)-Ca(2)-O(10)#4	109.72(16)	O(7)#9-Ca(2)-O(7)#6	176.92(10)
O(10)-Ca(2)-O(5)#4	168.22(9)	O(9)#2-B(1)-O(12)	124.3(4)
O(10)#4-Ca(2)-O(5)#4	81.57(12)	O(9)#2-B(1)-O(8)#1	122.3(4)
O(10)-Ca(2)-O(5)	81.57(12)	O(12)-B(1)-O(8)#1	113.4(4)
O(10)#4-Ca(2)-O(5)	168.22(9)	O(4)-B(2)-O(2)#3	124.3(4)
O(5)#4-Ca(2)-O(5)	87.39(15)	O(4)-B(2)-O(8)#10	119.1(4)
O(10)-Ca(2)-O(1)	79.68(12)	O(2)#3-B(2)-O(8)#10	116.5(4)
O(10)#4-Ca(2)-O(1)	105.53(12)	O(1)-B(3)-O(14)	119.7(4)
O(5)#4-Ca(2)-O(1)	94.29(11)	O(1)-B(3)-O(13)#6	121.0(4)
O(5)-Ca(2)-O(1)	79.27(11)	O(14)-B(3)-O(13)#6	118.8(4)
O(10)-Ca(2)-O(1)#4	105.53(12)	O(10)-B(4)-O(11)#8	120.7(4)
O(10)#4-Ca(2)-O(1)#4	79.68(12)	O(10)-B(4)-O(7)#9	117.5(3)
O(5)#4-Ca(2)-O(1)#4	79.27(11)	O(11)#8-B(4)-O(7)#9	121.0(4)
O(5)-Ca(2)-O(1)#4	94.29(11)	O(3)-B(5)-O(9)#12	114.7(3)
O(1)-Ca(2)-O(1)#4	171.16(13)	O(3)-B(5)-O(5)#4	106.7(3)
O(10)-Ca(2)-O(6)#7	53.27(10)	O(9)#12-B(5)-O(5)#4	110.6(3)
O(10)#4-Ca(2)-O(6)#7	75.37(11)	O(3)-B(5)-O(14)#4	105.2(3)

O(9)#12-B(5)-O(14)#4	107.9(3)	O(5)-B(7)-O(13)#4	106.3(3)
O(5)#4-B(5)-O(14)#4	111.7(3)	O(12)#13-B(7)-O(7)#9	107.6(3)
O(6)#7-B(6)-O(2)	112.7(3)	O(5)-B(7)-O(7)#9	111.7(3)
O(6)#7-B(6)-O(11)#6	111.4(3)	O(13)#4-B(7)-O(7)#9	108.4(3)
O(2)-B(6)-O(11)#6	106.3(3)	O(3)#6-B(8)-O(4)	112.2(3)
O(6)#7-B(6)-O(1)	106.4(3)	O(3)#6-B(8)-O(6)#14	109.1(3)
O(2)-B(6)-O(1)	110.2(3)	O(4)-B(8)-O(6)#14	111.8(3)
O(11)#6-B(6)-O(1)	109.8(3)	O(3)#6-B(8)-O(10)#3	109.8(3)
O(12)#13-B(7)-O(5)	113.0(3)	O(4)-B(8)-O(10)#3	108.5(3)
O(12)#13-B(7)-O(13)#4	109.7(3)	O(6)#14-B(8)-O(10)#3	105.2(3)

Symmetry transformations used to generate equivalent atoms:

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

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

#6 -x, -y+1, -z+1 #7 x, y+1, z #8 -x, y+1, -z+3/2

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

#11 -x+1/2, -y+3/2, -z+1 #12 x-1/2, -y+3/2, z+1/2

#13 -x+1/2, y-1/2, -z+3/2 #14 x, -y+1, z-1/2

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

#18 x+1/2, -y+3/2, z-1/2 #19 -x+1/2, y+1/2, -z+3/2

Table S2b. Selected bond distances (Å) and angles (deg) for $Cs_2Ca_3B_{16}O_{28}$.

Cs(1)-O(4)	2.978(4)	Ca(1)-O(11)	2.394(4)
Cs(1)-O(9)	3.057(4)	Ca(1)-O(5)#5	2.773(4)
Cs(1)-O(2)	3.178(4)	Ca(1)-O(3)#5	2.938(4)
Cs(1)-O(8)#1	3.187(5)	Ca(1)-O(13)#7	3.098(4)
Cs(1)-O(12)	3.190(4)	Ca(2)-O(10)	2.358(4)
Cs(1)-O(8)	3.369(6)	Ca(2)-O(10)#5	2.358(4)
Cs(1)-O(8)#2	3.605(5)	Ca(2)-O(5)#5	2.367(4)
Cs(1)-O(12)#1	3.609(4)	Ca(2)-O(5)	2.367(4)
Ca(1)-O(3)	2.276(4)	Ca(2)-O(1)	2.415(4)
Ca(1)-O(6)	2.342(4)	Ca(2)-O(1)#5	2.415(4)
Ca(1)-O(14)	2.354(4)	Ca(2)-O(6)#8	2.840(4)
Ca(1)-O(13)	2.376(4)	Ca(2)-O(6)#9	2.840(4)
Ca(1)-O(7)	2.379(4)	Ca(2)-O(7)#10	3.042(4)

Ca(2)-O(7)#7	3.042(4)	O(4)-Cs(1)-O(8)#2	40.32(10)
B(1)-O(9)#3	1.336(8)	O(9)-Cs(1)-O(8)#2	40.47(11)
B(1)-O(12)	1.358(8)	O(2)-Cs(1)-O(8)#2	135.67(11)
B(1)-O(8)#1	1.365(8)	O(8)#1-Cs(1)-O(8)#2	177.89(6)
B(2)-O(2)#4	1.344(8)	O(12)-Cs(1)-O(8)#2	139.15(10)
B(2)-O(4)	1.348(8)	O(8)-Cs(1)-O(8)#2	88.30(10)
B(2)-O(8)#2	1.384(8)	O(4)-Cs(1)-O(12)#1	81.25(10)
B(3)-O(14)	1.354(7)	O(9)-Cs(1)-O(12)#1	109.16(10)
B(3)-O(1)	1.355(8)	O(2)-Cs(1)-O(12)#1	73.76(10)
B(3)-O(13)#7	1.374(7)	O(8)#1-Cs(1)-O(12)#1	80.38(11)
B(4)-O(10)	1.358(7)	O(12)-Cs(1)-O(12)#1	97.64(9)
B(4)-O(11)#9	1.361(7)	O(8)-Cs(1)-O(12)#1	38.06(10)
B(4)-O(7)#10	1.387(7)	O(8)#2-Cs(1)-O(12)#1	100.74(10)
B(5)-O(9)#12	1.460(7)	O(3)-Ca(1)-O(6)	101.05(14)
B(5)-O(3)	1.461(7)	O(3)-Ca(1)-O(14)	112.60(14)
B(5)-O(14)#5	1.485(7)	O(6)-Ca(1)-O(14)	84.49(14)
B(5)-O(5)#5	1.486(7)	O(3)-Ca(1)-O(13)	85.66(14)
B(6)-O(6)#8	1.441(7)	O(6)-Ca(1)-O(13)	166.48(14)
B(6)-O(2)	1.464(8)	O(14)-Ca(1)-O(13)	103.91(15)
B(6)-O(1)	1.473(7)	O(3)-Ca(1)-O(7)	166.34(14)
B(6)-O(11)#7	1.484(7)	O(6)-Ca(1)-O(7)	82.31(13)
B(7)-O(12)#13	1.450(7)	O(14)-Ca(1)-O(7)	80.80(14)
B(7)-O(5)	1.454(7)	O(13)-Ca(1)-O(7)	88.53(14)
B(7)-O(7)#10	1.490(7)	O(3)-Ca(1)-O(11)	82.32(14)
B(7)-O(13)#5	1.496(7)	O(6)-Ca(1)-O(11)	90.98(14)
B(8)-O(3)#7	1.449(7)	O(14)-Ca(1)-O(11)	164.97(14)
B(8)-O(4)	1.456(7)	O(13)-Ca(1)-O(11)	78.19(14)
B(8)-O(6)#14	1.473(7)	O(7)-Ca(1)-O(11)	84.40(14)
B(8)-O(10)#4	1.512(7)	O(3)-Ca(1)-O(5)#5	54.71(12)
O(4)-Cs(1)-O(9)	80.38(11)	O(6)-Ca(1)-O(5)#5	139.31(12)
O(4)-Cs(1)-O(2)	96.27(11)	O(14)-Ca(1)-O(5)#5	78.08(13)
O(9)-Cs(1)-O(2)	175.02(11)	O(13)-Ca(1)-O(5)#5	53.90(12)
O(4)-Cs(1)-O(8)#1	138.58(11)	O(7)-Ca(1)-O(5)#5	129.55(13)
O(9)-Cs(1)-O(8)#1	140.89(11)	O(11)-Ca(1)-O(5)#5	113.87(13)
O(2)-Cs(1)-O(8)#1	42.84(11)	O(3)-Ca(1)-O(3)#5	80.19(14)
O(4)-Cs(1)-O(12)	178.39(11)	O(6)-Ca(1)-O(3)#5	52.26(12)
O(9)-Cs(1)-O(12)	98.93(11)	O(14)-Ca(1)-O(3)#5	51.14(12)
O(2)-Cs(1)-O(12)	84.52(11)	O(13)-Ca(1)-O(3)#5	141.13(13)
O(8)#1-Cs(1)-O(12)	42.03(11)	O(7)-Ca(1)-O(3)#5	111.69(13)
O(4)-Cs(1)-O(8)	94.26(11)	O(11)-Ca(1)-O(3)#5	134.38(13)
O(9)-Cs(1)-O(8)	76.38(11)	O(5)#5-Ca(1)-O(3)#5	88.97(11)
O(2)-Cs(1)-O(8)	107.67(11)	O(3)-Ca(1)-O(13)#7	137.11(13)
O(8)#1-Cs(1)-O(8)	93.65(12)	O(6)-Ca(1)-O(13)#7	112.51(13)
O(12)-Cs(1)-O(8)	84.17(11)	O(14)-Ca(1)-O(13)#7	48.72(12)

O(13)-Ca(1)-O(13)#7	67.78(15)	O(6)#9-Ca(2)-O(7)#10	79.22(11)
O(7)-Ca(1)-O(13)#7	49.98(12)	B(4)-Ca(2)-O(7)#10	26.49(14)
O(11)-Ca(1)-O(13)#7	121.45(13)	B(4)#5-Ca(2)-O(7)#10	156.33(15)
O(5)#5-Ca(1)-O(13)#7	82.42(11)	O(10)-Ca(2)-O(7)#7	132.79(12)
O(3)#5-Ca(1)-O(13)#7	99.46(11)	O(10)#5-Ca(2)-O(7)#7	49.53(12)
B(3)-Ca(1)-O(13)#7	25.95(13)	O(5)#5-Ca(2)-O(7)#7	51.87(11)
B(4)#6-Ca(1)-O(13)#7	144.36(14)	O(1)-Ca(2)-O(7)#7	69.39(12)
O(10)-Ca(2)-O(10)#5	109.0(2)	O(1)#5-Ca(2)-O(7)#7	110.38(13)
O(10)-Ca(2)-O(5)#5	168.70(14)	O(6)#8-Ca(2)-O(7)#7	79.22(11)
O(10)#5-Ca(2)-O(5)#5	81.80(13)	O(6)#9-Ca(2)-O(7)#7	103.03(11)
O(10)-Ca(2)-O(5)	81.80(13)	O(7)#10-Ca(2)-O(7)#7	177.01(16)
O(10)#5-Ca(2)-O(5)	168.70(15)	O(9)#3-B(1)-O(12)	124.0(5)
O(5)#5-Ca(2)-O(5)	87.70(19)	O(9)#3-B(1)-O(8)#1	121.8(6)
O(10)-Ca(2)-O(1)	80.54(14)	O(12)-B(1)-O(8)#1	114.2(5)
O(10)#5-Ca(2)-O(1)	104.37(14)	O(2)#4-B(2)-O(4)	124.7(6)
O(5)#5-Ca(2)-O(1)	93.64(14)	O(2)#4-B(2)-O(8)#2	116.9(6)
O(5)-Ca(2)-O(1)	80.36(13)	O(4)-B(2)-O(8)#2	118.1(6)
O(10)-Ca(2)-O(1)#5	104.37(14)	O(14)-B(3)-O(1)	119.6(5)
O(10)#5-Ca(2)-O(1)#5	80.54(14)	O(14)-B(3)-O(13)#7	118.9(5)
O(5)#5-Ca(2)-O(1)#5	80.36(14)	O(1)-B(3)-O(13)#7	120.9(5)
O(5)-Ca(2)-O(1)#5	93.64(14)	O(10)-B(4)-O(11)#9	121.3(5)
O(1)-Ca(2)-O(1)#5	171.7(2)	O(10)-B(4)-O(7)#10	117.5(5)
O(10)-Ca(2)-O(6)#8	53.58(12)	O(11)#9-B(4)-O(7)#10	120.4(5)
O(10)#5-Ca(2)-O(6)#8	74.70(13)	O(9)#12-B(5)-O(3)	114.0(5)
O(5)#5-Ca(2)-O(6)#8	129.23(12)	O(9)#12-B(5)-O(14)#5	108.2(5)
O(5)-Ca(2)-O(6)#8	115.60(12)	O(3)-B(5)-O(14)#5	105.5(4)
O(1)-Ca(2)-O(6)#8	51.76(12)	O(9)#12-B(5)-O(5)#5	110.4(5)
O(1)#5-Ca(2)-O(6)#8	136.50(14)	O(3)-B(5)-O(5)#5	106.5(4)
O(10)-Ca(2)-O(6)#9	74.70(13)	O(14)#5-B(5)-O(5)#5	112.1(5)
O(10)#5-Ca(2)-O(6)#9	53.58(12)	O(12)#13-B(7)-O(5)	113.4(5)
O(5)#5-Ca(2)-O(6)#9	115.60(12)	O(12)#13-B(7)-O(7)#10	107.9(5)
O(5)-Ca(2)-O(6)#9	129.23(11)	O(5)-B(7)-O(7)#10	112.1(5)
O(1)-Ca(2)-O(6)#9	136.50(14)	O(12)#13-B(7)-O(13)#5	109.9(5)
O(1)#5-Ca(2)-O(6)#9	51.76(12)	O(5)-B(7)-O(13)#5	106.2(4)
O(6)#8-Ca(2)-O(6)#9	84.87(16)	O(7)#10-B(7)-O(13)#5	107.2(4)
O(10)-Ca(2)-O(7)#10	49.53(12)	O(3)#7-B(8)-O(4)	112.2(5)
O(10)#5-Ca(2)-O(7)#10	132.79(12)	O(3)#7-B(8)-O(6)#14	109.5(5)
O(5)#5-Ca(2)-O(7)#10	125.44(12)	O(4)-B(8)-O(6)#14	111.7(5)
O(5)-Ca(2)-O(7)#10	51.87(11)	O(3)#7-B(8)-O(10)#4	109.0(4)
O(1)-Ca(2)-O(7)#10	110.38(12)	O(4)-B(8)-O(10)#4	108.3(5)
O(1)#5-Ca(2)-O(7)#10	69.39(12)	O(6)#14-B(8)-O(10)#4	105.9(4)
O(6)#8-Ca(2)-O(7)#10	103.03(11)	O(3)#7-B(8)-O(6)#14	109.5(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, -y+5/2, -z+1 #2 -x+1/2, y-1/2, -z+1/2 #3 x, -y+2, z+1/2 #4 x, -y+2, z-1/2

#5 -x, y, -z+3/2 #6 -x, y-1, -z+3/2 #7 -x, -y+1, -z+1 #8 x, y+1, z #9 -x, y+1, -z+3/2 #10 x, -y+1, z+1/2 #11 -x+1/2, -y+3/2, -z+1 #12 x-1/2, -y+3/2, z+1/2 #13 -x+1/2, y-1/2, -z+3/2 #14 x, -y+1, z-1/2 #15 -x, -y+2, -z+1 #16 x, y-1, z #17 -x+1/2, y+1/2, -z+1/2 #18 x+1/2, -y+3/2, z-1/2 #19 -x+1/2, y+1/2, -z+3/2

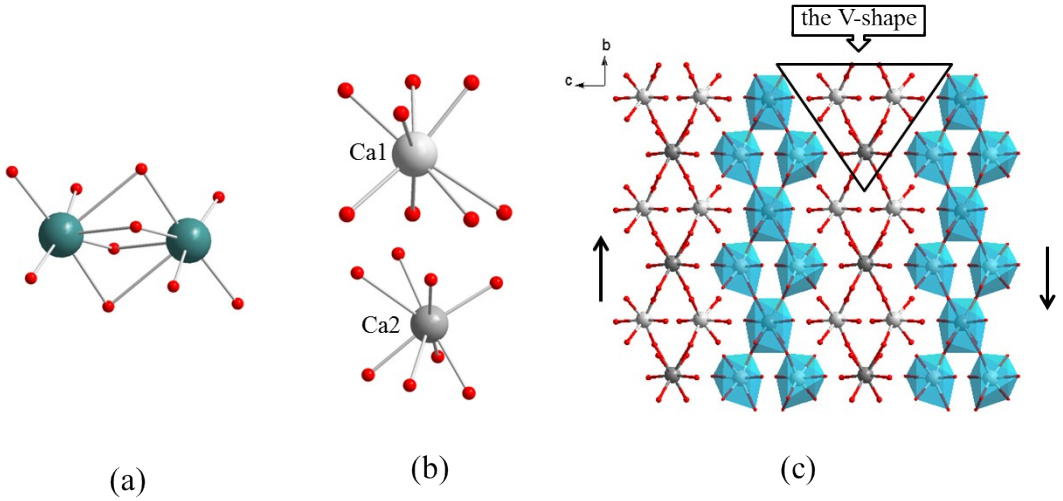


Figure S1. (a) The dimer of Rb-O group (b) The $Ca1O_8$ and the $Ca2O_8$ (c) The antiparallel Ca-O chains

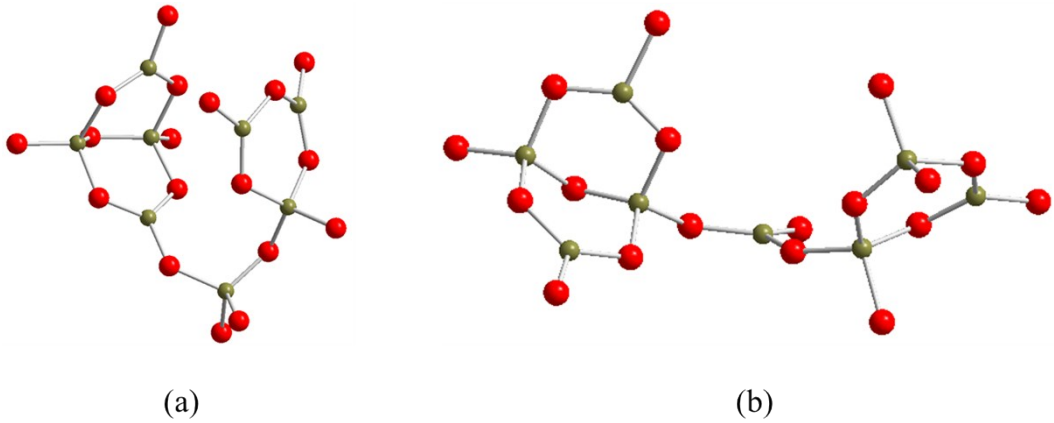
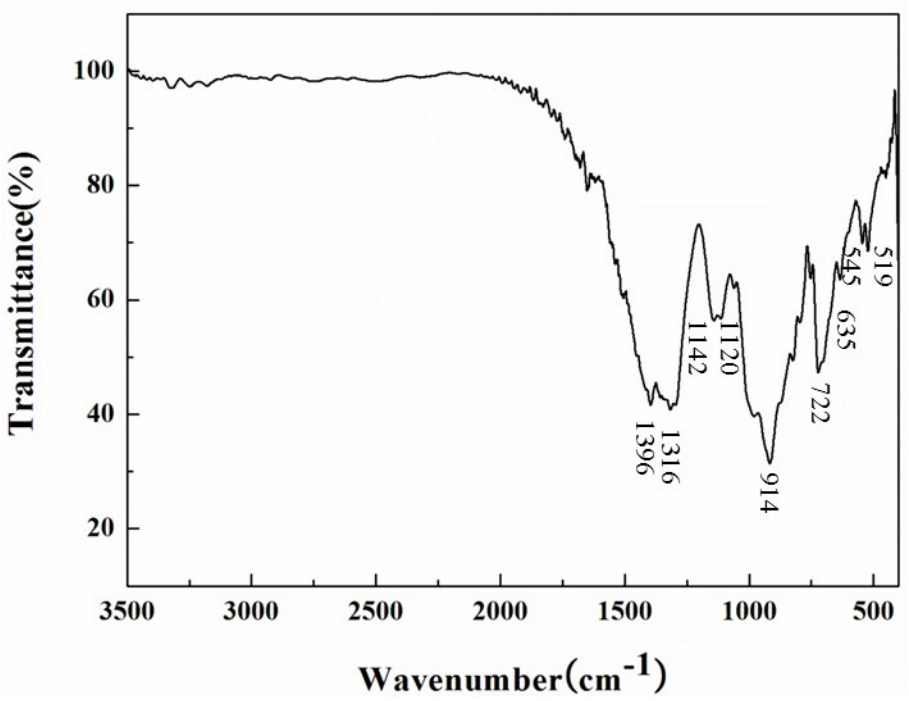
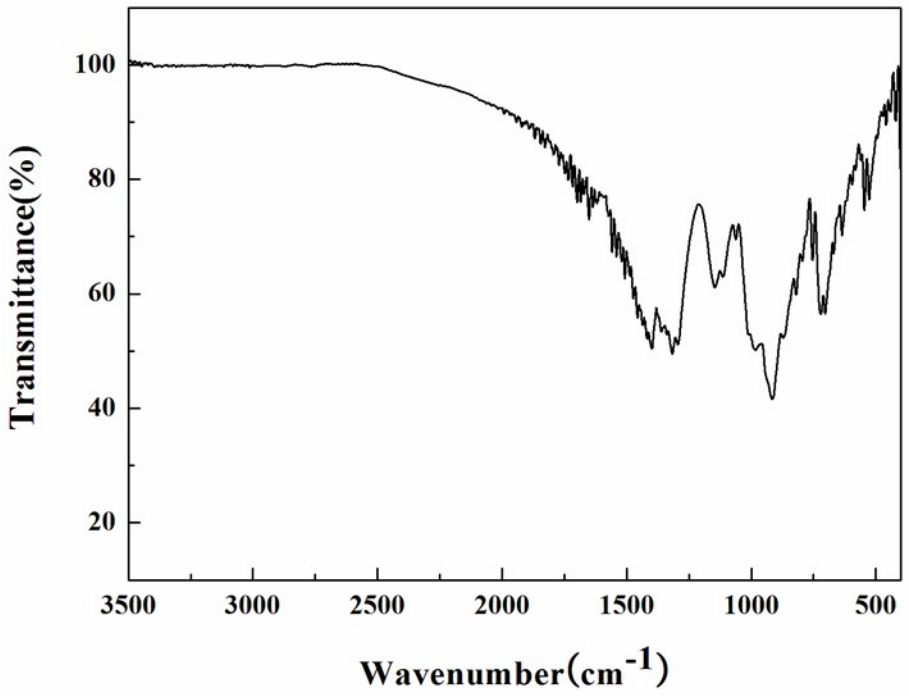


Figure S2. FBBs of α-CaB_4O_7 (a) and $Rb_2B_4O_7$ (b)

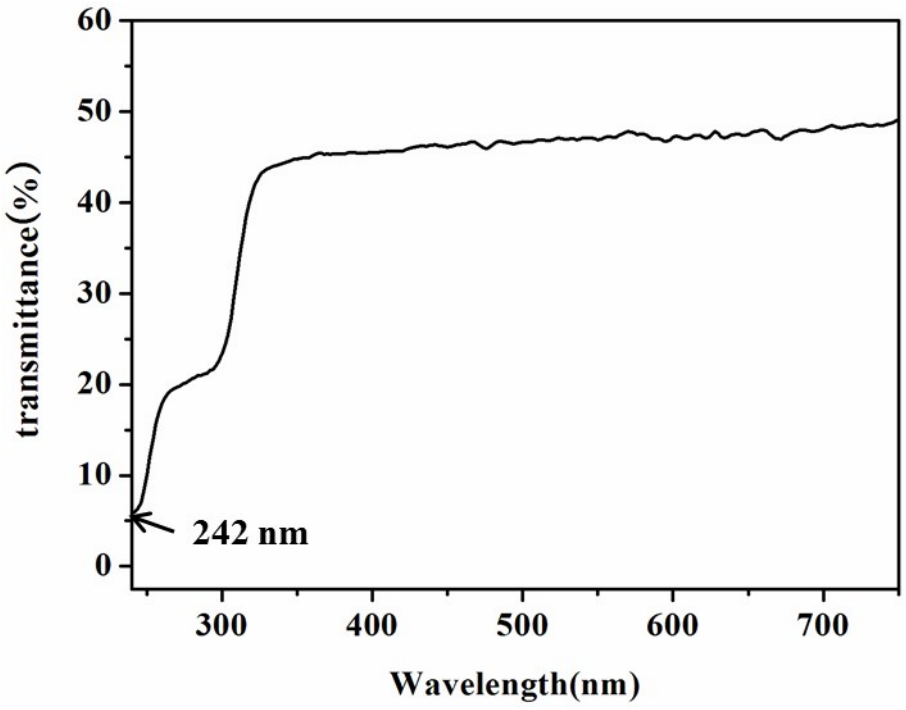


(a)

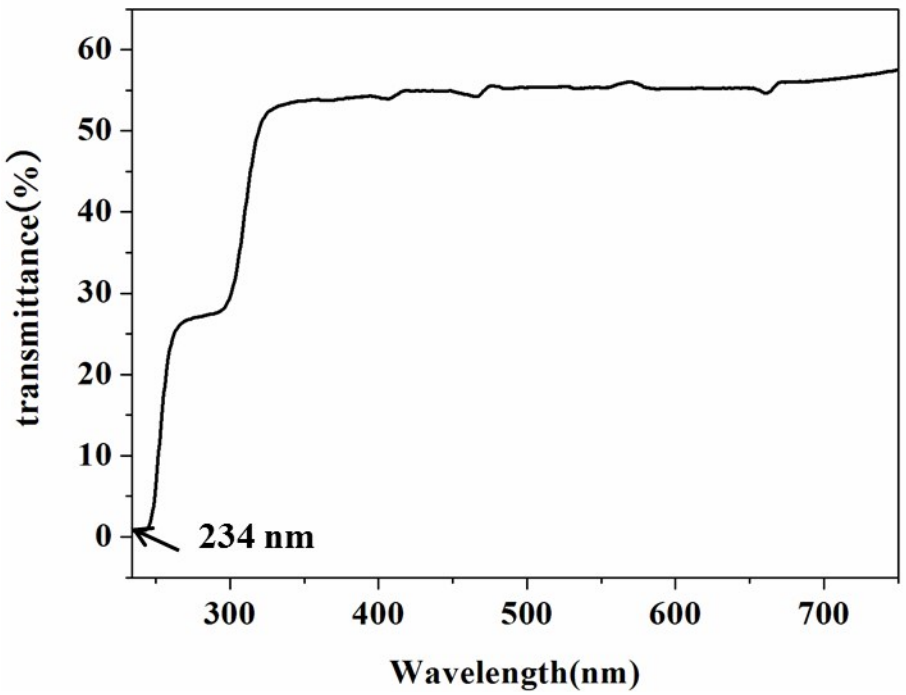


(b)

Figure S3. IR spectrum of $Rb_2Ca_3B_{16}O_{28}$ (a) and $Cs_2Ca_3B_{16}O_{28}$ (b)

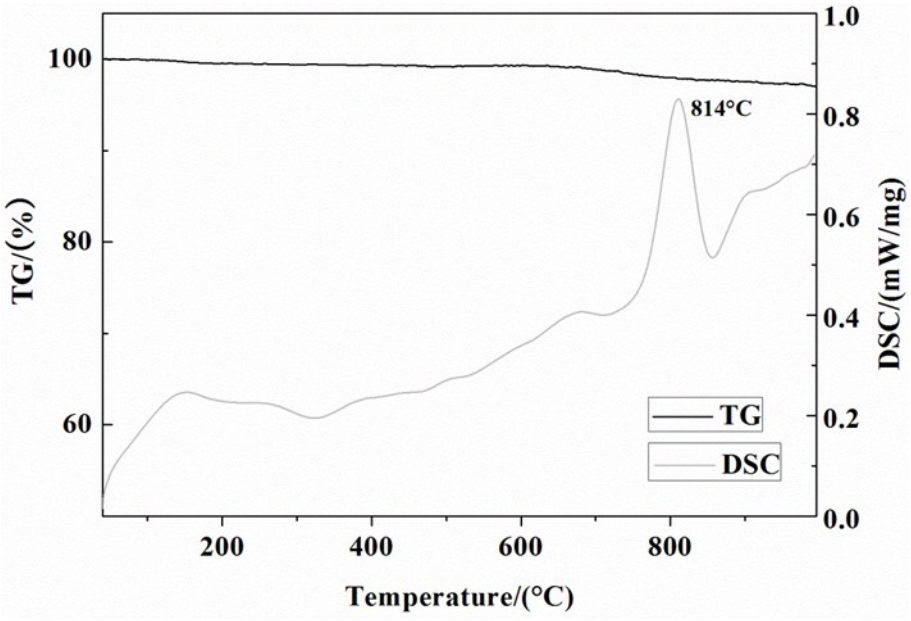


(a)

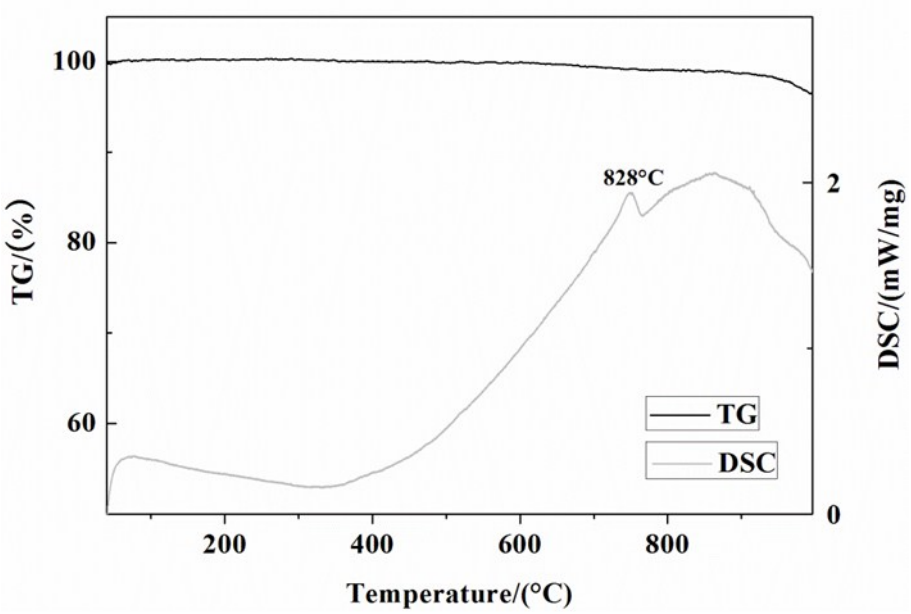


(b)

Figure S4. Transmittance spectrum of $Rb_2Ca_3B_{16}O_{28}$ (a) and $Cs_2Ca_3B_{16}O_{28}$ (b)



(a)



(b)

Figure S5. TG and DSC curves of $Rb_2Ca_3B_{16}O_{28}$ (a) and $Cs_2Ca_3B_{16}O_{28}$ (b)

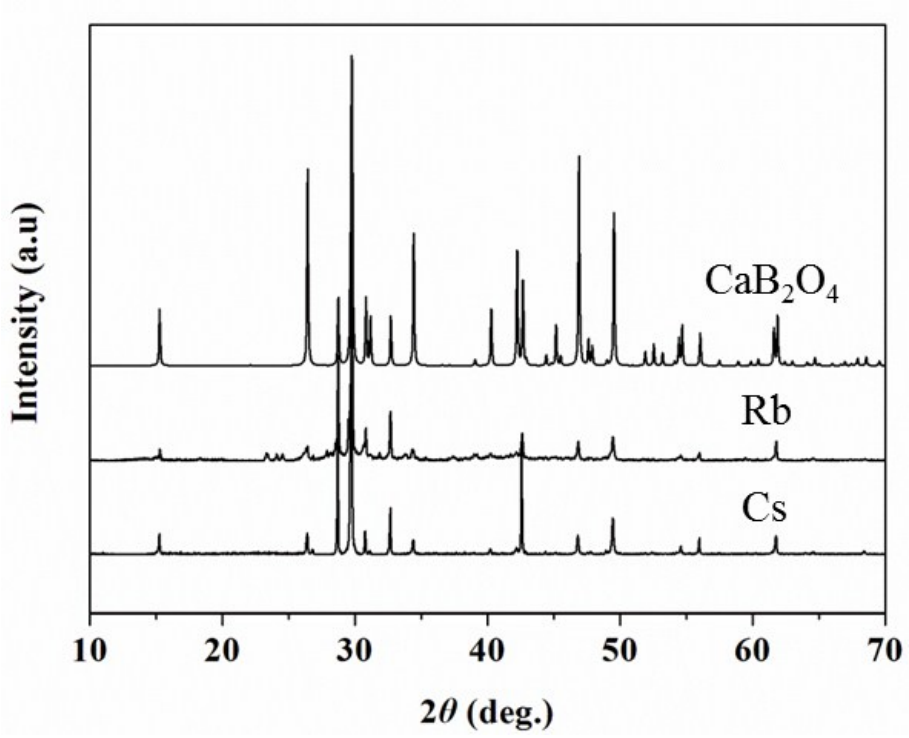


Figure S6. XRD patterns of $Rb_2Ca_3B_{16}O_{28}$ and $Cs_2Ca_3B_{16}O_{28}$ after melting

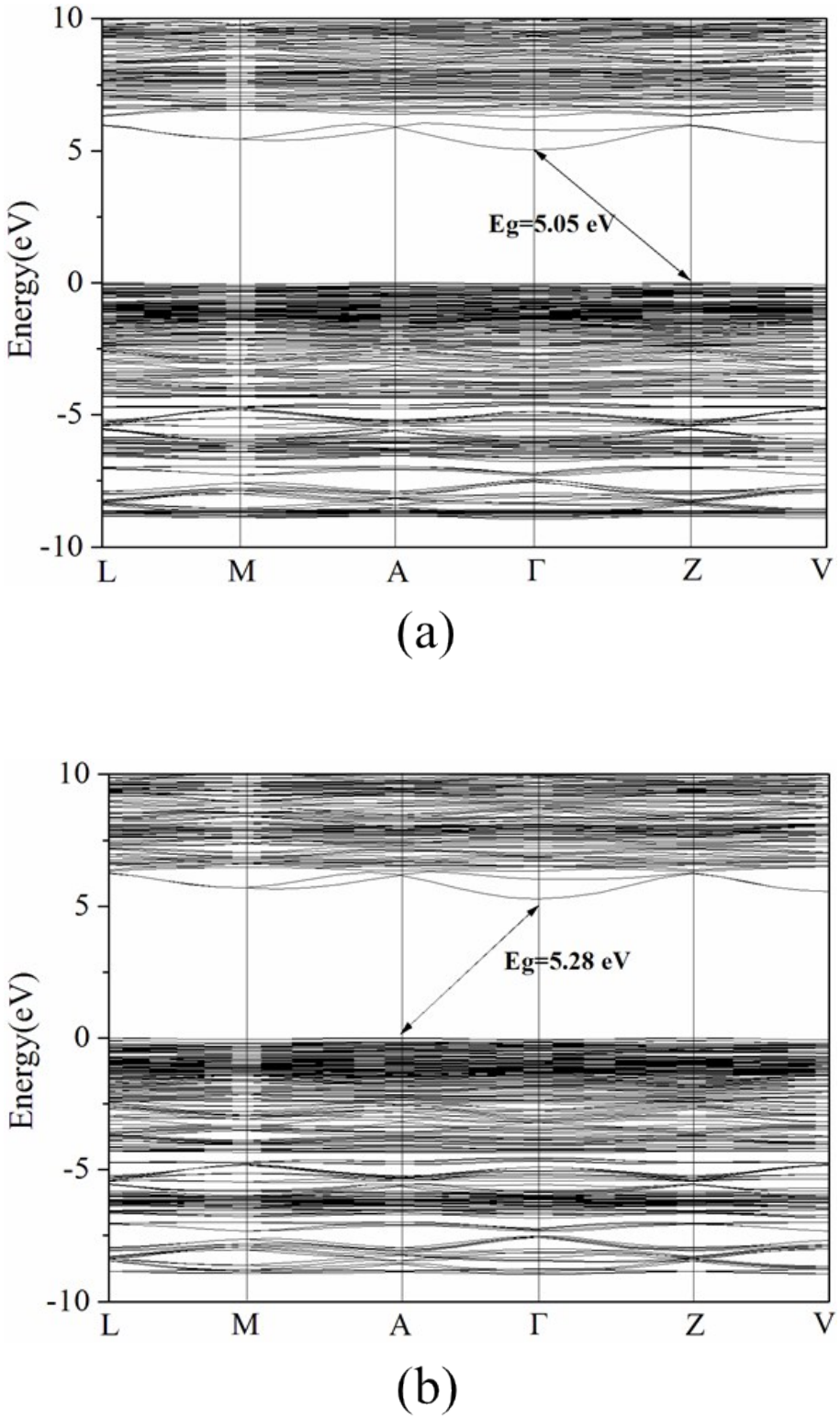


Figure S7. Calculated band structure of $Rb_2Ca_3B_{16}O_{28}$ (a) and $Cs_2Ca_3B_{16}O_{28}$ (b)