Supplementary Information
From Centrosymmetric to Noncentrosymmetric: Cation-Directed Structural Evolution in $X_3ZnB_5O_{10}$ (X=Na, K, Rb) and $Cs_{12}Zn_4(B_5O_{10})_4$ Crystals

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Table S1. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_{12}Zn_4(B_5O_{10})_4$, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the Bond Valence Sum (BVS) for each atom in asymmetric unit.

Atom	x	y	z	U(eq)	BVS
Cs(1)	9189(1)	4509(1)	3848(1)	27(1)	1.260
Cs(2)	6333(1)	6960(1)	4125(1)	44(1)	0.898
Cs(3)	2653(1)	4702(1)	7091(1)	50(1)	1.201
Cs(4)	4392(1)	4352(1)	4122(1)	63(1)	0.610
Cs(5)	7589(1)	5784(1)	2392(1)	28(1)	1.086
Cs(6)	818(1)	5660(1)	5310(1)	31(1)	0.824
Cs(7)	1891(1)	7000(1)	4151(1)	33(1)	1.068
Cs(8)	6008(1)	5650(1)	6018(1)	36(1)	0.863
Cs(9)	8585(1)	3294(1)	5621(1)	39(1)	1.122
Cs(10)	5190(1)	6925(1)	7508(1)	38(1)	0.993
Cs(11)	5034(1)	1657(1)	7296(1)	39(1)	0.781
Cs(12)	3338(1)	2914(1)	5708(1)	39(1)	1.003
Zn(1)	6652(1)	653(1)	8970(2)	20(1)	2.074
Zn(2)	4278(1)	1850(1)	3743(2)	24(1)	2.140
Zn(3)	7649(1)	3284(1)	2655(2)	22(1)	2.089
Zn(4)	5031(1)	4527(1)	7278(2)	23(1)	2.137
B(1)	5890(12)	1331(13)	10187(16)	21(5)	3.017
B(2)	7979(12)	5706(12)	6295(13)	17(5)	2.963
B(3)	8048(16)	2414(13)	7416(18)	31(6)	3.111
B(4)	5594(13)	2523(16)	5223(16)	29(6)	3.027
B(5)	5684(13)	1376(13)	1719(16)	23(5)	3.066
B(6)	7678(13)	5138(12)	4746(15)	21(5)	3.087
B(7)	5903(13)	187(14)	2452(15)	24(5)	3.028
B(8)	6312(13)	5150(15)	3839(17)	28(6)	2.937
B(9)	2834(13)	5413(13)	4894(16)	21(5)	2.960
B(10)	6612(14)	2146(15)	1409(16)	29(6)	3.096
B(11)	6644(12)	2507(13)	6857(15)	19(5)	3.016
B(12)	3723(13)	6224(14)	4443(17)	27(5)	3.046
B(13)	8548(13)	6150(16)	5057(16)	30(6)	2.986
B(14)	7019(15)	4120(15)	3777(17)	28(6)	3.131
B(15)	4113(14)	5599(13)	5984(17)	24(5)	3.124
B(16)	5778(13)	3545(13)	6321(17)	23(5)	2.998
B(17)	7349(13)	1692(14)	8217(17)	29(6)	3.108
B(18)	4939(14)	906(14)	2718(17)	26(6)	3.046
B(19)	4215(15)	3626(15)	8038(19)	34(6)	3.077
B(20)	8824(15)	2369(15)	3705(18)	34(6)	3.044
O(1)	8272(7)	5564(7)	4535(9)	22(3)	2.143
O(2)	6172(7)	1993(8)	1963(10)	27(3)	2.167
O(3)	6309(7)	3164(7)	7024(9)	25(3)	2.113
O(4)	2132(7)	5165(7)	4755(9)	22(3)	1.869

O(5)	3579(7)	6956(8)	4312(10)	28(3)	2.096
O(6)	6147(7)	2176(7)	5942(9)	25(3)	2.034
O(7)	6146(9)	761(8)	2073(12)	42(4)	2.059
O(8)	6708(7)	2033(7)	7671(10)	25(3)	2.097
O(9)	7678(7)	4449(7)	4345(9)	23(3)	2.109
O(10)	5100(7)	1434(7)	2184(9)	20(3)	2.096
O(11)	7837(8)	5105(8)	5807(9)	28(3)	2.106
O(12)	5633(7)	5492(8)	3664(10)	31(4)	1.816
O(13)	7399(8)	2656(8)	6795(10)	31(4)	2.092
O(14)	6962(8)	5499(8)	4326(10)	32(4)	2.124
O(15)	7007(8)	3482(7)	3450(10)	30(4)	1.985
O(16)	5593(8)	4196(8)	6426(10)	33(4)	1.925
O(17)	4660(7)	5448(8)	6861(10)	31(4)	1.892
O(18)	8721(8)	2674(10)	7551(11)	44(5)	2.133
O(19)	3442(8)	5245(8)	5751(11)	34(4)	1.899
O(20)	5384(8)	3198(9)	5437(11)	36(4)	2.122
O(21)	5348(7)	1306(8)	645(9)	26(3)	1.900
O(22)	7433(8)	1291(9)	8980(10)	41(4)	1.998
O(23)	8362(8)	6250(7)	5941(9)	25(3)	1.832
O(24)	8934(10)	6653(9)	4831(12)	50(5)	1.904
O(25)	4434(8)	964(9)	3192(11)	39(4)	1.961
O(26)	7124(10)	2648(10)	1614(12)	55(5)	1.865
O(27)	4298(10)	7087(10)	3245(12)	52(5)	2.039
O(28)	8002(8)	1811(11)	7981(13)	57(6)	2.042
O(29)	4299(10)	3838(10)	7207(11)	52(5)	2.034
O(30)	6349(9)	4467(9)	3553(13)	49(5)	2.075
O(31)	6272(8)	-419(8)	2568(10)	31(4)	1.937
O(32)	2986(7)	5856(8)	4248(9)	31(4)	2.074
O(33)	8626(9)	3034(8)	3550(11)	40(4)	2.057
O(34)	4262(8)	6046(9)	5378(11)	41(4)	2.181
O(35)	5280(9)	272(8)	2747(13)	42(5)	2.112
O(36)	4016(8)	5949(8)	3650(11)	35(4)	2.018
O(37)	7776(7)	5825(7)	7084(8)	24(3)	2.017
O(38)	5824(7)	973(8)	9374(10)	32(4)	2.013
O(39)	6517(8)	1753(8)	571(9)	29(4)	2.121
O(40)	5269(7)	2250(8)	4355(8)	27(3)	2.078

Table S2. Selected bond distances (Å) and angles (deg) for $Cs_{12}Zn_4(B_5O_{10})_4$.

Cs(1)-O(1)	3.040(13)	Cs(5)-O(37)#2	3.177(15)
Cs(1)-O(9)	3.149(13)	Cs(6)-O(4)	2.991(12)
Cs(1)-O(21)#4	3.193(13)	Cs(6)-O(6)#8	3.071(14)
Cs(1)-O(25)#3	3.052(16)	Cs(6)-O(7)#6	3.660(18)
Cs(1)-O(33)	3.019(16)	Cs(6)-O(25)#8	3.343(17)
Cs(1)-O(35)#3	3.329(14)	Cs(6)-O(31)#6	3.130(14)
Cs(1)-O(37)#2	3.073(12)	Cs(6)-O(35)#8	3.588(18)
Cs(1)-O(38)#1	3.045(13)	Cs(6)-O(38)#7	3.436(17)
Cs(2)-O(3)#2	3.040(13)	Cs(6)-O(40)#8	3.387(15)
Cs(2)-O(8)#2	3.117(14)	Cs(7)-O(2)#8	3.003(14)
Cs(2)-O(12)	3.104(16)	Cs(7)-O(4)	3.644(15)
Cs(2)-O(14)	3.036(14)	Cs(7)-O(5)	3.094(13)
Cs(2)-O(26)#5	3.495(18)	Cs(7)-O(6)#8	3.350(13)
Cs(2)-O(27)	3.602(18)	Cs(7)-O(7)#8	3.734(19)
Cs(2)-O(39)#5	3.196(15)	Cs(7)-O(15)#8	3.071(14)
Cs(3)-O(4)	3.318(13)	Cs(7)-O(32)	2.988(15)
Cs(3)-O(7)#6	2.953(14)	Cs(7)-O(40)#8	3.188(13)
Cs(3)-O(19)	2.998(14)	Cs(8)-O(11)	3.696(14)
Cs(3)-O(29)	3.463(19)	Cs(8)-O(12)	3.260(14)
Cs(3)-O(31)#6	3.207(15)	Cs(8)-O(14)	3.498(15)
Cs(3)-O(32)#5	3.166(14)	Cs(8)-O(16)	3.027(16)
Cs(3)-O(36)#5	3.059(15)	Cs(8)-O(17)	3.176(14)
Cs(3)-O(39)#6	3.763(16)	Cs(8)-O(30)#5	3.520(18)
Cs(4)-O(12)	3.425(15)	Cs(8)-O(34)	3.181(15)
Cs(4)-O(16)	3.361(15)	Cs(8)-O(37)	3.172(12)
Cs(4)-O(17)#2	3.498(14)	Cs(9)-O(5)#9	3.205(15)
Cs(4)-O(20)	3.113(15)	Cs(9)-O(9)	3.032(14)
Cs(4)-O(28)#7	3.419(17)	Cs(9)-O(10)#4	3.029(12)
Cs(4)-O(34)	3.794(18)	Cs(9)-O(13)	3.447(13)
Cs(4)-O(36)	3.189(15)	Cs(9)-O(15)	3.544(15)
Cs(5)-O(1)	2.968(13)	Cs(9)-O(18)	2.976(15)
Cs(5)-O(3)#2	3.053(14)	Cs(9)-O(21)#4	3.383(13)
Cs(5)-O(11)#2	3.026(13)	Cs(9)-O(33)	3.069(16)
Cs(5)-O(13)#2	3.123(16)	Cs(10)-O(2)#5	3.060(14)
Cs(5)-O(14)	3.427(15)	Cs(10)-O(10)#5	3.203(14)
Cs(5)-O(16)#2	3.530(15)	Cs(10)-O(15)#5	3.312(14)
Cs(5)-O(25)#3	3.277(15)	Cs(10)-O(17)	3.065(15)

Cs(10)-O(18)#8	3.130(16)	B(1)-O(39)#12	1.39(3)
Cs(10)-O(30)#5	3.471(16)	B(2)-O(11)	1.34(3)
Cs(10)-O(34)	3.442(16)	B(2)-O(23)	1.46(2)
Cs(10)-O(40)#5	3.077(12)	B(2)-O(37)	1.34(2)
Cs(11)-O(6)	3.457(13)	B(3)-O(13)	1.33(3)
Cs(11)-O(8)	3.087(12)	B(3)-O(18)	1.31(3)
Cs(11)-O(23)#10	3.191(14)	B(3)-O(28)	1.44(3)
Cs(11)-O(24)#10	3.478(18)	B(4)-O(6)	1.37(3)
Cs(11)-O(27)#5	3.309(16)	B(4)-O(20)	1.43(3)
Cs(11)-O(31)#11	3.263(15)	B(4)-O(40)	1.31(3)
Cs(11)-O(33)#6	3.717(16)	B(5)-O(2)	1.47(3)
Cs(11)-O(35)#11	3.786(17)	B(5)-O(7)	1.46(3)
Cs(11)-O(38)	3.167(15)	B(5)-O(10)	1.47(2)
Cs(12)-O(22)#7	2.945(14)	B(5)-O(21)	1.48(2)
Cs(12)-O(23)#10	3.232(14)	B(6)-O(1)	1.50(2)
Cs(12)-O(24)#10	3.122(17)	B(6)-O(9)	1.45(3)
Cs(12)-O(26)#6	3.176(16)	B(6)-O(11)	1.47(2)
Cs(12)-O(27)#5	3.513(18)	B(6)-O(14)	1.45(3)
Cs(12)-O(29)	2.921(16)	B(7)-O(7)	1.38(3)
Cs(12)-O(39)#6	3.412(14)	B(7)-O(31)	1.34(3)
Zn(1)-O(4)#4	1.981(13)	B(7)-O(35)	1.38(3)
Zn(1)-O(22)	1.909(15)	B(8)-O(12)	1.38(3)
Zn(1)-O(31)#11	1.968(14)	B(8)-O(14)	1.37(3)
Zn(1)-O(38)	1.934(14)	B(8)-O(30)	1.39(3)
Zn(2)-O(18)#7	1.927(16)	B(9)-O(4)	1.35(2)
Zn(2)-O(24)#10	1.931(14)	B(9)-O(19)	1.41(3)
Zn(2)-O(25)	1.952(16)	B(9)-O(32)	1.37(3)
Zn(2)-O(40)	1.932(13)	B(10)-O(2)	1.36(3)
Zn(3)-O(15)	1.962(13)	B(10)-O(26)	1.33(3)
Zn(3)-O(26)	1.940(15)	B(10)-O(39)	1.39(2)
Zn(3)-O(33)	1.919(16)	B(11)-O(3)	1.47(3)
Zn(3)-O(37)#2	1.959(14)	B(11)-O(6)	1.49(3)
Zn(4)-O(12)#5	1.949(14)	B(11)-O(8)	1.47(2)
Zn(4)-O(16)	1.976(14)	B(11)-O(13)	1.48(2)
Zn(4)-O(17)	1.932(15)	B(12)-O(5)	1.44(3)
Zn(4)-O(29)	1.890(16)	B(12)-O(32)	1.49(3)
B(1)-O(21)#12	1.39(2)	B(12)-O(34)	1.44(3)
B(1)-O(38)	1.34(2)	B(12)-O(36)	1.52(3)

B(13)-O(1)	1.36(3)	O(26)-Zn(3)-O(15)	109.2(6)
B(13)-O(23)	1.45(2)	O(26)-Zn(3)-O(37)#2	109.2(6)
B(13)-O(24)	1.32(3)	O(33)-Zn(3)-O(15)	106.6(6)
B(14)-O(9)	1.39(3)	O(33)-Zn(3)-O(26)	119.2(8)
B(14)-O(15)	1.32(3)	O(33)-Zn(3)-O(37)#2	106.5(6)
B(14)-O(30)	1.36(3)	O(37)#2-Zn(3)-O(15)	105.2(6)
B(15)-O(17)	1.37(3)	O(12)#5-Zn(4)-O(16)	113.1(6)
B(15)-O(19)	1.37(3)	O(17)-Zn(4)-O(12)#5	111.3(6)
B(15)-O(34)	1.33(3)	O(17)-Zn(4)-O(16)	108.3(6)
B(16)-O(3)	1.38(3)	O(29)-Zn(4)-O(12)#5	101.7(7)
B(16)-O(16)	1.33(3)	O(29)-Zn(4)-O(16)	105.4(7)
B(16)-O(20)	1.42(3)	O(29)-Zn(4)-O(17)	116.9(8)
B(17)-O(8)	1.37(3)	O(38)-B(1)-O(21)#12	122(2)
B(17)-O(22)	1.32(3)	O(38)-B(1)-O(39)#12	118.4(17)
B(17)-O(28)	1.40(3)	O(39)#12-B(1)-O(21)#12	119.1(18)
B(18)-O(10)	1.37(3)	O(11)-B(2)-O(23)	118.2(15)
B(18)-O(25)	1.35(2)	O(37)-B(2)-O(11)	122.4(19)
B(18)-O(35)	1.38(3)	O(37)-B(2)-O(23)	119.3(18)
B(19)-O(27)#5	1.41(3)	O(13)-B(3)-O(28)	117(2)
B(19)-O(29)	1.33(3)	O(18)-B(3)-O(13)	126(2)
B(19)-O(36)#5	1.35(3)	O(18)-B(3)-O(28)	117(2)
B(20)-O(5)#9	1.38(3)	O(6)-B(4)-O(20)	118.3(19)
B(20)-O(27)#9	1.39(3)	O(40)-B(4)-O(6)	122(2)
B(20)-O(33)	1.34(3)	O(40)-B(4)-O(20)	120(2)
O(22)-Zn(1)-O(4)#4	108.1(6)	O(2)-B(5)-O(21)	109.8(18)
O(22)-Zn(1)-O(31)#11	99.7(6)	O(7)-B(5)-O(2)	109.1(17)
O(22)-Zn(1)-O(38)	118.8(7)	O(7)-B(5)-O(10)	110.3(18)
O(31)#11-Zn(1)-O(4)#4	110.4(6)	O(7)-B(5)-O(21)	106.8(17)
O(38)-Zn(1)-O(4)#4	109.7(6)	O(10)-B(5)-O(2)	109.1(16)
O(38)-Zn(1)-O(31)#11	109.6(6)	O(10)-B(5)-O(21)	111.8(16)
O(18)#7-Zn(2)-O(24)#10	126.7(7)	O(9)-B(6)-O(1)	108.9(14)
O(18)#7-Zn(2)-O(25)	99.4(7)	O(9)-B(6)-O(11)	110.6(17)
O(18)#7-Zn(2)-O(40)	111.8(7)	O(11)-B(6)-O(1)	109.5(16)
O(24)#10-Zn(2)-O(25)	107.3(7)	O(14)-B(6)-O(1)	107.3(17)
O(14)-B(6)-O(9)	113.3(17)	O(31)-B(7)-O(7)	121.8(18)
O(14)-B(6)-O(11)	107.2(15)	O(31)-B(7)-O(35)	121(2)
O(24)#10-Zn(2)-O(40)	103.6(6)	O(35)-B(7)-O(7)	117(2)
O(40)-Zn(2)-O(25)	106.6(6)	O(12)-B(8)-O(30)	122(2)

O(14)-B(8)-O(12)	118(2)	O(24)-B(13)-O(23)	116(2)
O(14)-B(8)-O(30)	119.8(19)	O(15)-B(14)-O(9)	123(2)
O(4)-B(9)-O(19)	120.6(18)	O(15)-B(14)-O(30)	118(2)
O(4)-B(9)-O(32)	122.4(19)	O(30)-B(14)-O(9)	119(2)
O(32)-B(9)-O(19)	117.0(17)	O(17)-B(15)-O(19)	117.5(19)
O(2)-B(10)-O(39)	118(2)	O(34)-B(15)-O(17)	120(2)
O(26)-B(10)-O(2)	124.1(19)	O(34)-B(15)-O(19)	123(2)
O(26)-B(10)-O(39)	117.9(19)	O(3)-B(16)-O(20)	116.5(19)
O(3)-B(11)-O(6)	110.0(15)	O(16)-B(16)-O(3)	125(2)
O(3)-B(11)-O(13)	108.1(17)	O(16)-B(16)-O(20)	118.3(19)
O(8)-B(11)-O(3)	109.3(15)	O(8)-B(17)-O(28)	117(2)
O(8)-B(11)-O(6)	107.9(17)	O(22)-B(17)-O(8)	127(2)
O(8)-B(11)-O(13)	110.4(15)	O(22)-B(17)-O(28)	116(2)
O(13)-B(11)-O(6)	111.0(16)	O(10)-B(18)-O(35)	119.4(18)
O(5)-B(12)-O(32)	108.8(17)	O(25)-B(18)-O(10)	123(2)
O(5)-B(12)-O(36)	109.9(16)	O(25)-B(18)-O(35)	117(2)
O(32)-B(12)-O(36)	103.5(17)	O(29)-B(19)-O(27)#5	117(2)
O(34)-B(12)-O(5)	114(2)	O(29)-B(19)-O(36)#5	123(2)
O(34)-B(12)-O(32)	112.3(17)	O(36)#5-B(19)-O(27)#5	119(2)
O(34)-B(12)-O(36)	108.1(18)	O(5)#9-B(20)-O(27)#9	119(2)
O(1)-B(13)-O(23)	116.4(19)	O(33)-B(20)-O(5)#9	122(2)
O(24)-B(13)-O(1)	127.7(19)	O(33)-B(20)-O(27)#9	119(2)

Symmetry transformations used to generate equivalent atoms:

(1) x+1/2,-y+1/2,z-1/2 (2) x,-y+1,z-1/2 (3) x+1/2,y+1/2,z (4) x+1/2,-y+1/2,z+1/2

(5) x,-y+1,z+1/2 (6) x-1/2,-y+1/2,z+1/2 (7) x-1/2,-y+1/2,z-1/2 (8) x-1/2,y+1/2,z

(9) x+1/2,y-1/2,z (10) x-1/2,y-1/2,z (11) x,-y,z+1/2 (12) x,y,z+1

(13) x,-y,z-1/2 (14) x,y,z-1

Table S3. The anhydrous alkali-zinc borates with formula $X_3ZnB_5O_{10}$.

Ref No.	Formula	Space Group	B-O-Zn Framework	Code No.
1	$Na_3ZnB_5O_{10}$	*Pbca* (No.61)	2D $[ZnB_5O_{10}]_\infty$	423705
2	$Na_3ZnB_5O_{10}$	$P2_1/n$ (No.14)	2D $[ZnB_5O_{10}]_\infty$	417848
3	$NaK_2(ZnB_5O_{10})$	C2/c (No.15)	2D $[ZnB_5O_{10}]_\infty$	167139
4	$K_3ZnB_5O_{10}$	$P2_1/n$ (No.14)	2D $[ZnB_5O_{10}]_\infty$	262977
5	$Rb_3ZnB_5O_{10}$	$P2_1/n$ (No.14)	2D $[ZnB_5O_{10}]_\infty$	425890
This work	$Cs_{12}Zn_4(B_5O_{10})_4$	*Cc* (No.9)	3D $[ZnB_5O_{10}]_\infty$	1838047

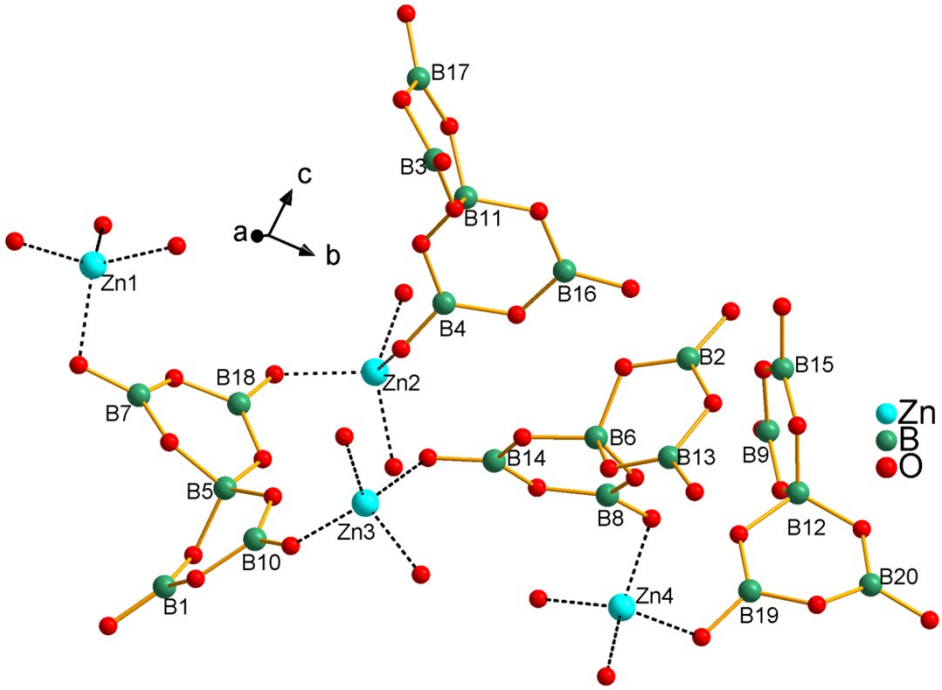

Figure S1. Crystallographic unique Zn, B and O atoms in $Cs_{12}Zn_4(B_5O_{10})_4$.

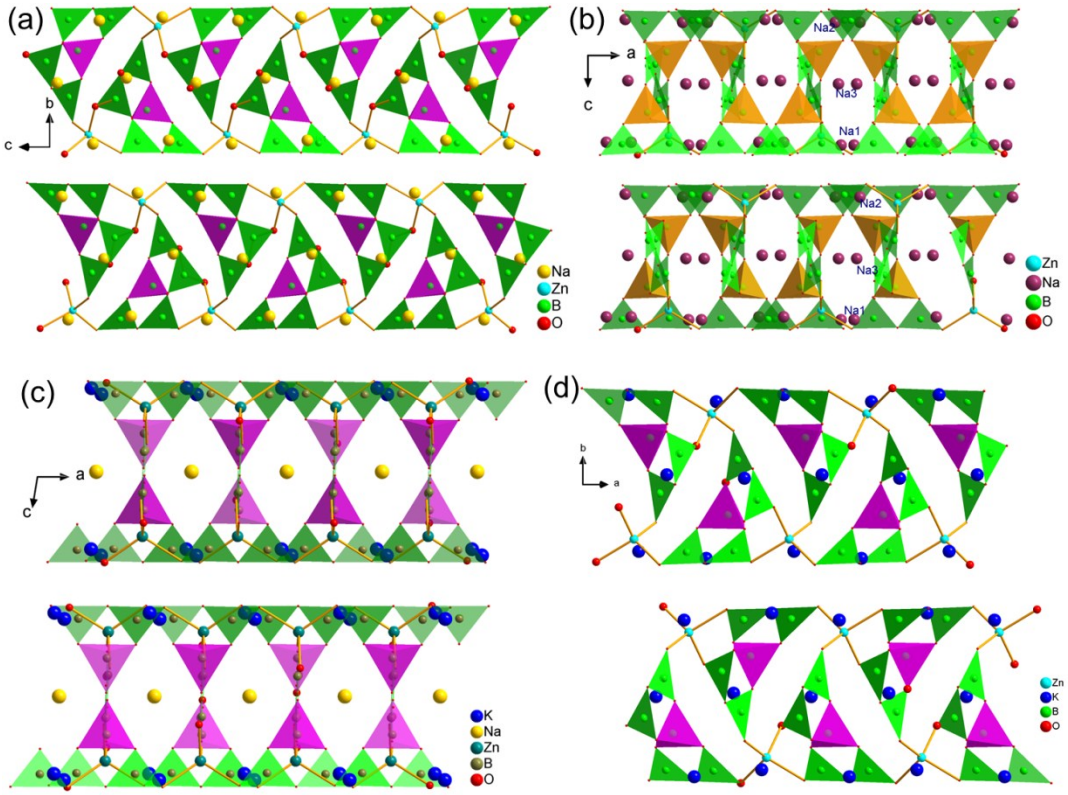

Figure S2. (a) Crystal structure of $Na_3ZnB_5O_{10}$ ($P2_1/n$). (b) Crystal structure of $Na_3ZnB_5O_{10}$ (*Pbca*). (c) Crystal structure of $NaK_2(ZnB_5O_{10})$. (d) Crystal structure of $K_3ZnB_5O_{10}$.

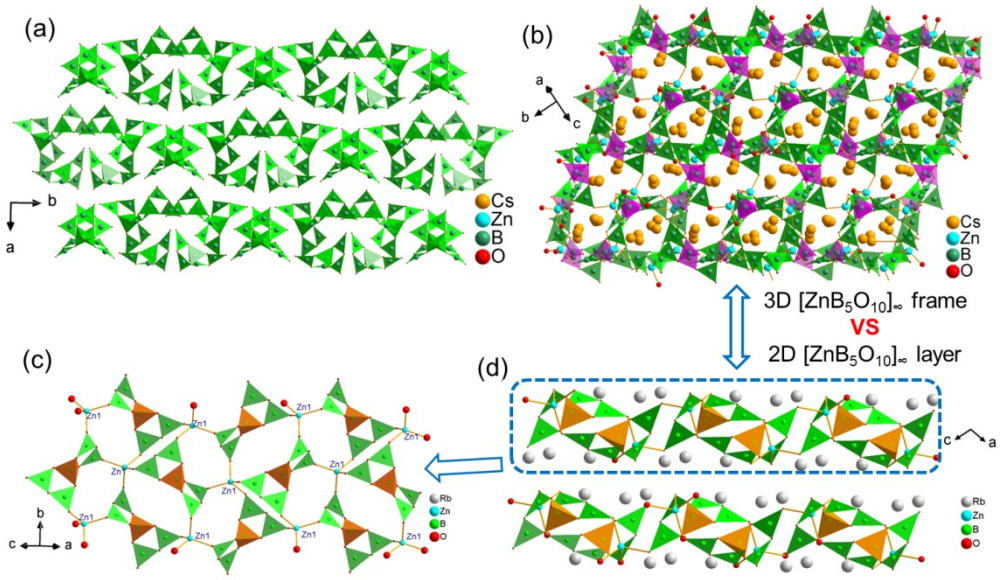

Figure S3. (a) Pseudo layer formed by the B_5O_{10} groups in $Cs_{12}Zn_4(B_5O_{10})_4$. (b) The 3D structure of $Cs_{12}Zn_4(B_5O_{10})_4$. (c) The 2D $[ZnB_5O_{10}]_\infty$ layer in $Rb_3ZnB_5O_{10}$. (d) The 3D structure of $Rb_3ZnB_5O_{10}$.

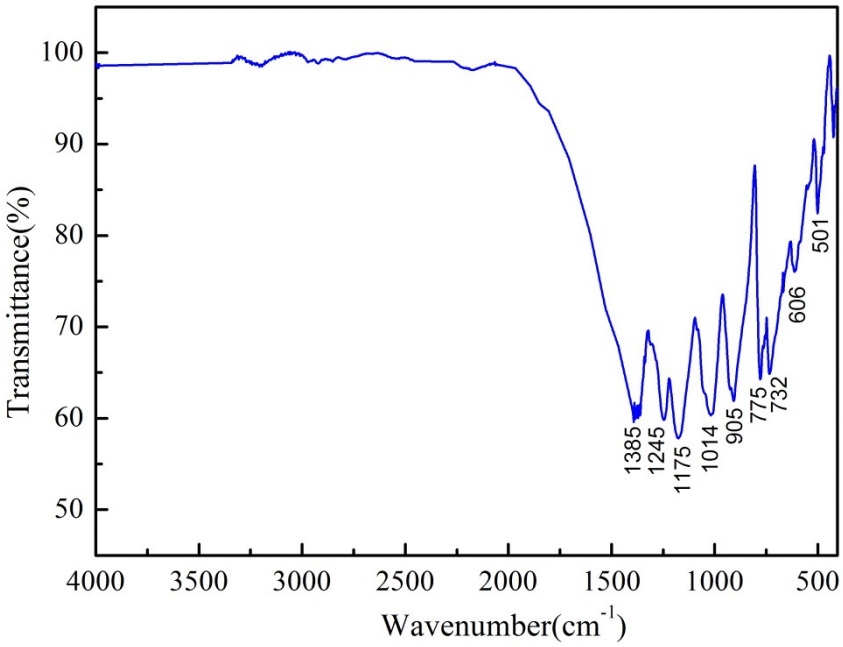

Figure S4. The IR spectrum of $Cs_{12}Zn_4(B_5O_{10})_4$.

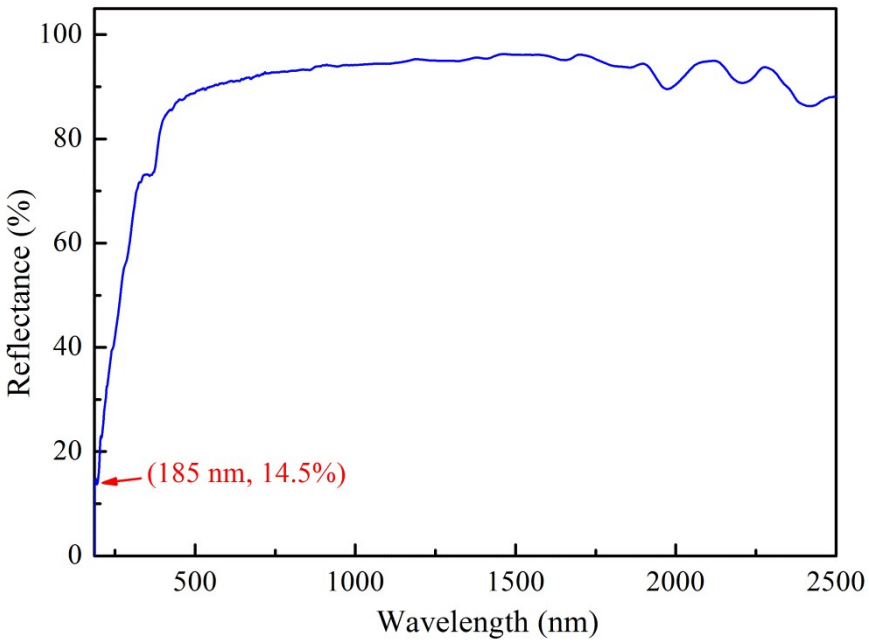

Figure S5. The UV-vis-NIR diffuse reflectance spectrum of $Cs_{12}Zn_4(B_5O_{10})_4$.

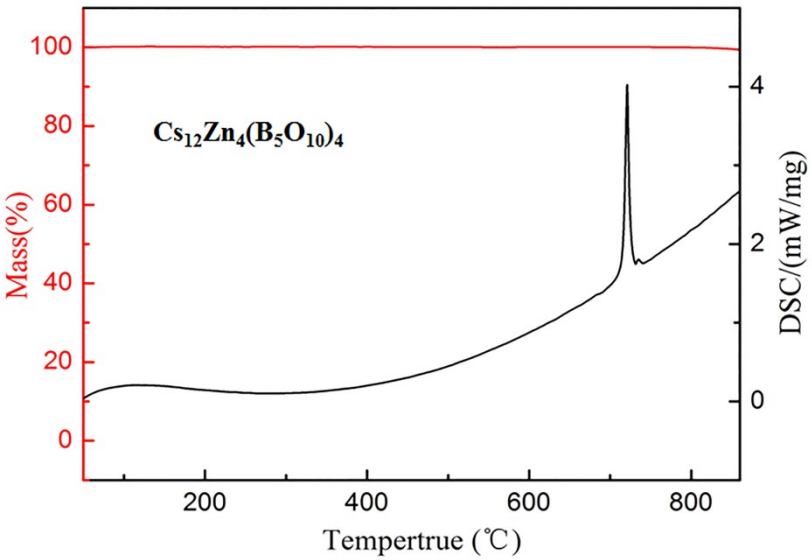

Figure S6. The TG-DSC curves of polycrystalline sample of $Cs_{12}Zn_4(B_5O_{10})_4$.

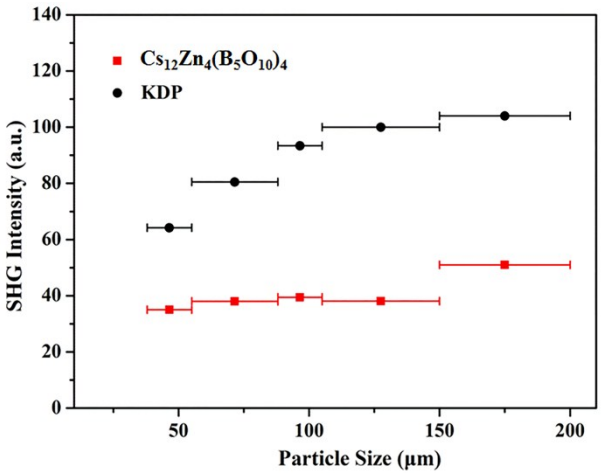

Figure S7. Powder SHG measurement result of $Cs_{12}Zn_4(B_5O_{10})_4$.