Electronic Supplementary Information

Insights of BO_3-PO_4 Replacement for the Design and Synthesis of a New Borate-Phosphate with Unique $^{1}_{\infty}[Zn4BO11]$ Chains and Two New Phosphates

Fengjiao Guo[a,b], Cong Hu[a,b], Ying Wang[a], Jian Han[a]*, Zhihua Yang[a], Shilie Pan[a]*

[a.] Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China

[b.] University of the Chinese Academy of Sciences, Beijing 100049, China

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $CsZn_4(BO_3)(PO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)	BVS
Cs(1)	1794(1)	2500	8406(1)	34(1)	0.93
Zn(1)	1969(1)	5589(1)	8226(1)	13(1)	2.11
Zn(2)	4064(1)	3561(1)	3881(1)	12(1)	2.04
P(1)	6623(2)	4378(1)	7692(1)	11(1)	5.05
B(1)	1314(10)	7500	6892(7)	9(1)	2.93
O(1)	5096(5)	5340(2)	7299(3)	17(1)	2.12
O(2)	6398(6)	4021(2)	9417(3)	23(1)	1.99
O(3)	5194(6)	3660(2)	6335(3)	20(1)	2.04
O(4)	9606(5)	4526(2)	7723(4)	26(1)	2.06
O(5)	4038(7)	7500	6846(4)	13(1)	1.92
O(6)	-20(5)	6669(2)	6930(3)	14(1)	1.96

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $CsZn_4(PO_4)_3$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)	BVS
Cs(1)	7491(1)	-1146(1)	9209(1)	33(1)	0.82
Zn(1)	10473(1)	-1478(1)	9118(1)	14(1)	2.08
Zn(2)	4319(1)	-1422(1)	9440(1)	14(1)	2.13
Zn(3)	6336(1)	1158(1)	6942(1)	13(1)	2.02
Zn(4)	8547(1)	1290(1)	7256(1)	13(1)	2.13
P(1)	9452(1)	1286(2)	8946(1)	12(1)	5.09
P(2)	5450(1)	1093(2)	8747(1)	12(1)	5.06
P(3)	7565(1)	-1198(2)	6573(1)	12(1)	4.98
O(1)	6156(3)	1076(5)	8066(3)	22(1)	2.00

O(2)	8767(3)	1846(4)	8339(3)	17(1)	2.09
O(3)	10430(3)	1909(5)	8811(3)	16(1)	2.11
O(4)	9118(3)	1689(5)	9784(3)	22(1)	1.97
O(5)	5278(3)	-298(5)	9063(3)	23(1)	2.03
O(6)	7523(3)	-2718(4)	6763(3)	14(1)	2.04
O(7)	8036(3)	-478(4)	7275(3)	19(1)	1.93
O(8)	8051(3)	-972(5)	5771(3)	20(1)	1.94
O(9)	9538(3)	-212(5)	8833(3)	25(1)	2.01
O(10)	5786(3)	2006(5)	9437(3)	18(1)	2.05
O(11)	4534(3)	1780(4)	8475(3)	17(1)	2.10
O(12)	6558(3)	-679(4)	6510(3)	12(1)	2.04

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $RbZn_4(PO_4)_3$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)	BVS
Rb(1)	7500(1)	-1191(1)	9103(1)	44(1)	0.91
Zn(1)	8546(1)	1290(1)	7248(1)	18(1)	2.31
Zn(2)	10452(1)	-1470(1)	9123(1)	18(1)	2.28
Zn(3)	6330(1)	1181(1)	6941(1)	15(1)	2.24
Zn(4)	10667(1)	1396(1)	4444(1)	18(1)	2.32
P(1)	7559(1)	-1183(2)	6562(1)	16(1)	5.48
P(2)	9409(1)	1321(2)	8960(1)	16(1)	5.54
P(3)	10504(1)	1110(2)	6249(1)	15(1)	5.53
O(1)	8702(4)	1854(5)	8350(3)	21(1)	2.29
O(2)	10395(3)	1935(5)	8769(3)	16(1)	2.31
O(3)	9086(4)	1787(6)	9794(3)	22(1)	2.14
O(4)	11231(4)	1077(6)	6915(3)	25(1)	2.17
O(5)	9586(3)	1783(5)	6545(3)	19(1)	2.30
O(6)	10326(4)	-280(5)	5916(3)	26(1)	2.16
O(7)	10829(4)	2042(5)	5561(3)	23(1)	2.24
O(8)	6543(3)	-658(5)	6512(3)	16(1)	2.27
O(9)	7521(3)	-2707(5)	6731(3)	16(1)	2.26
O(10)	8038(4)	-497(5)	7273(3)	23(1)	2.13
O(11)	8256(4)	-913(6)	5765(3)	28(1)	2.11
O(12)	9497(4)	-181(6)	8882(4)	28(1)	2.18

Table S4. Bond distances (Å) and angles (deg) for $CsZn_4(BO_3)(PO_4)_2$.

Cs(1)-O(4)#1	3.102(3)	O(3)-Cs(1)-O(3)#1	123.78(8)
Cs(1)-O(4)#2	3.102(3)	O(4)#2-Cs(1)-O(3)#2	42.53(6)
Cs(1)-O(2)#3	3.112(3)	O(2)#3-Cs(1)-O(3)#2	161.20(7)
Cs(1)-O(2)	3.112(3)	O(2)-Cs(1)-O(3)#2	107.70(7)
Cs(1)-O(3)#3	3.211(3)	O(3)#3-Cs(1)-O(3)#2	123.78(8)

Cs(1)-O(3)	3.211(3)	O(3)-Cs(1)-O(3)#2	94.64(7)
Cs(1)-O(3)#1	3.644(3)	O(3)#1-Cs(1)-O(3)#2	54.45(9)
Cs(1)-O(3)#2	3.644(3)	O(4)#1-Cs(1)-O(2)#1	41.76(7)
Cs(1)-O(2)#1	3.773(3)	O(4)#2-Cs(1)-O(2)#1	109.95(7)
Cs(1)-O(2)#2	3.773(3)	O(2)#3-Cs(1)-O(2)#1	93.82(8)
Zn(1)-O(4)#2	1.904(3)	O(2)-Cs(1)-O(2)#1	151.67(9)
Zn(1)-O(2)#4	1.919(3)	O(3)#3-Cs(1)-O(2)#1	110.47(7)
Zn(1)-O(6)	1.968(2)	O(3)-Cs(1)-O(2)#1	162.06(6)
Zn(1)-O(1)	1.978(3)	O(3)#1-Cs(1)-O(2)#1	38.38(6)
Zn(2)-O(3)	1.901(3)	O(3)#2-Cs(1)-O(2)#1	75.30(7)
Zn(2)-O(1)#5	1.959(3)	O(4)#1-Cs(1)-O(2)#2	109.95(7)
Zn(2)-O(6)#6	1.972(3)	O(4)#2-Cs(1)-O(2)#2	41.76(7)
Zn(2)-O(5)#5	1.983(2)	O(2)#3-Cs(1)-O(2)#2	151.67(9)
P(1)-O(4)	1.513(3)	O(2)-Cs(1)-O(2)#2	93.82(8)
P(1)-O(3)	1.519(3)	O(3)#3-Cs(1)-O(2)#2	162.06(6)
P(1)-O(2)	1.527(3)	O(3)-Cs(1)-O(2)#2	110.47(7)
P(1)-O(1)	1.567(3)	O(3)#1-Cs(1)-O(2)#2	75.30(7)
B(1)-O(6)#8	1.376(3	O(3)#2-Cs(1)-O(2)#2	38.38(6)
B(1)-O(6)	1.376(3)	O(2)#1-Cs(1)-O(2)#2	70.81(9)
B(1)-O(5)	1.387(6)	O(4)#2-Zn(1)-O(2)#4	119.83(13)
O(4)#1-Cs(1)-O(4)#2	139.52(10)	O(4)#2-Zn(1)-O(6)	109.53(12)
O(4)#1-Cs(1)-O(2)#3	65.45(8)	O(2)#4-Zn(1)-O(6)	107.21(11)
O(4)#2-Cs(1)-O(2)#3	154.46(7)	O(4)#2-Zn(1)-O(1)	107.08(12)
O(4)#1-Cs(1)-O(2)	154.46(7)	O(2)#4-Zn(1)-O(1)	106.34(12)
O(4)#2-Cs(1)-O(2)	65.45(8)	O(6)-Zn(1)-O(1)	106.03(11)
O(2)#3-Cs(1)-O(2)	89.22(11)	O(3)-Zn(2)-O(1)#5	114.24(11)
O(4)#1-Cs(1)-O(3)#3	68.74(7)	O(3)-Zn(2)-O(6)#6	108.10(11)
O(4)#2-Cs(1)-O(3)#3	127.71(8)	O(1)#5-Zn(2)-O(6)#6	109.19(10)
O(2)#3-Cs(1)-O(3)#3	45.38(7)	O(3)-Zn(2)-O(5)#5	110.56(13)
O(2)-Cs(1)-O(3)#3	91.54(8)	O(1)#5-Zn(2)-O(5)#5	106.14(11)
O(4)#1-Cs(1)-O(3)	127.71(8)	O(6)#6-Zn(2)-O(5)#5	108.48(12)
O(4)#2-Cs(1)-O(3)	68.74(7)	O(4)-P(1)-O(3)	110.94(16)
O(2)#3-Cs(1)-O(3)	91.54(8)	O(4)-P(1)-O(2)	112.58(17)
O(2)-Cs(1)-O(3)	45.38(7)	O(3)-P(1)-O(2)	106.51(15)
O(3)#3-Cs(1)-O(3)	62.56(10)	O(4)-P(1)-O(1)	107.73(15)
O(4)#1-Cs(1)-O(3)#1	42.53(6)	O(3)-P(1)-O(1)	110.88(15)
O(4)#2-Cs(1)-O(3)#1	96.98(7)	O(2)-P(1)-O(1)	108.19(15)
O(2)#3-Cs(1)-O(3)#1	107.70(7)	O(6)#8-B(1)-O(6)	120.4(4)
O(2)-Cs(1)-O(3)#1	161.20(6)	O(6)#8-B(1)-O(5)	119.8(2)
O(3)#3-Cs(1)-O(3)#1	94.64(7)	O(6)-B(1)-O(5)	119.8(2)

Symmetry transformations used to generate equivalent atoms:

#1 x-1, -y+1/2, z	#2 x-1, y, z	#3 x, -y+1/2, z	#4 -x+1, -y+1, -z+2
#5 -x+1, -y+1, -z+1	#6 -x, -y+1, -z+1	#7 x+1, y, z	#8 x, -y+3/2, z
#9 -x+1, y+1/2, -z+1			

Table S5. Bond distances (Å) and angles (deg) for $CsZn_4(PO_4)_3$.

Cs(1)-O(2)#1	3.069(5)	O(5)-Cs(1)-O(8)#2	70.99(12)
Cs(1)-O(10)#1	3.130(5)	O(7)-Cs(1)-O(8)#2	130.07(13)
Cs(1)-O(9)	3.170(6)	O(2)#1-Cs(1)-O(1)	80.68(15)
Cs(1)-O(4)#1	3.322(6)	O(10)#1-Cs(1)-O(1)	151.89(12)
Cs(1)-O(5)	3.325(6)	O(9)-Cs(1)-O(1)	102.98(14)
Cs(1)-O(7)	3.346(6)	O(4)#1-Cs(1)-O(1)	100.39(14)
Cs(1)-O(8)#2	3.423(5)	O(5)-Cs(1)-O(1)	42.71(11)
Cs(1)-O(1)	3.498(5)	O(7)-Cs(1)-O(1)	59.48(12)
Zn(4)-O(2)	1.894(5)	O(8)#2-Cs(1)-O(1)	83.20(13)
Zn(4)-O(7)	1.920(5)	O(2)-Zn(4)-O(7)	108.8(2)
Zn(4)-O(11)#5	1.931(5)	O(2)-Zn(4)-O(11)#5	112.7(2)
Zn(4)-O(6)#6	2.012(5)	O(7)-Zn(4)-O(11)#5	122.0(2)
Zn(1)-O(4)#7	1.913(5)	O(2)-Zn(4)-O(6)#6	111.3(2)
Zn(1)-O(9)	1.915(5)	O(7)-Zn(4)-O(6)#6	99.52(19)
Zn(1)-O(11)#1	2.041(5)	O(11)#5-Zn(4)-O(6)#6	101.1(2)
Zn(1)-O(12)#5	2.044(5)	O(4)#7-Zn(1)-O(9)	121.6(2)
Zn(3)-O(1)	1.869(5)	O(4)#7-Zn(1)-O(11)#1	113.4(2)
Zn(3)-O(3)#8	1.956(5)	O(9)-Zn(1)-O(11)#1	115.9(2)
Zn(3)-O(12)	2.000(5)	O(4)#7-Zn(1)-O(12)#5	106.4(2)
Zn(3)-O(6)#6	2.021(5)	O(9)-Zn(1)-O(12)#5	99.3(2)
Zn(2)-O(5)	1.893(5)	O(11)#1-Zn(1)-O(12)#5	94.42(18)
Zn(2)-O(8)#8	1.923(5)	O(4)#7-Zn(1)-O(10)#1	87.66(19)
Zn(2)-O(10)#4	1.944(5)	O(9)-Zn(1)-O(10)#1	86.3(2)
Zn(2)-O(3)#1	1.999(5)	O(11)#1-Zn(1)-O(10)#1	64.80(17)
P(3)-O(8)	1.514(5)	O(12)#5-Zn(1)-O(10)#1	158.59(17)
P(3)-O(7)	1.523(5)	O(1)-Zn(3)-O(3)#8	123.3(2)
P(3)-O(12)	1.552(5)	O(1)-Zn(3)-O(12)	109.5(2)
P(3)-O(6)	1.557(5)	O(3)#8-Zn(3)-O(12)	103.69(19)
P(1)-O(2)	1.515(5)	O(1)-Zn(3)-O(6)#6	106.5(2)
P(1)-O(4)	1.516(5)	O(3)#8-Zn(3)-O(6)#6	104.0(2)
P(1)-O(9)	1.517(5)	O(12)-Zn(3)-O(6)#6	109.23(19)
P(1)-O(3)	1.565(5)	O(5)-Zn(2)-O(8)#8	120.2(2)
P(2)-O(5)	1.508(5)	O(5)-Zn(2)-O(10)#4	123.2(2)
P(2)-O(1)	1.517(5)	O(8)#8-Zn(2)-O(10)#4	99.6(2)
P(2)-O(10)	1.537(5)	O(5)-Zn(2)-O(3)#1	101.3(2)
P(2)-O(11)	1.562(5)	O(8)#8-Zn(2)-O(3)#1	106.08(19)
O(2)#1-Cs(1)-O(10)#1	98.15(15)	O(10)#4-Zn(2)-O(3)#1	104.7(2)
O(2)#1-Cs(1)-O(9)	131.16(13)	O(8)-P(3)-O(7)	112.4(3)
O(10)#1-Cs(1)-O(9)	56.79(14)	O(8)-P(3)-O(12)	109.2(3)
O(2)#1-Cs(1)-O(4)#1	44.57(13)	O(7)-P(3)-O(12)	108.3(3)
O(10)#1-Cs(1)-O(4)#1	98.00(15)	O(8)-P(3)-O(6)	109.9(3)

O(9)-Cs(1)-O(4)#1	154.79(13)	O(7)-P(3)-O(6)	109.2(3)
O(2)#1-Cs(1)-O(5)	63.97(14)	O(12)-P(3)-O(6)	107.7(2)
O(10)#1-Cs(1)-O(5)	158.21(12)	O(2)-P(1)-O(4)	106.9(3)
O(9)-Cs(1)-O(5)	144.31(13)	O(2)-P(1)-O(9)	109.9(3)
O(4)#1-Cs(1)-O(5)	60.71(13)	O(4)-P(1)-O(9)	113.6(3)
O(2)#1-Cs(1)-O(7)	80.09(12)	O(2)-P(1)-O(3)	110.6(3)
O(10)#1-Cs(1)-O(7)	92.53(12)	O(4)-P(1)-O(3)	108.1(3)
O(9)-Cs(1)-O(7)	62.27(12)	O(9)-P(1)-O(3)	107.7(3)
O(4)#1-Cs(1)-O(7)	124.53(12)	O(5)-P(2)-O(1)	110.8(3)
O(5)-Cs(1)-O(7)	96.19(12)	O(5)-P(2)-O(10)	110.4(3)
O(2)#1-Cs(1)-O(8)#2	128.30(13)	O(1)-P(2)-O(10)	109.8(3)
O(10)#1-Cs(1)-O(8)#2	117.38(12)	O(5)-P(2)-O(11)	111.5(3)
O(9)-Cs(1)-O(8)#2	100.27(13)	O(1)-P(2)-O(11)	111.5(3)
O(4)#1-Cs(1)-O(8)#2	91.73(13)	O(10)-P(2)-O(11)	102.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y-1/2,z	#2 -x+3/2,-y,z+1/2	#3 x+1/2,-y-1/2,-z+2	#4 -x+1,-y,-z+2
#5 x+1/2,y,-z+3/2	#6 -x+3/2,y+1/2,z	#7 -x+2,-y,-z+2	#8 x-1/2,y,-z+3/2
#9 x-1/2,-y-1/2,-z+2	#10 -x+3/2,-y,z-1/2		

Table S6. Bond distances (Å) and angles (deg) for $RbZn_4(PO_4)_3$.

Zn(1)-O(1)	1.866(6)	O(12)-Zn(2)-O(7)#4	85.5(3)
Zn(1)-O(10)	1.895(6)	O(8)#3-Zn(2)-O(7)#4	158.83(19)
Zn(1)-O(5)	1.905(5)	O(5)#4-Zn(2)-O(7)#4	64.5(2)
Zn(1)-O(9)#1	1.973(5)	O(4)#5-Zn(3)-O(2)#5	125.8(2)
Zn(2)-O(3)#2	1.879(6)	O(4)#5-Zn(3)-O(8)	108.1(2)
Zn(2)-O(12)	1.881(6)	O(2)#5-Zn(3)-O(8)	104.2(2)
Zn(2)-O(8)#3	2.002(5)	O(4)#5-Zn(3)-O(9)#1	105.1(2)
Zn(2)-O(5)#4	2.024(6)	O(2)#5-Zn(3)-O(9)#1	103.8(2)
Zn(2)-O(7)#4	2.369(6)	O(8)-Zn(3)-O(9)#1	109.1(2)
Zn(3)-O(4)#5	1.844(6)	O(6)#6-Zn(4)-O(11)#6	120.4(3)
Zn(3)-O(2)#5	1.913(5)	O(6)#6-Zn(4)-O(7)	125.0(2)
Zn(3)-O(8)	1.956(6)	O(11)#6-Zn(4)-O(7)	97.9(2)
Zn(3)-O(9)#1	1.973(5)	O(6)#6-Zn(4)-O(2)#7	100.5(2)
Zn(4)-O(6)#6	1.862(6)	O(11)#6-Zn(4)-O(2)#7	107.4(2)
Zn(4)-O(11)#6	1.880(6)	O(7)-Zn(4)-O(2)#7	103.9(2)
Zn(4)-O(7)	1.915(6)	O(1)#9-Rb(1)-O(7)#4	98.6(2)
Zn(4)-O(2)#7	1.978(5)	O(1)#9-Rb(1)-O(12)	137.10(16)
Rb(1)-O(1)#9	2.825(6)	O(7)#4-Rb(1)-O(12)	58.49(19)
Rb(1)-O(7)#4	2.963(6)	O(1)#9-Rb(1)-O(10)	83.68(17)
Rb(1)-O(12)	2.988(7)	O(7)#4-Rb(1)-O(10)	96.28(15)
Rb(1)-O(10)	3.105(7)	O(12)-Rb(1)-O(10)	65.68(15)
Rb(1)-O(6)#5	3.173(8)	O(1)#9-Rb(1)-O(6)#5	67.45(18)
Rb(1)-O(3)#9	3.180(7)	O(7)#4-Rb(1)-O(6)#5	157.58(15)

Rb(1)-O(4)#5	3.285(7)	O(12)-Rb(1)-O(6)#5	143.42(18)
Rb(1)-O(11)#10	3.463(7)	O(10)-Rb(1)-O(6)#5	99.32(14)
Rb(1)-O(4)#4	3.609(7)	O(1)#9-Rb(1)-O(3)#9	46.22(16)
Rb(1)-P(3)#5	3.640(5)	O(7)#4-Rb(1)-O(3)#9	97.0(2)
P(1)-O(11)	1.480(6)	O(12)-Rb(1)-O(3)#9	154.48(15)
P(1)-O(10)	1.485(6)	O(10)-Rb(1)-O(3)#9	129.52(13)
P(1)-O(8)	1.515(5)	O(6)#5-Rb(1)-O(3)#9	60.62(17)
P(1)-O(9)	1.523(6)	O(1)#9-Rb(1)-O(4)#5	85.8(2)
P(2)-O(3)	1.485(6)	O(7)#4-Rb(1)-O(4)#5	156.23(14)
P(2)-O(1)	1.487(6)	O(12)-Rb(1)-O(4)#5	102.82(18)
P(2)-O(12)	1.487(6)	O(10)-Rb(1)-O(4)#5	60.82(15)
P(2)-O(2)	1.530(6)	O(6)#5-Rb(1)-O(4)#5	44.38(13)
P(3)-O(4)	1.477(6)	O(3)#9-Rb(1)-O(4)#5	102.69(19)
P(3)-O(6)	1.488(6)	O(1)#9-Rb(1)-O(11)#10	126.94(17)
P(3)-O(7)	1.505(6)	O(7)#4-Rb(1)-O(11)#10	112.78(16)
P(3)-O(5)	1.520(5)	O(12)-Rb(1)-O(11)#10	95.95(16)
O(1)-Rb(1)#1	2.825(6)	O(10)-Rb(1)-O(11)#10	130.64(17)
O(2)-Zn(3)#3	1.913(5)	O(6)#5-Rb(1)-O(11)#10	67.84(14)
O(2)-Zn(4)#11	1.978(5)	O(3)#9-Rb(1)-O(11)#10	86.97(17)
O(3)-Zn(2)#2	1.879(6)	O(4)#5-Rb(1)-O(11)#10	81.72(18)
O(3)-Rb(1)#1	3.180(7)	O(1)#9-Rb(1)-O(4)#4	66.04(18)
O(4)-Zn(3)#3	1.844(6)	O(7)#4-Rb(1)-O(4)#4	42.10(14)
O(4)-Rb(1)#3	3.285(7)	O(12)-Rb(1)-O(4)#4	74.51(17)
O(4)-Rb(1)#8	3.609(7)	O(10)-Rb(1)-O(4)#4	67.45(15)
O(5)-Zn(2)#8	2.024(6)	O(6)#5-Rb(1)-O(4)#4	132.66(14)
O(6)-Zn(4)#6	1.862(6)	O(3)#9-Rb(1)-O(4)#4	92.11(18)
O(6)-Rb(1)#3	3.173(8)	O(4)#5-Rb(1)-O(4)#4	123.09(19)
O(7)-Zn(2)#8	2.369(6)	O(11)#10-Rb(1)-O(4)#4	154.57(12)
O(7)-Rb(1)#8	2.963(6)	O(11)-P(1)-O(10)	111.7(3)
O(8)-Zn(2)#5	2.002(5)	O(11)-P(1)-O(8)	109.6(3)
O(9)-Zn(3)#9	1.973(5)	O(10)-P(1)-O(8)	108.1(3)
O(9)-Zn(1)#9	1.973(5)	O(11)-P(1)-O(9)	110.3(3)
O(11)-Zn(4)#6	1.880(6)	O(10)-P(1)-O(9)	109.0(3)
O(11)-Rb(1)#12	3.463(7)	O(8)-P(1)-O(9)	108.2(3)
O(1)-Zn(1)-O(10)	107.4(2)	O(3)-P(2)-O(1)	106.4(3)
O(1)-Zn(1)-O(5)	113.3(2)	O(3)-P(2)-O(12)	114.1(3)
O(10)-Zn(1)-O(5)	122.4(2)	O(1)-P(2)-O(12)	110.5(3)
O(1)-Zn(1)-O(9)#1	109.8(2)	O(3)-P(2)-O(2)	107.9(3)
O(10)-Zn(1)-O(9)#1	100.8(2)	O(1)-P(2)-O(2)	110.4(3)
O(5)-Zn(1)-O(9)#1	101.7(2)	O(12)-P(2)-O(2)	107.6(3)
O(3)#2-Zn(2)-O(12)	123.1(2)	O(4)-P(3)-O(6)	110.8(3)
O(3)#2-Zn(2)-O(8)#3	105.9(2)	O(4)-P(3)-O(7)	109.6(3)
O(12)-Zn(2)-O(8)#3	99.7(3)	O(6)-P(3)-O(7)	110.2(3)
O(3)#2-Zn(2)-O(5)#4	110.9(2)	O(4)-P(3)-O(5)	111.5(3)

O(12)-Zn(2)-O(5)#4	116.3(2)	O(6)-P(3)-O(5)	111.8(3)
O(8)#3-Zn(2)-O(5)#4	95.1(2)	O(7)-P(3)-O(5)	102.7(3)
O(3)#2-Zn(2)-O(7)#4	87.7(2)		

Symmetry transformations used to generate equivalent atoms:

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

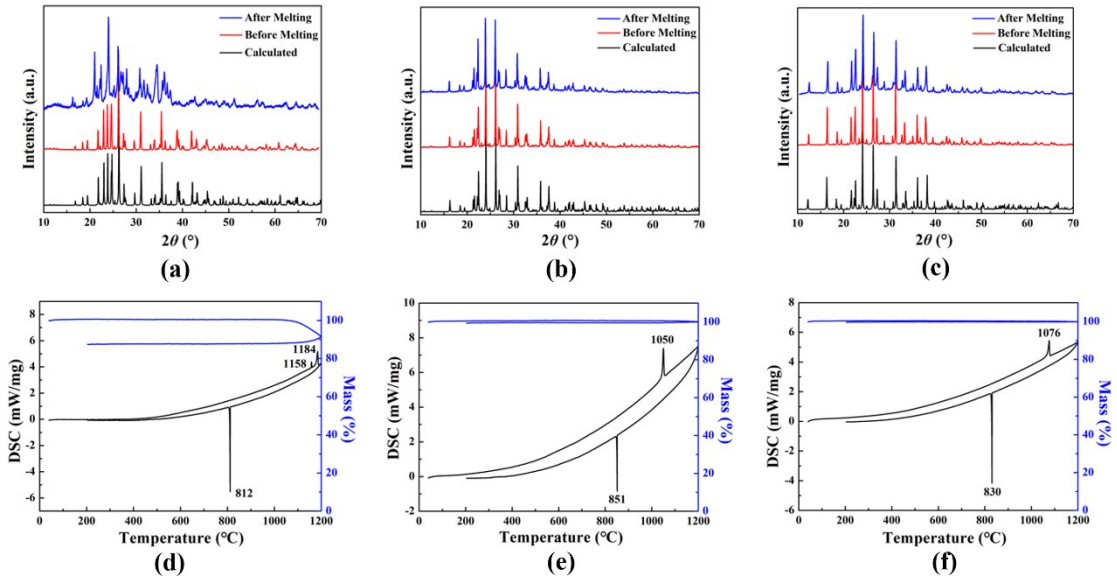

Fig. S1 XRD patterns and TG-DSC curves of: (a, d) $CsZn_4(BO_3)(PO_4)_2$, (b, e) $CsZn_4(PO_4)_3$ and (c, f) $RbZn_4(PO_4)_3$.

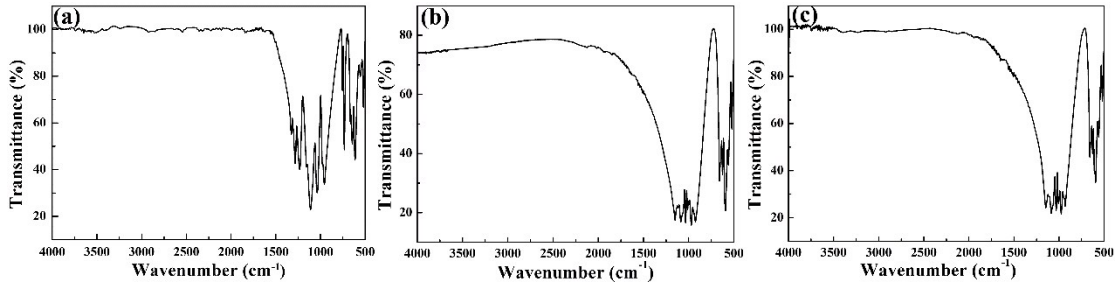

Fig. S2. IR spectrum of: (a) $CsZn_4(BO_3)(PO_4)_2$, (b) $CsZn_4(PO_4)_3$ and (c) $RbZn_4(PO_4)_3$.

Table S7 Assignments of the IR absorption peaks for $CsZn_4(BO_3)(PO_4)_2$, $CsZn_4(PO_4)_3$ and $RbZn_4(PO_4)_3$.

Mode description (cm^{-1})	$CsZn_4(BO_3)(PO_4)_2$	$CsZn_4(PO_4)_3$	$RbZn_4(PO_4)_3$
Stretching and bending of Zn-O	1154	1150	1146
Asymmetric stretching	1326-1232 (BO_3)	1112-931 (PO_4)	1116-926 (PO_4)

	1110-955 (BO_3 and PO_4)		
Out-of-plane bending of P-O	666-613	659-460	658-463
Out-of-plane bending of B-O	556, 519		