Electronic Supplementary Information

Effect of Anion Dimensionality on Optical Properties: $_{\infty}[B_7O_{10}(OH)_2]$ Layer in $CsB_7O_{10}(OH)_2$ vs $_{\infty}[B_7O_{12}]$ Framework in $CsBaB_7O_{12}$

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Contents

Reagents

CsF (Tianjin Baishi Chemical Reagent Co., Ltd, 99.5%), BaF_2 (Aladdin Reagent Co., Ltd., 99.99%), H_3BO_3 (Tianjin Baishi Chemical Reagent Co., Ltd, 99.5%), Na_2CO_3 (Shanghai Aladdin Reagent Co., Ltd., 99.5%), $BaCO_3$ (Shanghai Aladdin Reagent, Ltd., 99.0%), B_2O_3 (Shanghai Aladdin Reagent Co., Ltd., 98.0%), PbO (Tianjin Baishi Chemical Reagent Co., Ltd, 99.0%) and Cs_2CO_3 (Tianjin Baishi Chemical Reagent Co., Ltd, 99.0%) were of analytical grade and were obtained from commercial sources without further purification.

Table S1. (a) Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sums (BVSs) for $CsB_7O_{10}(OH)_2$.

Atoms	x	y	z	U(eq)	BVS
Cs(1)	10000	8134(1)	7500	25(1)	1.110
B(1)	5000	2787(4)	2500	18(1)	3.060
B(2)	5777(3)	3381(3)	4482(3)	19(1)	3.050
B(3)	7739(3)	5051(3)	5345(2)	18(1)	3.073
B(4)	8903(3)	6655(3)	4044(3)	19(1)	3.059
O(1)	5773(2)	3664(2)	3388(1)	20(1)	1.996
O(2)	6655(2)	4047(2)	5350(2)	24(1)	2.073
O(3)	7878(2)	5738(2)	4365(2)	24(1)	2.090
O(4)	8627(2)	5347(2)	6313(2)	31(1)	1.926
O(5)	8888(2)	6869(2)	2935(2)	20(1)	1.880
O(6)	9864(2)	7363(2)	4846(2)	26(1)	2.032

Table S1. (b) Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sums (BVSs) for $CsBaB_7O_{12}$.

Atoms	x	y	z	U(eq)	BVS
Ba(1)	4774(1)	2552(1)	1122(1)	15(1)	1.922
Cs(1)	136(1)	2558(1)	-19(1)	22(1)	1.051
B(1)	-2533(5)	4641(6)	503(4)	12(1)	3.071
B(2)	2992(5)	5573(6)	1648(4)	10(1)	3.049
B(3)	3996(5)	1242(6)	-1713(4)	11(1)	3.065
B(4)	2866(5)	1215(6)	2961(5)	14(1)	3.049
B(5)	1798(5)	4899(6)	2942(5)	12(1)	3.042
B(6)	-3719(5)	2427(6)	-643(4)	10(1)	3.061
B(7)	692(6)	86(6)	2596(5)	12(1)	3.071
O(1)	-629(3)	-70(4)	1806(3)	15(1)	2.057
O(2)	1595(3)	737(4)	2177(3)	16(1)	2.082
O(3)	2898(3)	851(4)	-1290(3)	13(1)	1.743
O(4)	5244(3)	1450(3)	-714(3)	11(1)	2.131
O(5)	3537(3)	2288(3)	2606(3)	12(1)	2.088
O(6)	4185(3)	4906(3)	2549(3)	10(1)	2.043
O(7)	2674(3)	4735(3)	586(3)	13(1)	2.09
O(8)	1804(3)	5583(4)	1991(3)	14(1)	2.055
O(9)	-1084(3)	4656(3)	1312(3)	12(1)	2.102
O(10)	-3367(3)	5620(4)	968(3)	17(1)	1.919
O(11)	-3063(3)	3074(4)	416(2)	12(1)	2.032
O(12)	-3369(3)	2790(3)	-1537(3)	11(1)	2.013

Table S2. (a) Bond lengths [Å] and angles [°] for $CsB_7O_{10}(OH)_2$.

Cs(1)-O(1)#1	3.291(2)	O(4)#5-Cs(1)-O(1)#1	167.23(5)
Cs(1)-O(1)#2	3.291(2)	O(4)-Cs(1)-O(1)#2	167.23(5)
Cs(1)-O(2)#3	3.269(2)	O(4)#5-Cs(1)-O(1)#2	125.74(6)
Cs(1)-O(2)#4	3.269(2)	O(4)-Cs(1)-O(1)#1	125.74(6)
Cs(1)-O(3)#1	3.369(2)	O(4)-Cs(1)-O(2)#3	112.23(6)
Cs(1)-O(3)#2	3.369(2)	O(4)#5-Cs(1)-O(2)#3	93.98(6)
Cs(1)-O(4)	3.195(2)	O(4)#5-Cs(1)-O(2)#4	112.23(6)
Cs(1)-O(4)#5	3.195(2)	O(4)-Cs(1)-O(2)#4	93.98(6)
Cs(1)-O(5)#1	3.498(3)	O(4)#5-Cs(1)-O(3)#1	141.35(5)
Cs(1)-O(5)#2	3.498(3)	O(4)#5-Cs(1)-O(3)#2	75.86(6)
Cs(1)-O(6)	3.239(2)	O(4)-Cs(1)-O(3)#2	141.35(5)
Cs(1)-O(6)#5	3.239(2)	O(4)-Cs(1)-O(3)#1	75.86(6)
B(1)-O(1)	1.455(3)	O(4)#5-Cs(1)-O(4)	66.56(8)
B(1)-O(1)#6	1.455(3)	O(4)#5-Cs(1)-O(5)#1	112.93(5)
B(1)-O(5)#7	1.486(3)	O(4)#5-Cs(1)-O(5)#2	67.00(5)
B(1)-O(5)#8	1.486(3)	O(4)-Cs(1)-O(5)#1	67.00(5)
B(2)-O(1)	1.333(3)	O(4)-Cs(1)-O(5)#2	112.93(5)
B(2)-O(2)	1.374(3)	O(4)-Cs(1)-O(6)#5	101.71(6)
B(2)-O(6)#7	1.389(3)	O(4)#5-Cs(1)-O(6)#5	54.26(5)
B(3)-O(2)	1.377(3)	O(4)#5-Cs(1)-O(6)	101.71(6)
B(3)-O(3)	1.363(3)	O(4)-Cs(1)-O(6)	54.26(5)
B(3)-O(4)	1.346(3)	O(5)#2-Cs(1)-O(5)#1	179.92(6)
B(4)-O(3)	1.373(3)	O(6)-Cs(1)-O(1)#1	85.41(5)
B(4)-O(5)	1.338(4)	O(6)#5-Cs(1)-O(1)#1	120.34(5)
B(4)-O(6)	1.381(3)	O(6)#5-Cs(1)-O(1)#2	85.41(5)
O(1)#2-Cs(1)-O(1)#1	42.31(7)	O(6)-Cs(1)-O(1)#2	120.34(5)
O(1)#1-Cs(1)-O(3)#2	91.43(5)	O(6)-Cs(1)-O(2)#3	150.43(5)
O(1)#1-Cs(1)-O(3)#1	51.41(4)	O(6)-Cs(1)-O(2)#4	41.61(5)
O(1)#2-Cs(1)-O(3)#2	51.41(4)	O(6)#5-Cs(1)-O(2)#4	150.43(5)
O(1)#2-Cs(1)-O(3)#1	91.43(5)	O(6)#5-Cs(1)-O(2)#3	41.61(5)
O(1)#1-Cs(1)-O(5)#2	102.40(4)	O(6)-Cs(1)-O(3)#1	60.36(6)
O(1)#2-Cs(1)-O(5)#2	77.68(4)	O(6)#5-Cs(1)-O(3)#2	60.35(6)
O(1)#2-Cs(1)-O(5)#1	102.40(4)	O(6)#5-Cs(1)-O(3)#1	129.86(5)
O(1)#1-Cs(1)-O(5)#1	77.68(4)	O(6)-Cs(1)-O(3)#2	129.86(5)
O(2)#3-Cs(1)-O(1)#2	66.32(5)	O(6)-Cs(1)-O(5)#1	87.32(4)
O(2)#4-Cs(1)-O(1)#2	84.39(5)	O(6)#5-Cs(1)-O(5)#2	87.32(4)
O(2)#4-Cs(1)-O(1)#1	66.32(5)	O(6)#5-Cs(1)-O(5)#1	92.67(4)
O(2)#3-Cs(1)-O(1)#1	84.39(5)	O(6)-Cs(1)-O(5)#2	92.67(4)
O(2)#3-Cs(1)-O(2)#4	148.94(7)	O(6)-Cs(1)-O(6)#5	153.65(7)
O(2)#4-Cs(1)-O(3)#2	91.95(6)	O(1)-B(1)-O(5)#7	111.75(10)

O(2)#4-Cs(1)-O(3)#1	78.12(6)	O(1)-B(1)-O(5)#8	108.27(11)
O(2)#3-Cs(1)-O(3)#2	78.12(6)	O(1)#6-B(1)-O(5)#7	108.27(11)
O(2)#3-Cs(1)-O(3)#1	91.95(6)	O(5)#7-B(1)-O(5)#8	107.4(3)
O(2)#4-Cs(1)-O(5)#1	116.62(5)	O(1)-B(2)-O(2)	124.5(2)
O(2)#3-Cs(1)-O(5)#1	63.40(5)	O(1)-B(2)-O(6)#7	121.9(2)
O(2)#4-Cs(1)-O(5)#2	63.40(5)	O(2)-B(2)-O(6)#7	113.5(2)
O(2)#3-Cs(1)-O(5)#2	116.62(5)	O(3)-B(3)-O(2)	119.5(2)
O(3)#2-Cs(1)-O(3)#1	142.55(7)	O(4)-B(3)-O(2)	119.1(2)
O(3)#2-Cs(1)-O(5)#1	140.68(4)	O(4)-B(3)-O(3)	121.4(2)
O(3)#1-Cs(1)-O(5)#2	140.68(4)	O(3)-B(4)-O(6)	120.6(2)
O(3)#1-Cs(1)-O(5)#1	39.36(4)	O(5)-B(4)-O(3)	117.3(2)
O(3)#2-Cs(1)-O(5)#2	39.36(4)	O(5)-B(4)-O(6)	122.0(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+3/2,-z+1 #2 x+1/2,-y+3/2,z+1/2
#3 -x+3/2,y+1/2,-z+3/2 #4 x+1/2,y+1/2,z
#5 -x+2,y,-z+3/2 #6 -x+1,y,-z+1/2
#7 x-1/2,y-1/2,z #8 -x+3/2,y-1/2,-z+1/2

Table S2. (b) Bond lengths [Å] and angles [°] for $CsBaB_7O_{12}$.

Ba(1)-O(3)	3.286(3)	O(11)#3-Ba(1)-O(6)	118.33(8)
Ba(1)-O(4)	2.727(3)	O(11)#3-Ba(1)-O(6)#1	98.12(9)
Ba(1)-O(5)	2.680(3)	O(11)#3-Ba(1)-O(7)	119.06(9)
Ba(1)-O(6)	2.948(3)	O(11)#3-Ba(1)-O(10)#4	79.78(8)
Ba(1)-O(6)#1	2.811(3)	O(12)#5-Ba(1)-O(3)	147.38(8)
Ba(1)-O(7)	2.802(3)	O(12)#5-Ba(1)-O(4)	124.37(8)
Ba(1)-O(10)#4	2.951(3)	O(12)#5-Ba(1)-O(5)	66.15(9)
Ba(1)-O(11)#3	2.797(3)	O(12)#5-Ba(1)-O(6)	70.30(8)
Ba(1)-O(12)#5	2.875(3)	O(12)#5-Ba(1)-O(6)#1	48.90(8)
Cs(1)-O(1)#6	3.309(3)	O(12)#5-Ba(1)-O(7)	119.07(8)
Cs(1)-O(2)	3.052(3)	O(12)#5-Ba(1)-O(10)#4	152.83(9)
Cs(1)-O(7)	3.134(3)	O(12)#5-Ba(1)-O(11)#3	91.35(8)
Cs(1)-O(8)#4	3.022(3)	O(2)-Cs(1)-O(1)#6	97.21(8)
Cs(1)-O(9)	3.080(3)	O(7)-Cs(1)-O(1)#6	102.42(8)
Cs(1)-O(9)#4	3.285(3)	O(7)-Cs(1)-O(2)	90.09(8)
Cs(1)-O(12)	3.475(3)	O(8)#4-Cs(1)-O(1)#6	91.16(8)
B(1)-O(7)#4	1.433(6)	O(8)#4-Cs(1)-O(2)	167.31(8)
B(1)-O(9)	1.484(6)	O(8)#4-Cs(1)-O(7)	97.42(8)
B(1)-O(10)	1.499(6)	O(9)#4-Cs(1)-O(1)#6	88.99(8)
B(1)-O(11)	1.461(6)	O(9)-Cs(1)-O(1)#6	165.49(7)
B(2)-O(6)	1.460(6)	O(9)-Cs(1)-O(2)	88.96(8)
B(2)-O(7)	1.449(6)	O(9)#4-Cs(1)-O(2)	133.57(8)
B(2)-O(8)	1.481(6)	O(9)-Cs(1)-O(7)	90.64(8)
B(2)-O(12)#4	1.498(6)	O(9)#4-Cs(1)-O(7)	43.93(8)

B(3)-O(3)	1.493(6)	O(9)#4-Cs(1)-O(8)#4	55.75(7)
B(3)-O(4)	1.449(6)	O(9)-Cs(1)-O(8)#4	80.78(8)
B(3)-O(5)#7	1.512(6)	O(12)-Cs(1)-O(1)#6	94.32(7)
B(3)-O(6)#7	1.431(6)	O(12)-Cs(1)-O(2)	126.51(7)
B(4)-O(2)	1.396(6)	O(12)-Cs(1)-O(7)	137.46(7)
B(4)-O(5)	1.349(6)	O(12)-Cs(1)-O(8)#4	42.84(7)
B(4)-O(10)#8	1.354(6)	O(12)-Cs(1)-O(9)#4	98.55(7)
B(5)-O(1)#9	1.392(6)	O(12)-Cs(1)-O(9)	71.56(7)
B(5)-O(3)#2	1.364(6)	O(9)-B(1)-O(7)#4	111.1(4)
B(5)-O(8)	1.343(6)	O(10)-B(1)-O(7)#4	107.6(4)
B(6)-O(4)#10	1.364(6)	O(10)-B(1)-O(9)	109.6(4)
B(6)-O(11)	1.372(6)	O(11)-B(1)-O(7)#4	112.6(4)
B(6)-O(12)	1.354(5)	O(11)-B(1)-O(9)	109.0(4)
B(7)-O(1)	1.381(6)	O(11)-B(1)-O(10)	106.9(4)
B(7)-O(2)	1.381(6)	O(7)-B(2)-O(6)	110.4(4)
B(7)-O(9)#8	1.334(6)	O(8)-B(2)-O(6)	110.7(4)
O(4)-Ba(1)-O(3)	45.17(8)	O(8)-B(2)-O(7)	110.7(4)
O(5)-Ba(1)-O(3)	109.09(8)	O(12)#4-B(2)-O(6)	105.5(4)
O(5)-Ba(1)-O(4)	149.78(9)	O(12)#4-B(2)-O(7)	111.5(4)
O(6)#1-Ba(1)-O(3)	98.49(8)	O(12)#4-B(2)-O(8)	108.0(4)
O(6)-Ba(1)-O(3)	133.24(8)	O(4)-B(3)-O(3)	107.0(4)
O(6)-Ba(1)-O(4)	156.20(8)	O(5)#7-B(3)-O(3)	105.7(3)
O(6)#1-Ba(1)-O(4)	93.72(9)	O(5)#7-B(3)-O(4)	112.2(4)
O(6)-Ba(1)-O(5)	49.84(8)	O(6)#7-B(3)-O(3)	113.5(4)
O(6)#1-Ba(1)-O(5)	72.33(9)	O(6)#7-B(3)-O(4)	110.2(4)
O(7)-Ba(1)-O(3)	86.38(8)	O(6)#7-B(3)-O(5)#7	108.1(4)
O(7)-Ba(1)-O(4)	114.73(9)	O(5)-B(4)-O(2)	117.3(4)
O(7)-Ba(1)-O(5)	70.75(9)	O(10)#8-B(4)-O(2)	119.9(4)
O(7)-Ba(1)-O(6)#1	142.26(8)	O(10)#8-B(4)-O(5)	122.8(4)
O(7)-Ba(1)-O(6)	49.01(8)	O(3)#2-B(5)-O(1)#9	116.1(4)
O(10)#4-Ba(1)-O(3)	59.43(8)	O(8)-B(5)-O(1)#9	120.4(4)
O(10)#4-Ba(1)-O(4)	67.72(9)	O(8)-B(5)-O(3)#2	123.5(4)
O(10)#4-Ba(1)-O(5)	117.23(8)	O(11)-B(6)-O(4)#10	114.4(4)
O(10)#4-Ba(1)-O(6)	91.27(8)	O(12)-B(6)-O(4)#10	124.1(4)
O(10)#4-Ba(1)-O(6)#1	157.41(9)	O(12)-B(6)-O(11)	121.4(4)
O(10)#4-Ba(1)-O(7)	48.49(8)	O(2)-B(7)-O(1)	115.0(4)
O(11)#3-Ba(1)-O(3)	93.18(8)	O(9)#8-B(7)-O(1)	123.4(4)
O(11)#3-Ba(1)-O(4)	49.18(9)	O(9)#8-B(7)-O(2)	121.7(4)
O(11)#3-Ba(1)-O(5)	156.64(9)		

Symmetry transformations used to generate equivalent atoms:

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

#4 -x,-y+1,-z #5 x,-y+1/2,z+1/2 #6 -x,-y,-z
#7 -x,y-1/2,-z+1/2 #8 -x,y+1/2,-z+1/2
#9 x-1,y,z #10 x,-y+1/2,z-1/2

Table S3. Disorder-free alkali- and/or alkaline-earth metal cations-containing caesium borates.

NO	Compound	Space group	M/B	FBBs	Anionic Groups
1	$Cs_4Mg_{4(}BO_3)_4$[1]	*P*2$_1$/*c*	2	BO_3	0D Isolated BO_3 Unit
2	$CsNa_2(BO_3)$[2]	*Pmmn*	3	BO_3	0D Isolated BO_3 Unit
3	$Na_2CsBe_6B_5O_{15}$[3]	*C*2/*c*	1.8	BO_3	0D Isolated BO_3 Unit
4	$Cs_3(BO_3)$[4]	*Pbam*	3	BO_3	0D Isolated BO_3 Unit
5	$CsBe_4(BO_3)_3$[5]	*Pnma*	1.667	BO_3	0D Isolated BO_3 Unit
6	$CsCaBO_3$[6]	*P*2$_1$3	2	BO_3	0D Isolated BO_3 Unit
7	$Cs[B(OH)_4]\cdot 2H_2O$[7]	$I\bar{4}$	1	$B(OH)_4$	0D Isolated $B(OH)_4$
8	$CsLi_5(BO_3)_2$[8]	*C*2/*c*	3	BO_3	0D Isolated BO_3 Unit
9	$Cs_3Na[Li_2(BO_3)_2]$[9]	$P\bar{1}$	3	BO_3	0D Isolated BO_3 Unit
10	$CsBO_2$[10]	$R\bar{3}c$	1	B_3O_6	0D Isolated B_3O_6 Ring
11	$CsBaB_3O_6$[11]	*P*321	0.667	B_3O_6	0D Isolated B_3O_6 Ring
12	$Cs_2(B_3O_5)_2$[12]	*P*2$_1$2$_1$2$_1$	0.333	B_3O_7	3D B_3O_5 Framework
13	$CsLiB_6O_{10}$[13-15]	$I\bar{4}2d$	0.333	B_3O_7	3D B_3O_5 Framework
14	$Cs_2(B_3O_5)_2$[16]	*P*2$_1$2$_1$2$_1$	0.333	B_3O_7	3D B_3O_5 Framework
15	$NaCs[B_4O_5(OH)_4]\cdot 4H_2O$[17]	*P*2$_1$/*c*	0.5	$B_4O_5(OH)_4$	0D Isolated $B_4O_5(OH)_4$ Unit
16	$Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$[18]	*P*2$_1$2$_1$2$_1$	0.375	$B_4O_5(OH)_4$	0D Isolated $B_4O_5(OH)_4$ Unit
17	$Cs_2[B_4O_5(OH)_4]\cdot 3H_2O$[19]	*P*2$_1$/*c*	0.5	$B_4O_5(OH)_4$	0D Isolated $B_4O_5(OH)_4$ Unit
18	$Li_3Cs_2B_5O_{10}$[20]	*C*222$_1$	1	B_5O_{10}	0D Isolated B_5O_{10} Unit
19	$Na_2Cs_2B_{20}O_{32}$[21]	*C*2/*c*	0.2	B_5O_{10}	3D B_5O_8 Framework
20	$Cs[B_5O_6(OH)_4]\cdot 2H_2O$[22, 23]	*C*2/*c*	0.2	$B_5O_6(OH)_4$	0D Isolated $B_5O_6(OH)_4$ Unit
21	$K_3CsB_{20}O_{32}$[24]	*Pbca*	0.2	B_5O_{10}	3D $B_{20}O_{32}$ Framework
22	*α*-CsB_5O_8[25, 26]	*P*2$_1$/*c*	0.2	B_5O_{10}	3D B_5O_8 Framework
23	*β*-CsB_5O_8[26, 27]	*Pbca*	0.2	B_5O_{10}	3D B_5O_8 Framework
24	*γ*-CsB_5O_8[26]	*Pbca*	0.2	B_5O_{10}	3D B_5O_8 Framework
25	*HP*- CsB_5O_8[28]	*Pnma*	0.2	B_5O_{11}	3D B_5O_8 Framework
26	$Cs_2Na_2B_{10}O_{17}$[29]	*C*2/*c*	0.4	B_5O_{11}	2D $B_{10}O_{17}$ Layer
27	$Cs_2K_2B_{10}O_{17}$[29]	*C*2/*c*	0.4	B_5O_{11}	2D $B_{10}O_{17}$ Layer
28	$Li_5Cs_2B_7O_{14}$[30]	*Ama*2	1	B_5O_{12} and BO_3	1D B_5O_{10} Chain and BO_2 Chain
29	$Li_4Cs_3B_7O_{14}$[31]	*P*3$_1$21	1	B_7O_{14}	0D Isolated B_7O_{14} Unit
30	*α*-CsB_9O_{14}[32]	*P*222$_1$	0.111	B_9O_{17}	3D B_9O_{14} Framework
31	*β*-CsB_9O_{14}[33]	*P*2$_1$/*c*	0.111	B_9O_{18}	2D B_9O_{14} Layer

32	$Cs_2(B_9O_{14})_2$[34]	$P222_1$	0.111	B_9O_{17}	3D B_9O_{14} Framework
33	$Na_2Cs_2Sr(B_9O_{15})_2$[35]	$P2_1/c$	0.278	B_9O_{19}	3D B_9O_{15} Framework
34	$Na_2Cs_2BaB_{18}O_{30}$[24]	$Pmn2_1$	0.278	B_9O_{19}	3D $B_{18}O_{30}$ Framework
35	δ-CsB_5O_8[36]	$Pccn$	0.2	$B_{10}O_{19}$	3D B_5O_8 Framework
36	$NaCs[B_{10}O_{14}(OH)_4]$[37]	$P2/c$	0.2	$B_{10}O_{15}(OH)_4$	1D $B_{10}O_{14}(OH)_4$ Chain
37	$Na_2Cs_4Ba_2[B_{12}O_{18}(OH)_6]\cdot4(OH)$[38]	$Pmn2_1$	0.667	$B_{12}O_{18}(OH)_6$	0D Isolated $B_{12}O_{18}(OH)_6$ Unit
38	$Cs_3B_{13}O_{21}$[39]	$C2/c$	0.230	$B_{26}O_{51}$	3D $B_{13}O_{21}$ Layer
39	$Na_8CsB_{21}O_{36}$[40]	$I\bar{4}$	0.429	$B_{21}O_{44}$	3D $B_{21}O_{36}$ Framework
40	$Li_4Cs_4B_{40}O_{64}$[21]	$P\bar{1}$	0.2	$B_{40}O_{77}$	3D $B_{40}O_{64}$ Framework
41	$Cs_3B_7O_{12}$[41]	$C2/c$	0.429	$B_{63}O_{133}$	3D $B_{63}O_{108}$ Framework

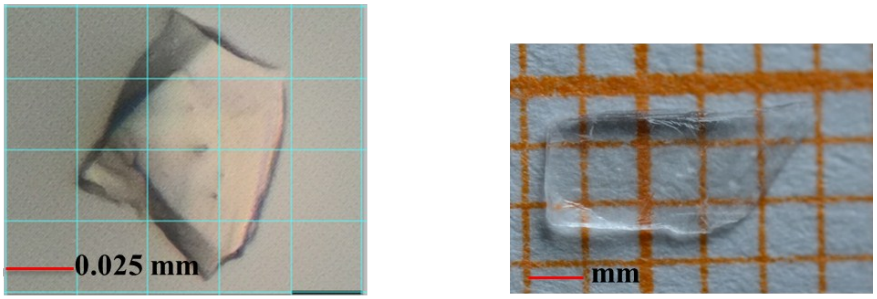

Figure S1. The crystal photographs of $CsB_7O_{10}(OH)_2$ (a) and $CsBaB_7O_{12}$ (b).

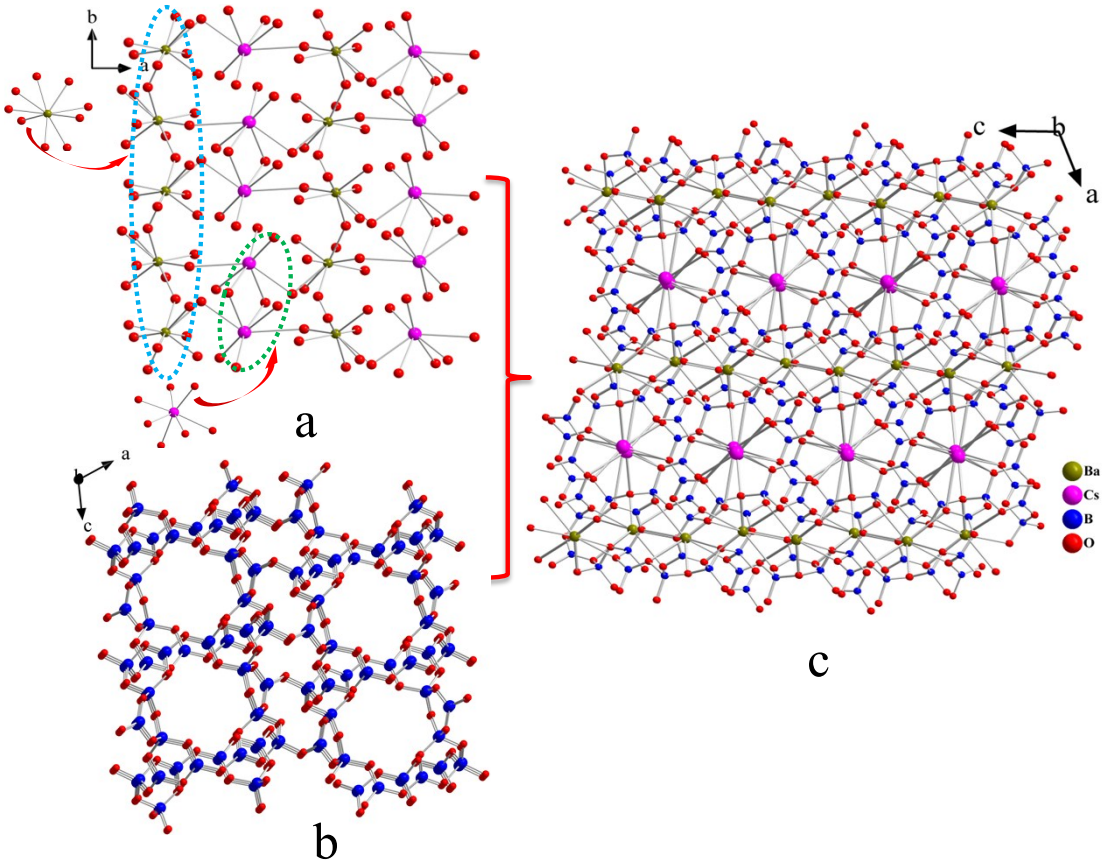

Figure S2. (a) $_{\infty}[CsBaO_{12}]$ layer; the $_{\infty}[BaO_8]$ chain is surrounded by blue circle; the $[Cs_2O_{12}]$ dimer is surrounded by green circle. (b) The 3D $_{\infty}[B_7O_{12}]$ anionic open-framework. (c) The whole 3D framework of $CsBaB_7O_{12}$.

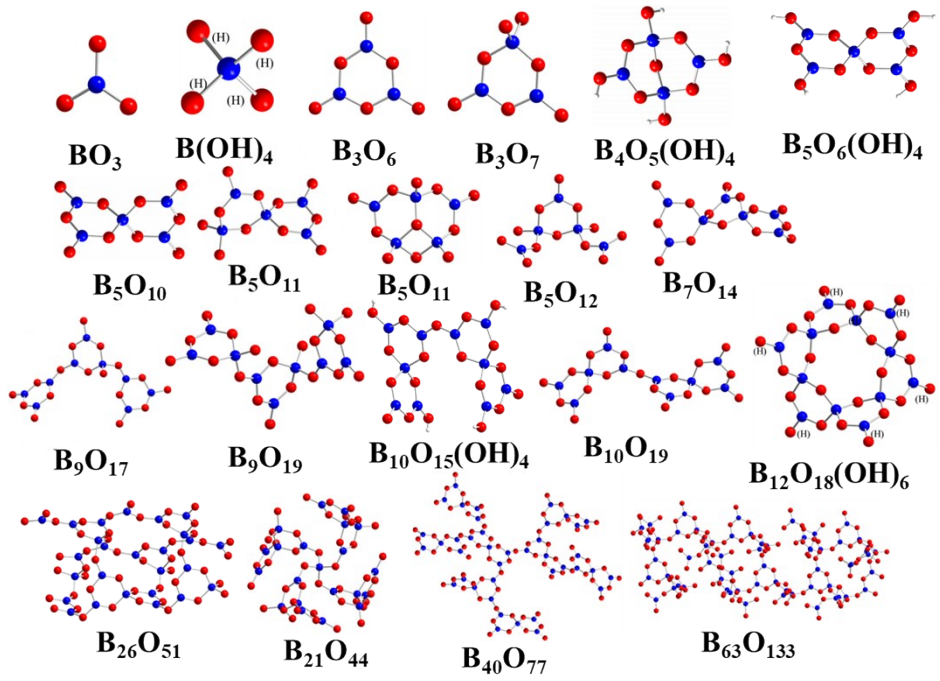

Figure S3. The fundamental building blocks (FBBs) of the investigated compounds.

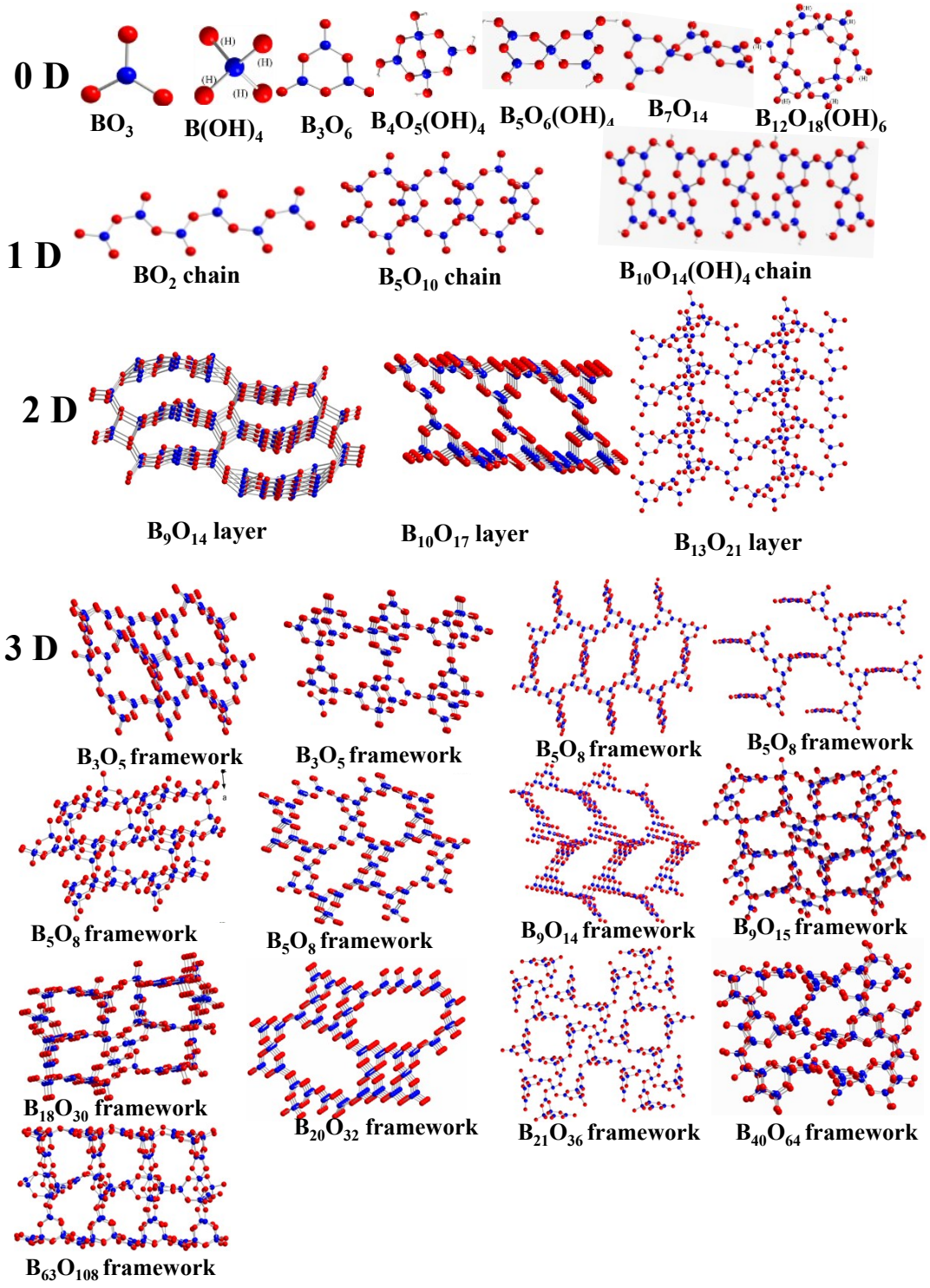

Figure S4. The anionic structures of the investigated compounds.

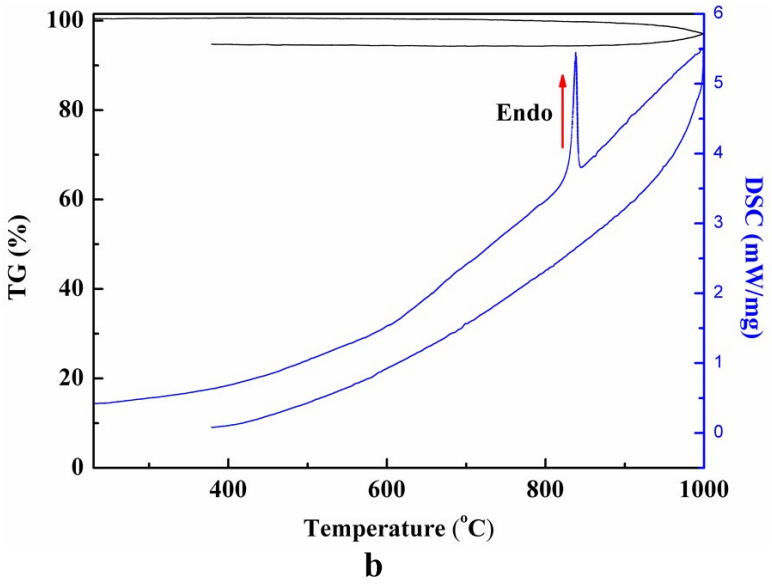

Figure S5. TG-DSC curves of $CsBaB_7O_{12}$.

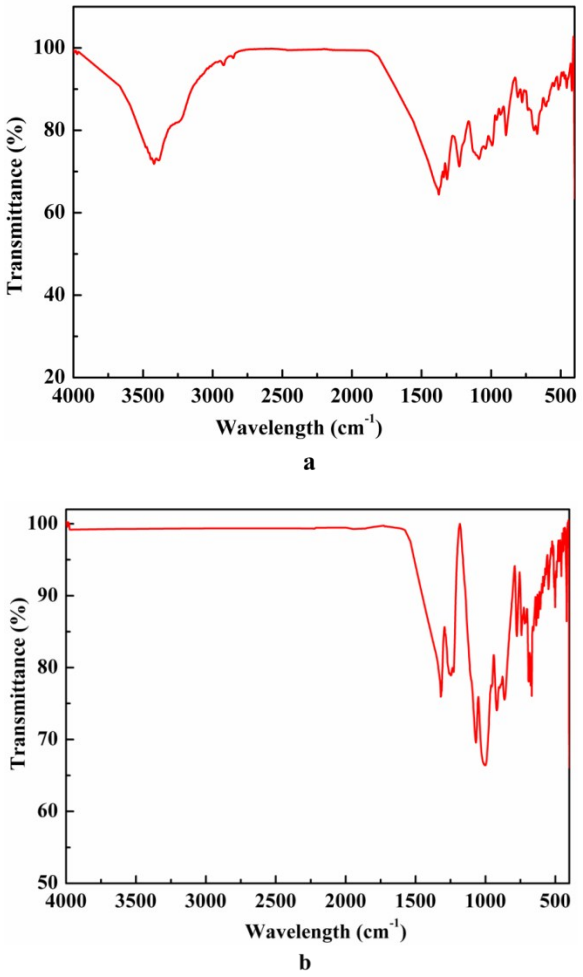

Figure S6. (a) The IR spectrum of $CsB_7O_{10}(OH)_2$. (b) The IR spectrum of $CsBaB_7O_{12}$.

Mode description	IR (cm^{-1}) for $CsB_7O_{10}(OH)_2$	IR (cm^{-1}) for $CsBaB_7O_{12}$
stretching vibrations of OH groups	3382	/
asymmetric stretching vibration of BO_3 groups	1377, 1314, and 1224	1317, 1243, 1227
asymmetric stretching vibration of BO_4 groups	1086 and 989	1066, 1000 and 914
symmetric extension of BO_3 groups	886 to 803	856
symmetric stretching vibration of BO_4 groups	775	737 and 778
out-of-plane bending of BO_3 groups	671	620 to 720
bending of in-plane bending of BO_3 groups	595 and 512	551
bending of BO_4 groups	400 to 500	400 to 500

Notes and References

1 Z. Wang, M. Zhang, S. L. Pan, Z. H. Yang, H. Zhang, B. B. Zhang, Y. Wang, J. Kang and X. X. Lin, *New J. Chem.*, 2014, **38**, 3035.

2 M. Schlager and R. Hoppe, *Aust. J. Chem.*, 1992, **45**, 1427-1439.

3 S. Wang and N. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 11458-11461.

4 C. Hoch, *Z. Naturforsch. B*, 2011, **66b**, 1248-1254.

5 H. W. Huang, W. J. Yao, R. He, C. T. Chen, X. Y. Wang and Y. H. Zhang, *Solid State Sci.*, 2013, **18**, 105-109.

6 M. Wen, H. P. Wu, X. Su, J. J. Lu, Z. H. Yang, X. H. Wu and S. L.Pan, *Dalton T.*, 2017, **46**, 4968-4974.

7 I. I. Zviedre and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser*, 1974, **1974**, 401-405.

8 M. Miessen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1986, **536**, 92-100.

9 M. Schlager and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1991, **605**, 25-34.

10 M. Schliiger and H. Hoppe, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1867-1871.

11 G. J. Chen, Y. C. Wu and P. Z. Fu, *J. Solid State Chem.*, 2007, **180**, 2194-2201.

12 J. K. MOE, *Acta Crystallogr. B*, 1974, **30**, 1178-1180.

13 J.M. Tu and D. A. Keszler, *Mater. Res. Bull.*, 1995, **30**, 209-215.

14 A. Sasaki, Y. Mori, I. Kuroda, S. Nakajima, K. Yamaguchi and S. Watanabe, *Acta Crystallogr. C*, 1995, **51**, 2222-2224.

15 N. A. Sennova, G. Cordier, B. Albert, S. K. Filatov, R. S. Bubnova, L. I. Isaenko, L. I. Gubenko, J. P. Klöckner and M. H. Prosenc, *Z. Kristallogr. Cryst. Mater.*, 2014, **229**, 741-751.

16 J. Krogh-Moe, *Acta Crystallogr. B*, 1974, **30**, 1178-1180.

17 J. G. Zhou, F. Y. Zhao, S. P. Xia and S. Y. Gao, *J. Mol. Struct.*, 2004, **688**, 143-148.

18 L. X. Zhu, T. Yue, S. P. Xia and K. B. Yu, *J. Alloy. Compd.*, 2004, **372**, 97-102.

19 M. Touboul, N. Penin and G. Nowogrocki, *J. Solid State Chem.*, 1999, **143**, 260-265.

20 Y. Yang, S. L. Pan, X. L. Hou, C. Y. Wang, K. R. Poeppelmeier, Z. H. Chen, H. P. Wu and Z. X. Zhou, *J. Mater. Chem.*, 2011, **21**, 2890-2894.

21 M. Abudoureheman, S. J. Han, Y. Wang, Q. Liu, Z. H. Yang and S. L. Pan, *Inorg. Chem.*, 2017, **56**, 13456-13463.

22 N. Penin, L. Seguin, B. Gerand, M. Touboul and G. Nowogrocki, *J. Alloy. Compd.*, 2002, **334**, 97-109.

23 H. Behm, *Acta Crystallogr. C* , 1984, **40**, 1114-1116.

24 M. Mutailipu, M. Zhang, X. Su, Z. Yang, Y. Chen and S. Pan, *Chem. Eur. J.,* 2017, **23**, 13910-13918.

25 S. Filatov, R. Bubnova, Y. Shepelev, J. Anderson and Y. Smolin, *Cryst. Res. Technol.*, 2005, **40**, 65-72.

26 N. Penin, L. Seguin, M. Touboul and G. Nowogrocki, *J. Solid State Chem.*, 2001, **161**, 205-213.

27 R. Bubnova, R. E. Dinnebier, S. Filatov and J. Anderson, *Cryst. Res. Technol.*, 2007, **42**, 143-150.

28 G. Sohr, D. M. Többens, J. Schmedt auf der Günne and H. Huppertz, *Chem. Eur. J.*, 2014, **20**, 17059-17067.

29 J. M. Tu and D. A. Keszler, *Inorg. Chem.*, 1996, **35**, 463-466.

30 L. Li, S. J. Han, B. H. Lei, X. Y. Dong, H. P. Wu, Z. X. Zhou, Z. H. Yang and S. L. Pan, *Inorg. Chem.*, 2015, **54**, 7381-7387.

31 Y. Yang, S. L. Pan, H. Y. Li, J. Han, Z. Chen, W. W. Zhao and Z. X. Zhou, *Inorg. Chem.*, 2011, **50**, 2415-2419.

32 N. Penin, M. Touboul and G. Nowogrocki, *J. Solid State Chem.*, 2003, **175**, 348-352.

33 S. J. Han, C. M. Huang, A. Tudi, S. S. Hu, Z. H. Yang and S. L. Pan, *Chem. Eur. J.*, 2019, **25**, 11614-11619.
34 J. Krogh-Moe, *Acta Crystallogr.*, 1967, **23**, 427-430.
35 X. Chen, L. Wu, K. Wang, X. Chang and W. Xiao, *J. Alloy. Compd.*, 2015, **623**, 157-163.
36 A. Q. Jiao, H. W. Yu, H. P. Wu, S. L. Pan and X. W. Zhang, *Inorg. Chem.*, 2014, **53**, 2358-2360.
37 L. Q. Li, Q. Song, P. Li, H. S. Huang and Z. H. Liu, *J. Therm. Anal. Calorim.*, 2014, **116**, 1019-1025.
38 T. J. Zhang, R. Pan, H. He, B. F. Yang and G. Y. Yang, *J. Clust. Sci.*, 2015, **27**, 625-633.
39 N. Penin, L. Seguin, M. Touboul and G. Nowogrocki, *Solid State Sci.*, 2002, **4**, 67-76.
40 M. Mutailipu, M. Zhang, X. Su, Z. H. Yang and S. L.Pan, *Inorg. Chem.*, 2017, **56**, 5506-5509.
41 G. Nowogrocki, N. Penin and M. Touboul, *Solid State Sci.*, 2003, **5**, 795-803.