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# $Pb_3Ba_3Zn_6(BO_3)_8$ and $\alpha$-$BaZn_2(BO_3)_2$ : New Members of the Zincoborates Containing Two Different Dimensional Zn-O Units

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**Table S1.** Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for $Pb_3Ba_3Zn_6(BO_3)_8$.

| Atoms | x | y | z | *U(eq)*[a] | BVS[b, c] |
|---|---|---|---|---|---|
| Pb(1) | 3555(1) | 2309(2) | 7170(1) | 18(1) | 2.062 |
| Pb(2) | 5000 | 1585(2) | 7500 | 20(1) | 1.994 |
| Ba(1) | 4202(1) | 2295(2) | 5411(1) | 14(1) | 2.153 |
| Ba(2) | 2500 | 2500 | 5000 | 10(1) | 2.055 |
| Zn(1) | 2451(1) | 7793(4) | 3031(1) | 11(1) | 2.105 |
| Zn(2) | 3419(1) | 7440(4) | 4416(1) | 12(1) | 2.098 |
| Zn(3) | 4671(1) | -2907(4) | 8597(1) | 16(1) | 1.979 |
| B(1) | 3012(8) | 12570(40) | 3592(11) | 7(4) | 3.089 |
| B(2) | 4327(8) | 6890(40) | 6939(10) | 9(4) | 2.951 |
| B(3) | 3190(9) | 7460(40) | 5948(12) | 17(5) | 3.007 |
| B(4) | 4477(9) | 2100(40) | 9215(12) | 18(5) | 3.093 |
| O(1) | 3227(5) | 11230(20) | 4255(6) | 13(3) | 1.970 |
| O(2) | 4250(5) | -1710(30) | 7554(6) | 16(3) | 1.818 |
| O(3) | 4145(5) | 6570(30) | 4584(7) | 21(3) | 1.926 |
| O(4) | 5375(5) | -1780(30) | 8469(7) | 17(3) | 1.919 |
| O(5) | 1981(5) | 9080(30) | 3565(7) | 17(3) | 2.102 |
| O(6) | 2175(5) | 6100(20) | 2060(6) | 13(3) | 2.023 |
| O(7) | 4153(5) | 4420(30) | 6742(7) | 24(3) | 2.349 |
| O(8) | 4743(6) | -6670(30) | 8829(9) | 30(4) | 2.171 |
| O(9) | 2977(5) | 5230(30) | 3598(6) | 18(3) | 2.114 |
| O(10) | 3337(6) | 140(30) | 6073(7) | 27(3) | 2.047 |
| O(11) | 4495(6) | -630(30) | 9311(7) | 25(3) | 2.115 |
| O(12) | 3223(6) | 6310(30) | 5299(7) | 29(3) | 2.007 |

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa, S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: Si = exp[(R0-Ri)/B], where Si = valence of bond “i” and B = 0.37.

**Table S2.** Selected bond distances (Å) and angles (deg) for $Pb_3Ba_3Zn_6(BO_3)_8$.

| | | | |
|---|---|---|---|
| Pb(1)-O(10) | 2.231(12) | O(3)-Ba(1)-O(1)#5 | 79.8(4) |
| Pb(1)-O(7) | 2.232(13) | O(7)-Ba(1)-O(1)#5 | 118.6(4) |
| Pb(1)-O(5)#1 | 2.450(12) | O(8)#4-Ba(1)-O(1)#5 | 163.6(4) |
| Pb(1)-O(2) | 2.677(13) | O(4)#2-Ba(1)-O(1)#5 | 119.0(4) |
| Pb(2)-O(4) | 2.454(13) | O(11)#3-Ba(1)-O(10) | 130.1(4) |
| Pb(2)-O(4)#2 | 2.454(14) | O(3)-Ba(1)-O(10) | 126.4(4) |
| Pb(2)-O(2) | 2.602(13) | O(7)-Ba(1)-O(10) | 62.6(4) |
| Pb(2)-O(2)#2 | 2.602(13) | O(8)#4-Ba(1)-O(10) | 127.7(4) |
| Pb(2)-O(7)#2 | 2.686(14) | O(4)#2-Ba(1)-O(10) | 69.6(4) |
| Pb(2)-O(7) | 2.686(14) | O(1)#5-Ba(1)-O(10) | 67.9(3) |
| Ba(1)-O(11)#3 | 2.525(12) | O(11)#3-Ba(1)-O(3)#5 | 46.1(4) |
| Ba(1)-O(3) | 2.600(13) | O(3)-Ba(1)-O(3)#5 | 117.0(5) |
| Ba(1)-O(7) | 2.727(13) | O(7)-Ba(1)-O(3)#5 | 140.1(4) |
| Ba(1)-O(8)#4 | 2.800(16) | O(8)#4-Ba(1)-O(3)#5 | 107.9(4) |
| Ba(1)-O(4)#2 | 2.894(12) | O(4)#2-Ba(1)-O(3)#5 | 71.3(4) |
| Ba(1)-O(1)#5 | 2.902(11) | O(1)#5-Ba(1)-O(3)#5 | 64.8(3) |
| Ba(1)-O(10) | 3.091(14) | O(10)-Ba(1)-O(3)#5 | 86.9(3) |
| Ba(1)-O(3)#5 | 3.220(14) | O(11)#3-Ba(1)-O(12) | 125.3(4) |
| Ba(1)-O(12) | 3.237(16) | O(3)-Ba(1)-O(12) | 63.1(4) |

| | | | |
|---|---|---|---|
| Ba(2)-O(12) | 2.641(14) | O(7)-Ba(1)-O(12) | 64.8(4) |
| Ba(2)-O(12)#6 | 2.641(14) | O(8)#4-Ba(1)-O(12) | 126.0(4) |
| Ba(2)-O(1)#5 | 2.751(12) | O(4)#2-Ba(1)-O(12) | 128.2(3) |
| Ba(2)-O(1)#1 | 2.751(12) | O(1)#5-Ba(1)-O(12) | 62.3(3) |
| Ba(2)-O(10) | 2.785(14) | O(10)-Ba(1)-O(12) | 64.2(4) |
| Ba(2)-O(10)#6 | 2.785(14) | O(3)#5-Ba(1)-O(12) | 126.0(3) |
| Ba(2)-O(5)#5 | 3.130(13) | O(12)-Ba(2)-O(12)#6 | 179.998(1) |
| Ba(2)-O(5)#1 | 3.130(13) | O(12)-Ba(2)-O(1)#5 | 72.5(4) |
| Zn(1)-O(5) | 1.914(12) | O(12)#6-Ba(2)-O(1)#5 | 107.5(4) |
| Zn(1)-O(6) | 1.936(11) | O(12)-Ba(2)-O(1)#1 | 107.5(4) |
| Zn(1)-O(6)#7 | 1.953(12) | O(12)#6-Ba(2)-O(1)#1 | 72.5(4) |
| Zn(1)-O(9) | 1.960(12) | O(1)#5-Ba(2)-O(1)#1 | 180.0(6) |
| Zn(2)-O(3) | 1.914(13) | O(12)-Ba(2)-O(10) | 76.6(4) |
| Zn(2)-O(12) | 1.940(13) | O(12)#6-Ba(2)-O(10) | 103.4(4) |
| Zn(2)-O(1) | 1.951(12) | O(1)#5-Ba(2)-O(10) | 74.5(4) |
| Zn(2)-O(9) | 1.967(12) | O(1)#1-Ba(2)-O(10) | 105.5(4) |
| Zn(3)-O(11) | 1.903(12) | O(12)-Ba(2)-O(10)#6 | 103.4(4) |
| Zn(3)-O(8) | 1.919(14) | O(12)#6-Ba(2)-O(10)#6 | 76.6(4) |
| Zn(3)-O(4) | 2.029(13) | O(1)#5-Ba(2)-O(10)#6 | 105.5(4) |
| Zn(3)-O(2) | 2.031(12) | O(1)#1-Ba(2)-O(10)#6 | 74.5(4) |
| B(1)-O(9)#8 | 1.33(2) | O(10)-Ba(2)-O(10)#6 | 179.998(2) |

| | | | |
|---|---|---|---|
| B(1)-O(1) | 1.37(2) | O(12)-Ba(2)-O(5)#5 | 133.3(4) |
| B(1)-O(6)#7 | 1.38(2) | O(12)#6-Ba(2)-O(5)#5 | 46.7(4) |
| B(2)-O(7) | 1.33(2) | O(1)#5-Ba(2)-O(5)#5 | 69.4(3) |
| B(2)-O(2)#8 | 1.40(2) | O(1)#1-Ba(2)-O(5)#5 | 110.6(3) |
| B(2)-O(4)#4 | 1.41(2) | O(10)-Ba(2)-O(5)#5 | 116.7(3) |
| B(3)-O(5)#1 | 1.36(2) | O(10)#6-Ba(2)-O(5)#5 | 63.3(3) |
| B(3)-O(12) | 1.36(3) | O(12)-Ba(2)-O(5)#1 | 46.7(4) |
| B(3)-O(10)#8 | 1.39(2) | O(12)#6-Ba(2)-O(5)#1 | 133.3(4) |
| B(4)-O(8)#8 | 1.30(3) | O(1)#5-Ba(2)-O(5)#1 | 110.6(3) |
| B(4)-O(11) | 1.37(3) | O(1)#1-Ba(2)-O(5)#1 | 69.4(3) |
| B(4)-O(3)#11 | 1.42(3) | O(10)-Ba(2)-O(5)#1 | 63.3(3) |
| O(10)-Pb(1)-O(7) | 85.7(5) | O(10)#6-Ba(2)-O(5)#1 | 116.7(3) |
| O(10)-Pb(1)-O(5)#1 | 83.4(5) | O(5)#5-Ba(2)-O(5)#1 | 180.0(4) |
| O(7)-Pb(1)-O(5)#1 | 79.4(5) | O(5)-Zn(1)-O(6) | 120.0(5) |
| O(10)-Pb(1)-O(2) | 82.1(4) | O(5)-Zn(1)-O(6)#7 | 100.7(5) |
| O(7)-Pb(1)-O(2) | 86.5(5) | O(6)-Zn(1)-O(6)#7 | 110.6(3) |
| O(5)#1-Pb(1)-O(2) | 160.4(4) | O(5)-Zn(1)-O(9) | 114.1(5) |
| O(4)-Pb(2)-O(4)#2 | 93.9(6) | O(6)-Zn(1)-O(9) | 104.0(5) |
| O(4)-Pb(2)-O(2) | 72.3(4) | O(6)#7-Zn(1)-O(9) | 106.9(5) |
| O(4)#2-Pb(2)-O(2) | 56.2(4) | O(3)-Zn(2)-O(12) | 107.3(6) |
| O(4)-Pb(2)-O(2)#2 | 56.2(4) | O(3)-Zn(2)-O(1) | 116.8(5) |

| | | | |
|---|---|---|---|
| O(4)#2-Pb(2)-O(2)#2 | 72.3(4) | O(12)-Zn(2)-O(1) | 106.7(6) |
| O(2)-Pb(2)-O(2)#2 | 101.9(6) | O(3)-Zn(2)-O(9) | 110.5(6) |
| O(4)-Pb(2)-O(7)#2 | 82.5(4) | O(12)-Zn(2)-O(9) | 104.4(6) |
| O(4)#2-Pb(2)-O(7)#2 | 147.9(4) | O(1)-Zn(2)-O(9) | 110.4(5) |
| O(2)-Pb(2)-O(7)#2 | 147.7(4) | O(11)-Zn(3)-O(8) | 117.0(6) |
| O(2)#2-Pb(2)-O(7)#2 | 79.4(4) | O(11)-Zn(3)-O(4) | 109.6(6) |
| O(4)-Pb(2)-O(7) | 147.9(4) | O(8)-Zn(3)-O(4) | 104.9(6) |
| O(4)#2-Pb(2)-O(7) | 82.5(4) | O(11)-Zn(3)-O(2) | 108.3(5) |
| O(2)-Pb(2)-O(7) | 79.4(4) | O(8)-Zn(3)-O(2) | 119.5(6) |
| O(2)#2-Pb(2)-O(7) | 147.7(4) | O(4)-Zn(3)-O(2) | 94.7(5) |
| O(7)#2-Pb(2)-O(7) | 116.7(6) | O(9)#8-B(1)-O(1) | 119.2(15) |
| O(11)#3-Ba(1)-O(3) | 76.7(4) | O(9)#8-B(1)-O(6)#7 | 121.7(16) |
| O(11)#3-Ba(1)-O(7) | 165.2(4) | O(1)-B(1)-O(6)#7 | 119.0(14) |
| O(3)-Ba(1)-O(7) | 102.1(4) | O(7)-B(2)-O(2)#8 | 124.4(17) |
| O(11)#3-Ba(1)-O(8)#4 | 88.5(4) | O(7)-B(2)-O(4)#4 | 119.3(16) |
| O(3)-Ba(1)-O(8)#4 | 91.7(4) | O(2)#8-B(2)-O(4)#4 | 116.3(16) |
| O(7)-Ba(1)-O(8)#4 | 76.7(4) | O(5)#1-B(3)-O(12) | 118.0(17) |
| O(11)#3-Ba(1)-O(4)#2 | 101.9(4) | O(5)#1-B(3)-O(10)#8 | 124.3(18) |
| O(3)-Ba(1)-O(4)#2 | 160.5(4) | O(12)-B(3)-O(10)#8 | 117.8(18) |
| O(7)-Ba(1)-O(4)#2 | 74.2(4) | O(8)#8-B(4)-O(11) | 122(2) |
| O(8)#4-Ba(1)-O(4)#2 | 68.8(4) | O(8)#8-B(4)-O(3)#11 | 123.9(19) |

| | | | |
|---|---|---|---|
| O(11)#3-Ba(1)-O(1)#5 | 75.9(4) | O(11)-B(4)-O(3)#11 | 113.7(18) |

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

#9 -x+1,y-1,-z+3/2 #10 x,-y,z+1/2

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

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

**Table S3.** Atomic coordinates ( $\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $\alpha$-$BaZn_2(BO_3)_2$.

| Atom | x | y | z | *U*(eq) | BVS |
|---|---|---|---|---|---|
| Ba(1) | -628(1) | 10398(1) | 1591(1) | 12(1) | 1.917 |
| Zn(1) | 2904(1) | 10528(1) | 1790(1) | 12(1) | 2.084 |
| Zn(2) | -1398(1) | 11036(1) | 4490(1) | 13(1) | 1.999 |
| B(1) | 1814(5) | 5737(11) | 678(4) | 14(1) | 2.944 |
| B(2) | -590(5) | 5811(11) | 3587(4) | 13(1) | 2.964 |
| O(1) | 2260(4) | 4203(6) | 1702(3) | 20(1) | 1.997 |
| O(2) | -297(3) | 8484(6) | 3954(2) | 14(1) | 2.002 |
| O(3) | 1832(3) | 4691(6) | -366(3) | 14(1) | 1.908 |
| O(4) | 1377(3) | 8331(6) | 726(2) | 13(1) | 2.068 |
| O(5) | 4762(3) | 9611(6) | 1932(3) | 20(1) | 2.013 |
| O(6) | -1710(3) | 4483(6) | 3699(3) | 18(1) | 1.922 |

**Table S4.** Selected bond distances (Å) and angles (deg) for $\alpha$-$BaZn_2(BO_3)_2$.

| | | | |
|---|---|---|---|
| Ba(1)-O(6)#1 | 2.651(3) | O(4)#3-Ba(1)-O(2) | 169.65(9) |
| Ba(1)-O(5)#2 | 2.686(3) | O(4)-Ba(1)-O(2) | 114.19(8) |
| Ba(1)-O(4)#3 | 2.711(3) | O(3)#3-Ba(1)-O(2) | 130.96(8) |
| Ba(1)-O(4) | 2.814(3) | O(6)#1-Ba(1)-O(3)#4 | 64.48(9) |
| Ba(1)-O(3)#3 | 2.885(3) | O(5)#2-Ba(1)-O(3)#4 | 167.04(9) |
| Ba(1)-O(2) | 2.927(3) | O(4)#3-Ba(1)-O(3)#4 | 76.50(9) |
| Ba(1)-O(3)#4 | 2.959(3) | O(4)-Ba(1)-O(3)#4 | 74.16(9) |
| Ba(1)-O(5)#5 | 3.328(3) | O(3)#3-Ba(1)-O(3)#4 | 115.99(10) |
| Zn(1)-O(5) | 1.898(3) | O(2)-Ba(1)-O(3)#4 | 95.53(8) |
| Zn(1)-O(1)#7 | 1.926(3) | O(6)#1-Ba(1)-O(5)#5 | 88.98(9) |
| Zn(1)-O(4) | 1.956(3) | O(5)#2-Ba(1)-O(5)#5 | 110.53(11) |
| Zn(1)-O(1)#2 | 2.011(3) | O(4)#3-Ba(1)-O(5)#5 | 132.86(9) |
| Zn(2)-O(3)#8 | 1.914(3) | O(4)-Ba(1)-O(5)#5 | 78.58(8) |
| Zn(2)-O(6)#7 | 1.929(3) | O(3)#3-Ba(1)-O(5)#5 | 170.15(8) |
| Zn(2)-O(2) | 1.955(3) | O(2)-Ba(1)-O(5)#5 | 43.75(8) |
| Zn(2)-O(2)#9 | 2.060(3) | O(3)#4-Ba(1)-O(5)#5 | 61.15(8) |
| B(1)-O(4) | 1.369(6) | O(5)-Zn(1)-O(1)#7 | 122.79(15) |
| B(1)-O(3) | 1.377(6) | O(5)-Zn(1)-O(4) | 117.20(14) |

| | | | |
|---|---|---|---|
| B(1)-O(1) | 1.387(6) | O(1)#7-Zn(1)-O(4) | 108.39(13) |
| B(2)-O(5)#5 | 1.361(6) | O(5)-Zn(1)-O(1)#2 | 104.59(14) |
| B(2)-O(6) | 1.370(6) | O(1)#7-Zn(1)-O(1)#2 | 102.68(9) |
| B(2)-O(2) | 1.395(6) | O(4)-Zn(1)-O(1)#2 | 96.35(12) |
| O(6)#1-Ba(1)-O(5)#2 | 107.07(10) | O(3)#8-Zn(2)-O(6)#7 | 102.81(13) |
| O(6)#1-Ba(1)-O(4)#3 | 90.80(9) | O(3)#8-Zn(2)-O(2) | 125.92(13) |
| O(5)#2-Ba(1)-O(4)#3 | 114.47(10) | O(6)#7-Zn(2)-O(2) | 114.68(14) |
| O(6)#1-Ba(1)-O(4) | 137.64(9) | O(3)#8-Zn(2)-O(2)#9 | 116.31(12) |
| O(5)#2-Ba(1)-O(4) | 115.24(9) | O(6)#7-Zn(2)-O(2)#9 | 106.65(13) |
| O(4)#3-Ba(1)-O(4) | 70.38(10) | O(2)-Zn(2)-O(2)#9 | 89.31(12) |
| O(6)#1-Ba(1)-O(3)#3 | 81.48(9) | O(4)-B(1)-O(3) | 120.5(4) |
| O(5)#2-Ba(1)-O(3)#3 | 70.37(10) | O(4)-B(1)-O(1) | 118.8(4) |
| O(4)#3-Ba(1)-O(3)#3 | 50.31(8) | O(3)-B(1)-O(1) | 120.7(4) |
| O(4)-Ba(1)-O(3)#3 | 110.21(9) | O(5)#5-B(2)-O(6) | 121.2(4) |
| O(6)#1-Ba(1)-O(2) | 79.70(9) | O(5)#5-B(2)-O(2) | 117.8(4) |
| O(5)#2-Ba(1)-O(2) | 72.71(10) | O(6)-B(2)-O(2) | 120.9(4) |

Symmetry transformations used to generate equivalent atoms:

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

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

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

#8 x-1/2,-y+3/2,z+1/2 #9 -x,-y+2,-z+1

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

**Table S5.** The basic information of the existed anhydrous-zincoborates.[d]

| No. | Chemical formula | Coordination of the Zn atom | No. | Chemical formula | Coordination of the Zn atom |
|---|---|---|---|---|---|
| 1 | $Ba_2Zn(BO_3)_2$ | isolated $ZnO_4$ | 31 | $NdZnB_5O_{10}$ | isolated $Zn_2O_{10}$ |
| 2 | $Ba_2ZnSc(BO_3)_3$ | isolated $ZnO_4$ | 32 | $TbZnB_5O_{10}$ | isolated $Zn_2O_{10}$ |
| 3 | $Ba_3Zn(BO_3)(B_2O_5)F$ | isolated $ZnO_4$ | 33 | $EuZn(BO_2)_5$ | isolated $Zn_2O_{10}$ |
| 4 | $Ba_3Zn_2B_3O_9F$ | isolated $ZnO_4$ | 34 | $Zn_3B_7O_{13}Cl$ | isolated $Zn_3O_{12}Cl$ |
| 5 | $Ba_5Zn_2B_4O_{12}F_2$ | isolated $ZnO_4$ | 35 | $Zn_3B_7O_{13}Br$ | isolated $Zn_3O_{12}Br$ |
| 6 | $Bi_2ZnB_2O_7$ | isolated $ZnO_4$ | 36 | $Zn_4(B_6O_{12})O$ | isolated $Zn_4O_{13}$ |
| 7 | $K_3ZnB_5O_{10}$ | isolated $ZnO_4$ | 37 | $Zn_8(BO_2)_{12}Se_2$ | isolated $Zn_4O_{12}Se$ |
| 8 | $K_2NaZnB_5O_{10}$ | isolated $ZnO_4$ | 38 | **$KBa_2Zn_3(B_3O_6)(B_6O_{13})$** | **isolated $Zn_2O_7$ and isolated $Zn_2O_6$** |
| 9 | $Li_6Zn_3(BO_3)_4$ | isolated $ZnO_4$ | 39 | **$K_2Ba_4Zn_5(B_3O_6)_3(B_9O_{19})$** | **isolated $Zn_2O_7$ and isolated $Zn_3O_{10}$** |
| 10 | $Na_3ZnB_5O_{10}$- Ⅰ | isolated $ZnO_4$ | 40 | ***α*-$Pb_2Ba_4Zn_4B_{14}O_{31}$** | **isolated $ZnO_4$ and isolated $Zn_2O_6$** |
| 11 | $Na_3ZnB_5O_{10}$- Ⅱ | isolated $ZnO_4$ | 41 | ***β*-$Pb_2Ba_4Zn_4B_{14}O_{31}$** | **isolated $ZnO_4$ and isolated $Zn_2O_6$** |
| 12 | $Pb_4Zn_2B_{10}O_{21}$ | isolated $ZnO_4$ | 42 | ***γ*-$Pb_2Ba_4Zn_4B_{14}O_{31}$** | **isolated $ZnO_4$ and isolated $Zn_2O_6$** |

| | | | | | |
|---|---|---|---|---|---|
| 13 | $Rb_3ZnB_5O_{10}$ | isolated $ZnO_4$ | 43 | $LiZnBO_3$-Ⅱ | 1D $Zn_2O_6$ chain |
| 14 | $Cs_{12}Zn_4(B_5O_{10})_4$ | isolated $ZnO_4$ | 44 | $LiZnBO_3$-Ⅲ | 1D $Zn_2O_6$ chain |
| 15 | $ZnV_{12}B_{18}O_{63}$ | isolated $ZnO_4$ | 45 | $Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$ | 1D $Zn_2O_7$ chain |
| 16 | $Zn(B_4O_7)$-Ⅰ | isolated $ZnO_4$ | 46 | $PbZn_2(BO_3)_2$ | 1D $Zn_2O_7$ chain |
| 17 | $BaZnBO_3F$ | isolated $ZnO_3F_2$ | 47 | $Ba_4Zn_5Sc_2(BO_3)_8$ | 1D $Zn_3O_{11}$ chain |
| 18 | $K_7ZnSc_2B_{15}O_{30}$ | isolated $ZnO_6$ | 48 | $Ba_2ZnSc(BO_3)_3$ | isolated $ZnO_4$ |
| 19 | $Zn(B_4O_7)$-Ⅱ | isolated $ZnO_5$ | 49 | $BaZn_2(BO_3)_2$ | 1D $Zn_4O_{12}$ chain |
| 20 | $Ba_2Zn(B_3O_6)_2$ | isolated $Zn_2O_6$ | 50 | $CsZn_2B_3O_7$ | 2D layer |
| 21 | $KZnB_3O_6$ | isolated $Zn_2O_6$ | 51 | $CsZn_4(BO_3)_3$ | 2D layer |
| 22 | $KCdZn_2B_2O_6F$ | isolated $Zn_2O_6F$ | 52 | $Cs_3Zn_6B_9O_{21}$ | 2D layer |
| 23 | $Ba_5Zn_4(BO_3)_6$ | isolated $Zn_2O_7$ | 53 | $KZn_4B_3O_9$ | 2D layer |
| 24 | $LiZnBO_3$-Ⅰ | isolated $Zn_2O_7$ | 54 | $KZn_2BO_3Cl_2$ | 2D layer |
| 25 | $Na_2Ba_4Zn_4(B_3O_6)_2(B_{12}O_{24})$ | isolated $Zn_2O_7$ | 55 | $RbZn_4(BO_3)_3$ | 2D layer |
| 26 | $\alpha$-$Pb_5Zn_4B_6O_{18}$ | isolated $Zn_2O_7$ | 56 | $RbZn_2BO_3Cl_2$ | 2D layer |

| | | | | | |
|---|---|---|---|---|---|
| 27 | $\beta$-$Pb_5Zn_4B_6O_{18}$ | isolated $Zn_2O_7$ | 57 | $RbZn_2BO_3Br_2$ | 2D layer |
| 28 | $\gamma$-$Pb_5Zn_4B_6O_{18}$ | isolated $Zn_2O_7$ | 58 | $Zn_3(BO_3)_2$-Ⅰ | 3D |
| 29 | $CeZnB_5O_{10}$ | isolated $Zn_2O_{10}$ | 59 | $Zn_3(BO_3)_2$-Ⅱ | 3D |
| 30 | $LaZnB_5O_{10}$ | isolated $Zn_2O_{10}$ | 60 | $Zn_3(BO_3)_2$-Ⅲ | 3D |

[d]. Inorganic Crystal Structure Database (ICSD-3.7.0, the latest release of ICSD-2019/08/26)

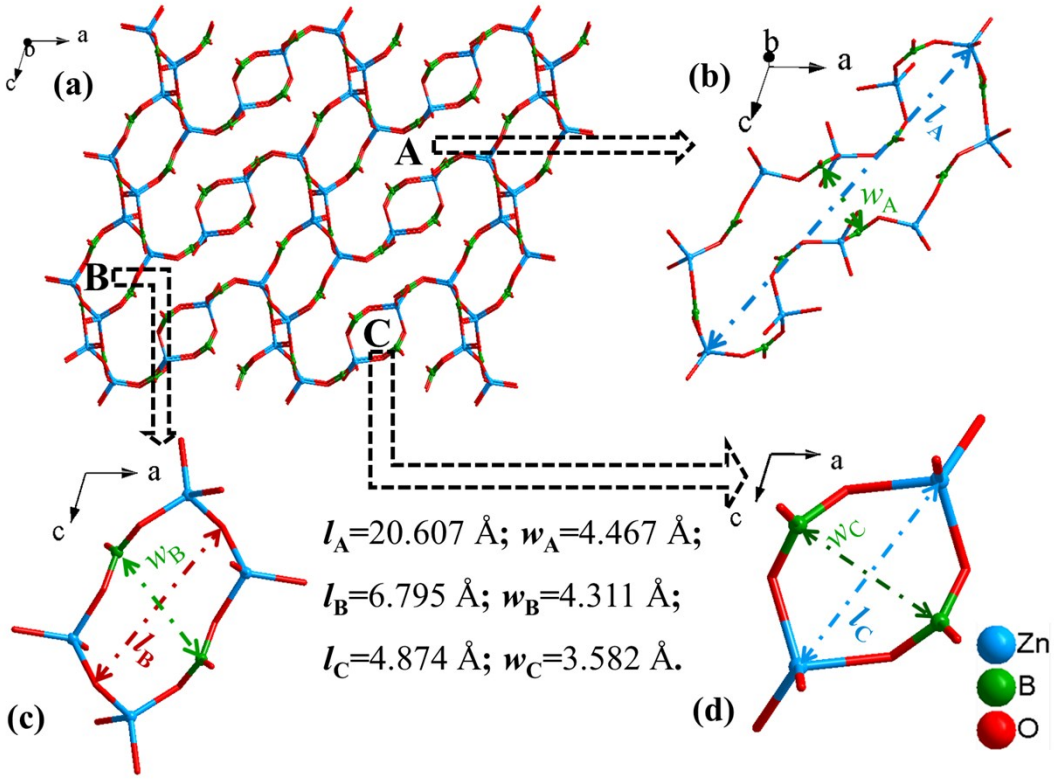


**Figure S1.** (a). Three types of tunnels in $Pb_3Ba_3Zn_6(BO_3)_8$; (b) A-type tunnel; (c) B-type tunnel; (d) C-type tunnel.

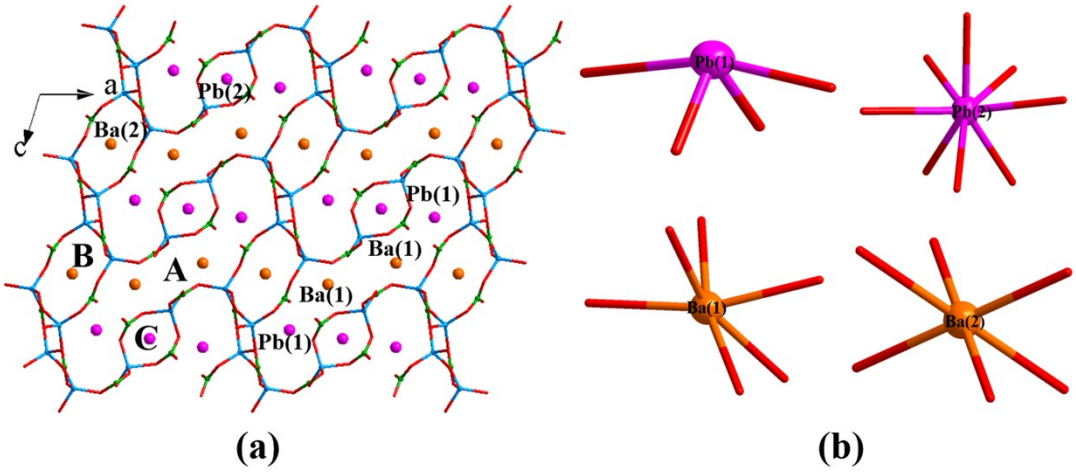


**Figure S2.** (a). Crystal structure of $Pb_3Ba_3Zn_6(BO_3)_8$ viewed along the *b*-axis; (b) Coordination environments of the Pb and the Ba atoms.

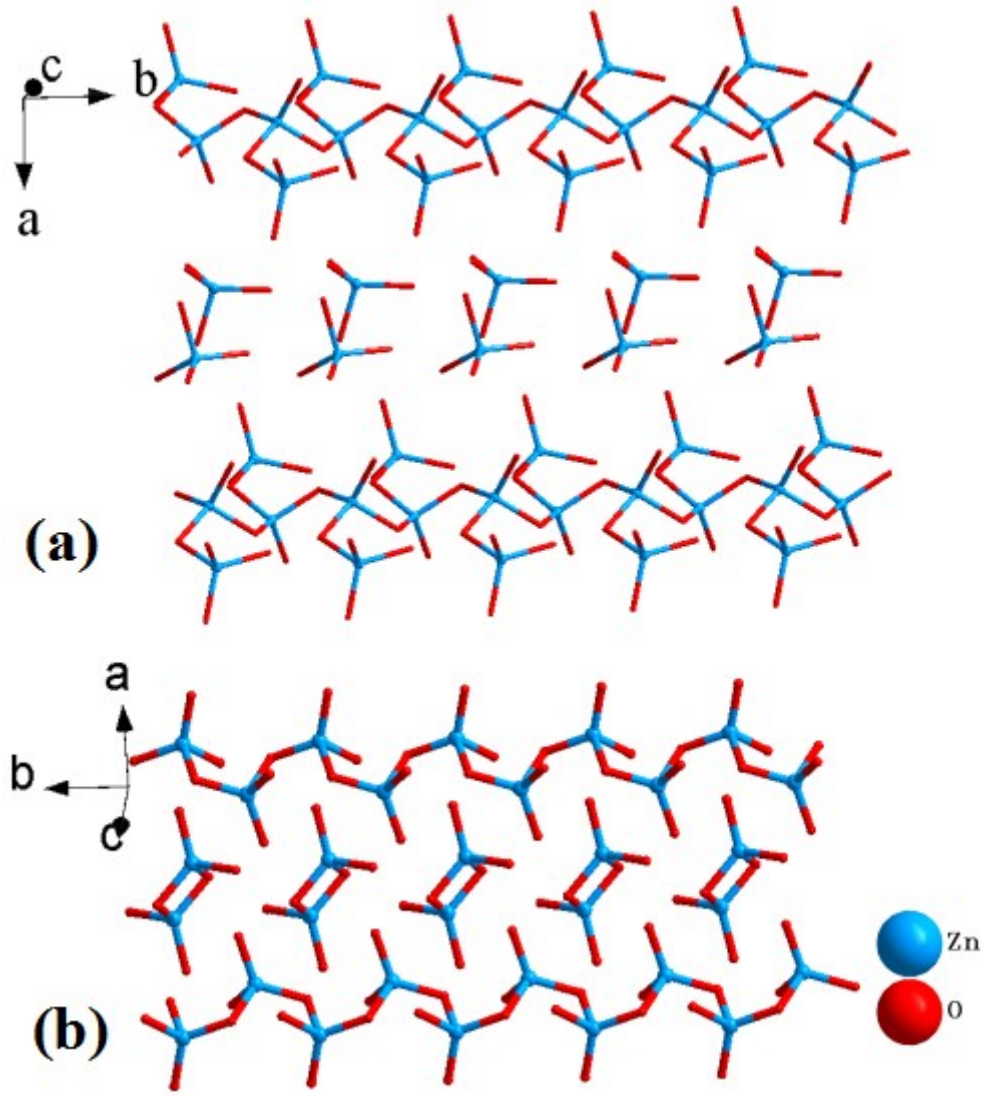


**Figure S3.** Coordination of the Zn atom: 0D isolated $ZnO_4$ and 1D $[Zn_4O_{12}]$ chain in $Pb_3Ba_3Zn_6(BO_3)_8$, (a); 0D isolated $Zn_2O_6$ dipolymer and 1D $[Zn_2O_7]$ chain in $\alpha$-$BaZn_2(BO_3)_2$, (b).

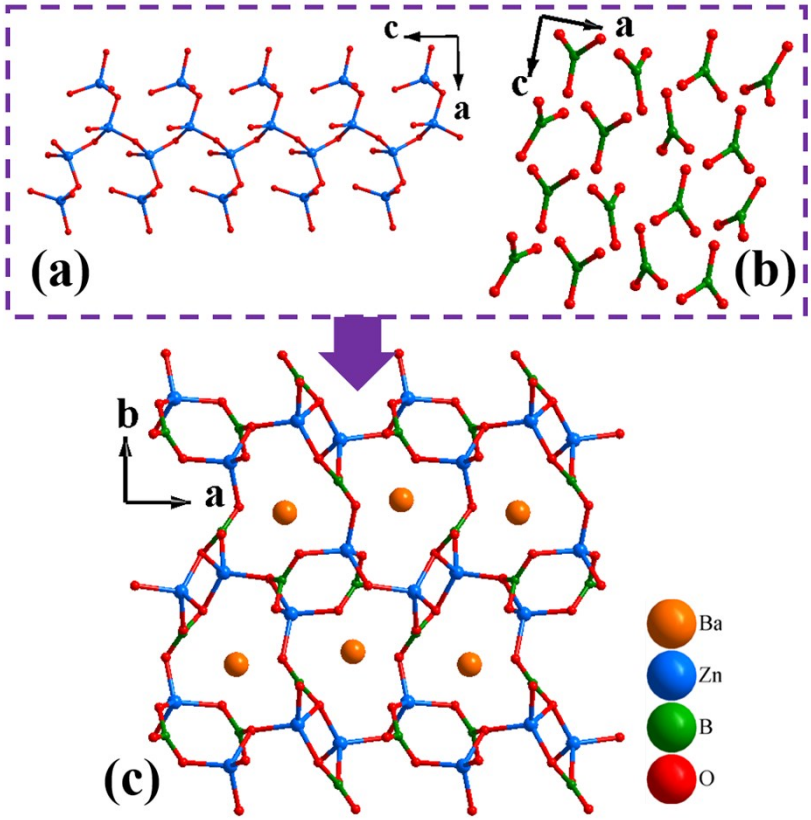


**Figure S4** (a) $[Zn_4O_{12}]$ chain; (b) isolated $BO_3$ triangles; (c) crystal structure of $\beta$-$BaZn_2(BO_3)_2$ viewing along the *c*-axis; All the Ba-O bonds are removed for clarity.

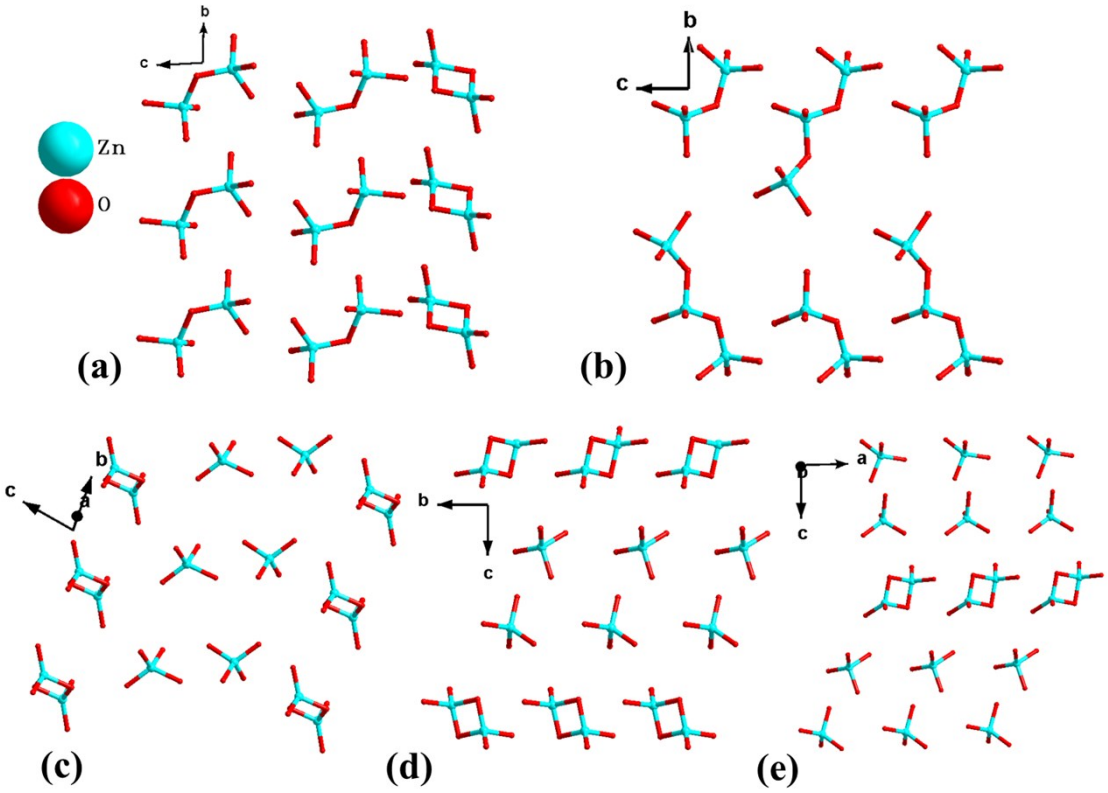


**Figure S5.** Coordination of the Zn atom: isolated $Zn_2O_7$ and $Zn_2O_6$ in $KBa_2Zn_3(B_3O_6)(B_6O_{13})$, (a); isolated $Zn_2O_7$ and $Zn_3O_{10}$ in $K_2Ba_4Zn_5(B_3O_6)_3(B_9O_{19})$, (b); isolated $ZnO_4$ and $Zn_2O_6$ in $\alpha$-, $\beta$- and $\gamma$- $Pb_2Ba_4Zn_4B_{14}O_{31}$, (c)(d)&(e).

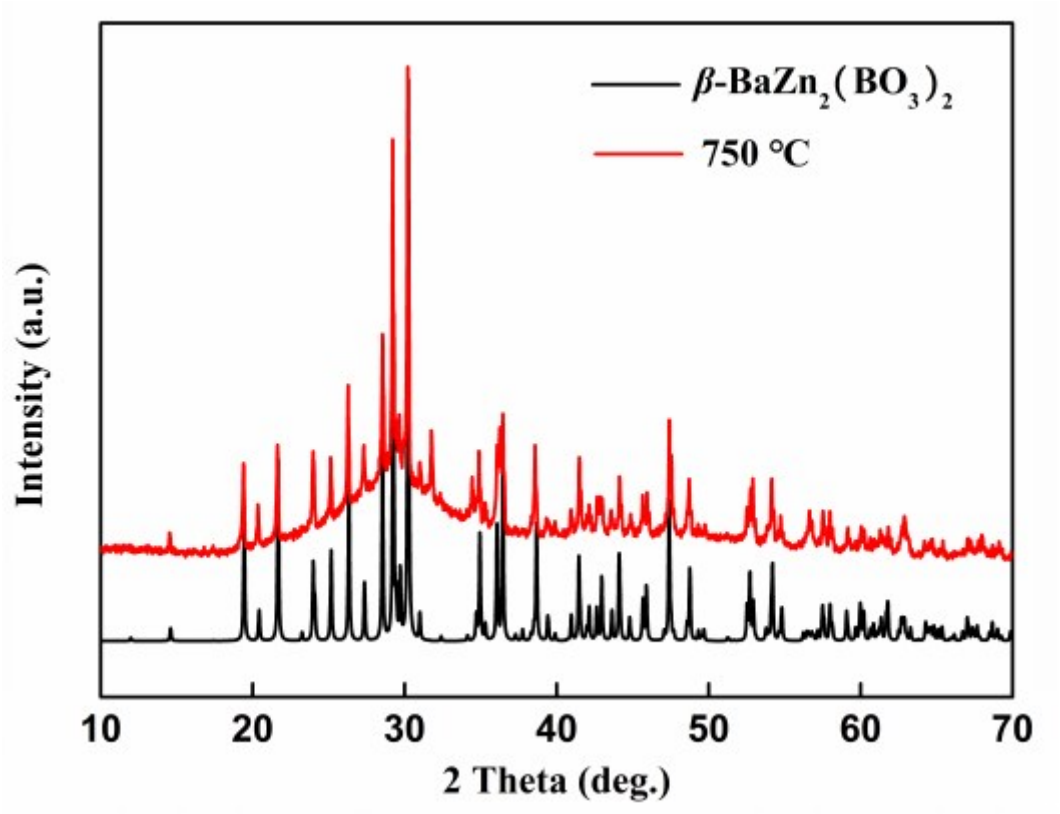


**Figure S6.** The powder XRD patterns of $Pb_3Ba_3Zn_6(BO_3)_8$ after holding at 750 °C.