Electronic Supplementary Material (ESI) for Dalton Transactions.

$CaZn(HPO_3)_2$ and $Ba_2Zn(HPO_3)_3$: Novel Alkaline-Earth Zincophosphites with Diversified Anionic Frameworks

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Table S1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $CaZn(HPO3)_2$ and $Ba_2Zn(HPO_3)_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	Symmetry	x	y	z	U_{eq}	Occu
			$CaZn(HPO3)_2$			
Zn1	4e	8923.6(5)	1065.4(4)	5856.3(2)	11.12(9)	1
Ca1	4e	4726.5(9)	2519.7(6)	2384.3(4)	8.79(11)	1
P1	4e	3899.3(12)	2479.6(9)	4883.6(5)	9.46(13)	1
P2	4e	10071.8(11)	4808.1(8)	7012.3(5)	8.50(13)	1
O1	4e	5231(4)	2432(3)	3973.5(13)	19.2(4)	1
O2	4e	1680(3)	1204(2)	4892.9(13)	14.0(4)	1
O3	4e	5624(3)	2202(3)	5752.2(12)	13.0(4)	1
O4	4e	10768(3)	3067(2)	6578.4(13)	13.4(4)	1
O5	4e	7487(3)	4854(2)	7380.6(14)	14.3(4)	1
O6	4e	12074(3)	5220(2)	7781.7(13)	12.1(4)	1
H1	4e	2920(50)	4100(40)	5017(19)	6(7)	1
			$Ba_2Zn(HPO_3)_3$			
Ba1	4c	4042.2(4)	2500	4322.4(5)	17.89(18)	0.5
Ba2	4c	5027.9(4)	-2500	1794.2(5)	18.82(18)	0.5
Zn1	4c	6714.5(7)	2500	668.8(9)	16.9(3)	0.5
P1	4c	5997.3(18)	2500	3346(2)	20.8(6)	0.5
P2	4c	6193.3(17)	-2500	-878(2)	18.1(6)	0.5
P3	4c	7854.1(17)	-2500	1463(2)	20.6(6)	0.5
O1	4c	6074(6)	2500	2053(7)	68(3)	0.5
O2	8d	5572(4)	156(10)	3760(5)	40.7(17)	1
O3	4c	5720(5)	-2500	-1996(6)	26.8(19)	0.5
O4	8d	6011(4)	-146(9)	-181(4)	33.6(14)	1
O5	4c	8749(4)	-2500	1615(6)	24.6(18)	0.5
O6	8d	7592(3)	-65(9)	853(4)	28.1(13)	1
H1	4c	6730(20)	2500	3730(80)	25	0.5
H2	4c	6970(60)	-2500	-1140(80)	20(30)	0.5
H3	4c	7500(50)	-2500	2460(40)	30(30)	0.5

Table S2: Bond Lengths in Å with calculated bond valence units for $CaZn(HPO3)_2$ and $Ba_2Zn(HPO_3)_3$.

Bond Lengths	(Å)	Bond Valence	
		contributions	sum
	$CaZn(HPO_3)_2$		
P1-O1	1.4982(19)	1.379	3.817
P1-O2	1.5522(19)	1.191	

Bond Lengths	(Å)	Bond Valence	
		contributions	sum
P1-O3	1.5353(19)	1.247	
P2-O4	1.5241(19)	1.285	3.827
P2-O5	1.5121(18)	1.328	
P2-O6	1.5451(19)	1.214	
Zn1-O2^{2}	2.0604(18)	0.382	1.906
Zn1-O2^{3}	2.0592(17)	0.383	
Zn1-O3	1.9920(18)	0.459	
Zn1-O4	2.0834(18)	0.359	
Zn1-O6^{1}	2.1216(18)	0.323	
Ca1-O1	2.2585(19)	0.455	2.161
Ca1-O3^{4}	2.3865(18)	0.322	
Ca1-O4^{5}	2.4396(19)	0.279	
Ca1-O5^{6}	2.3756(19)	0.331	
Ca1-O5^{4}	2.3590(18)	0.347	
Ca1-O6^{5}	2.6199(19)	0.171	
Ca1-O6^{7}	2.4710(19)	0.256	
$Ba_2Zn(HPO_3)_3$			
P1-O1	1.496(8)	1.387	4.043
P1-O2	1.512(5)	1.328	
P1-O2^{2}	1.512(5)	1.328	
P2-O3	1.515(7)	1.317	3.931
P2-O4	1.518(5)	1.307	
P2-O4^{2}	1.518(5)	1.307	
P3-O5	1.513(7)	1.325	3.815
P3-O6	1.536(5)	1.245	
P3-O6^{11}	1.536(5)	1.245	
Zn1-O1^{8}	1.925(8)	0.55	2.13
Zn1-O4^{9}	2.080(5)	0.362	
Zn1-O4^{10}	2.080(5)	0.362	
Zn1-O6	2.018(5)	0.428	
Zn1-O6^{2}	2.018(5)	0.428	
Ba1-O2	2.927(6)	0.176	2.191
Ba1-O2^{2}	2.927(6)	0.176	
Ba1-O2^{3}	2.701(5)	0.325	
Ba1-O2^{4}	2.701(5)	0.325	
Ba1-O3	2.712(7)	0.315	

Bond Lengths	(Å)	Bond Valence	
		contributions	sum
Ba1-O5	2.908(3)	0.186	
Ba1-O5[1]	2.908(3)	0.186	
Ba1-O6	2.797(5)	0.251	
Ba1-O6[2]	2.797(5)	0.251	
Ba2-O1[5]	3.197(5)	0.085	1.809
Ba2-O1[6]	3.197(5)	0.085	
Ba2-O2[6]	2.822(5)	0.234	
Ba2-O2[7]	2.822(5)	0.234	
Ba2-O3[5]	2.946(3)	0.168	
Ba2-O3[6]	2.946(3)	0.168	
Ba2-O4	3.078(6)	0.117	
Ba2-O4[2]	3.078(6)	0.117	
Ba2-O4[6]	2.912(5)	0.184	
Ba2-O4[7]	2.912(5)	0.184	
Ba2-O5[6]	2.824(7)	0.233	

Symmetry transformations used to generate equivalent atoms. For **$CaZn(HPO3)_2$**: [1]2-x,-1/2+y,3/2-z; [2]1+x,+y,+z; [3]1-x,-y,1-z; [4]2-x,1/2+y,3/2-z; [5]-1+x,+y,+z. For **$Ba_2Zn(HPO_3)_3$**: [1]+x,1+y,+z; [2]+x,1/2-y,+z; [3]1-x,-y,1-z; [4]1-x,1/2+y,1-z; [5]1-x,1-y,-z; [6]1-x,-y,-z; [7]1-x,1/2+y,-z; [8]-1/2+x,+y,1/2-z; [9]1/2-x,-y,1/2+z; [10]1/2-x,1/2+y,1/2+z; [11]+x,-1/2-y,+z.

Table S3: Bond Angles in ° for $CaZn(HPO_3)_2$ and $Ba_2Zn(HPO_3)_3$.

Bond Angle	(°)	Bond Angle	(°)
$CaZn(HPO_3)_2$			
O3-Zn1-O6[1]	86.91(7)	O1-P1-O3	112.78(11)
O3-Zn1-O2[2]	126.75(8)	O3-P1-O2	110.97(11)
O3-Zn1-O2[3]	101.85(8)	O4-P2-O6	106.61(10)
O3-Zn1-O4	97.40(7)	O5-P2-O4	113.86(11)
O2[2]-Zn1-O6[1]	146.11(7)	O5-P2-O6	112.96(10)
O2[3]-Zn1-O6[1]	99.68(7)	P1-O3-Zn1	129.96(11)
O2[2]-Zn1-O2[3]	79.00(8)	P2-O6-Zn1[4]	120.60(10)
O2[2]-Zn1-O4	86.54(7)	Zn1[5]-O2-Zn1[3]	101.00(8)
O2[3]-Zn1-O4	160.39(7)	P1-O2-Zn1[3]	129.76(10)
O4-Zn1-O6[1]	84.98(7)	P1-O2-Zn1[5]	128.18(11)

Bond Angle	(°)	Bond Angle	(°)
O1-P1-O2	112.83(11)	P2-O4-Zn1	136.34(11)
$Ba_2Zn(HPO_3)_3$			
$O6_1$-Zn1-O6	84.9(3)	O1-P1-O2	110.8(3)
O6-Zn1-$O4^2$	90.5(2)	O1-P1-$O2^1$	110.8(3)
$O6^1$-Zn1-$O4^3$	90.5(2)	O3-P2-O4	110.2(3)
O6-Zn1-$O4^3$	156.9(2)	O3-P2-$O4^1$	110.2(3)
$O6^1$-Zn1-$O4^2$	156.9(2)	$O4^1$-P2-O4	110.9(5)
$O1^4$-Zn1-$O6^1$	108.7(2)	O5-P3-O6	109.7(3)
$O1^4$-Zn1-O6	108.7(2)	O5-P3-$O6^5$	109.7(3)
$O1^4$-Zn1-$O4^2$	94.2(3)	$O6^5$-P3-O6	114.6(4)
$O1^4$-Zn1-$O4^3$	94.2(3)	P1-O1-$Zn1^6$	150.9(6)
$O4^2$-Zn1-$O4^3$	84.9(3)	P2-O4-$Zn1^7$	133.7(4)
$O2^1$-P1-O2	110.8(5)	P3-O6-Zn1	145.6(3)

Symmetry transformations used to generate equivalent atoms. For **$CaZn(HPO3)_2$**: ^{1}2-x,-1/2+y,3/2-z; ^{2}1+x,+y,+z; ^{3}1-x,-y,1-z; ^{4}2-x,1/2+y,3/2-z; ^{5}-1+x,+y,+z. For **$Ba_2Zn(HPO_3)_3$**: ^{1}+x,1/2-y,+z; ^{2}1/2-x,-y,1/2+z; ^{3}1/2-x,1/2+y,1/2+z; ^{4}-1/2+x,+y,1/2-z; ^{5}+x,-1/2-y,+z; ^{6}1/2+x,+y,1/2-z; ^{7}1/2-x,-y,-1/2+z.

Table S4: Anisotropic Displacement Parameters ($Å^2×10^3$) for $CaZn(HPO3)_2$ and $Ba_2Zn(HPO_3)_3$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$CaZn(HPO3)_2$						
Zn1	9.29(14)	13.57(16)	10.58(15)	-2.99(12)	1.65(11)	-0.54(11)
Ca1	7.8(2)	10.4(2)	8.2(2)	0.08(18)	0.44(17)	0.22(18)
P1	9.1(3)	11.0(3)	8.3(3)	0.1(2)	-0.8(2)	-1.0(2)
P2	6.7(3)	8.8(3)	10.0(3)	-0.1(2)	-0.1(2)	0.2(2)
O1	19.4(9)	30.0(12)	8.3(9)	0.4(8)	3.0(8)	-6.7(9)
O2	13.0(8)	15.1(9)	14.1(9)	-5.4(7)	4.4(7)	-3.6(7)
O3	11.7(8)	19.8(10)	7.4(8)	-0.4(7)	-0.5(7)	2.3(7)
O4	9.5(8)	13.3(9)	17.3(10)	-6.5(7)	-1.0(7)	0.8(7)
O5	7.6(8)	13.3(9)	22.0(10)	-3.6(8)	2.6(7)	-0.4(7)
O6	9.3(8)	15.0(9)	12.0(9)	-1.5(7)	-0.4(7)	-0.2(7)
$Ba_2Zn(HPO_3)_3$						
Ba1	22.4(4)	16.4(3)	14.9(3)	0	-0.2(3)	0
Ba2	23.5(4)	19.4(3)	13.6(3)	0	-0.4(3)	0
Zn1	19.9(7)	15.7(7)	15.1(5)	0	-0.7(5)	0
P1	24.0(16)	23.9(16)	14.5(13)	0	-0.7(12)	0
P2	20.7(16)	16.1(15)	17.5(13)	0	-0.7(11)	0

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P3	21.9(17)	13.2(15)	26.8(13)	0	1.5(13)	0
O1	36(6)	149(10)	19(4)	0	14(4)	0
O2	62(5)	20(3)	41(3)	14(3)	-24(3)	-11(3)
O3	35(5)	30(4)	15(3)	0	-2(3)	0
O4	30(3)	30(3)	41(3)	-19(3)	-12(3)	6(3)
O5	23(4)	10(4)	40(4)	0	-13(4)	0
O6	22(3)	13(3)	49(3)	2(3)	-4(3)	6(2)

Table S5. State energies(eV) of lowest conduction band (LCB) and the highest valence band (HVB) of $CaZn(HPO_3)_2$ and $Ba_2Zn(HPO_3)_3$.

Formular	K-point	LCB	HVB
$CaZn(HPO_3)_2$	Z (0.0, 0.0, 0.5)	5.4052	-0.11204
	G (0.0, 0.0, 0.0)	5.20954	-0.000563004
	(0, 0.125, 0)	5.19911	0
	(0, 0.25, 0)	5.18555	-0.00453
	Y (0.0, 0.5, 0.0)	5.263	-0.06033
	A (-0.5, 0.5, 0.0)	5.7438	-0.13173
	B (-0.5, 0.0, 0.0)	5.7979	-0.03759
	D (-0.5, 0.0, 0.5)	5.79497	-0.12212
	E (-0.5, 0.5, 0.5)	5.76559	-0.15824
	C (0.0, 0.5, 0.5)	5.27145	-0.13093
$Ba_2Zn(HPO_3)_3$	G (0.0, 0.0, 0.0)	5.29109	0
	Z (0.0, 0.0, 0.5)	5.3396	-0.03615
	T (-0.5, 0.0, 0.5)	5.37882	-0.03905
	Y (-0.5, 0.0, 0.0)	5.3503	-0.00129
	S (-0.5, 0.5, 0.0)	5.51843	-0.39595
	X (0.0, 0.5, 0.0)	5.53638	-0.39141
	U (0.0, 0.5, 0.5)	5.53382	-0.39524
	R (-0.5, 0.5, 0.5)	5.53137	-0.4071

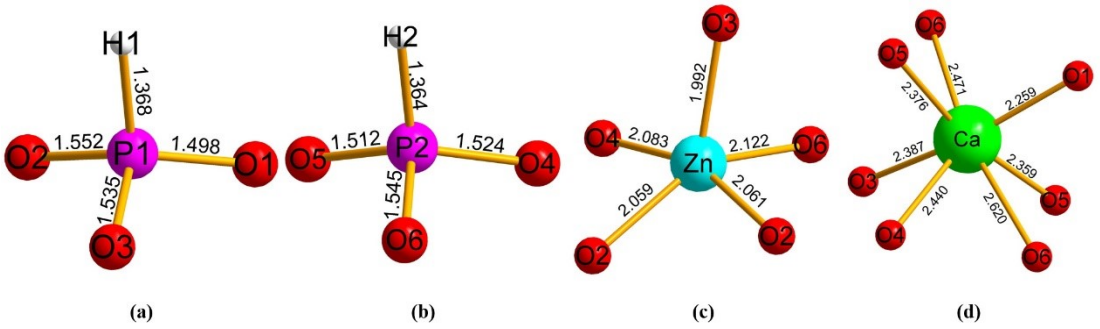

Figure S1. Coordination environments of P(1) (a), P(2) (b), Zn(c) and Ca(d) with bond lengths marked (Å) in $CaZn(HPO_3)_2$.

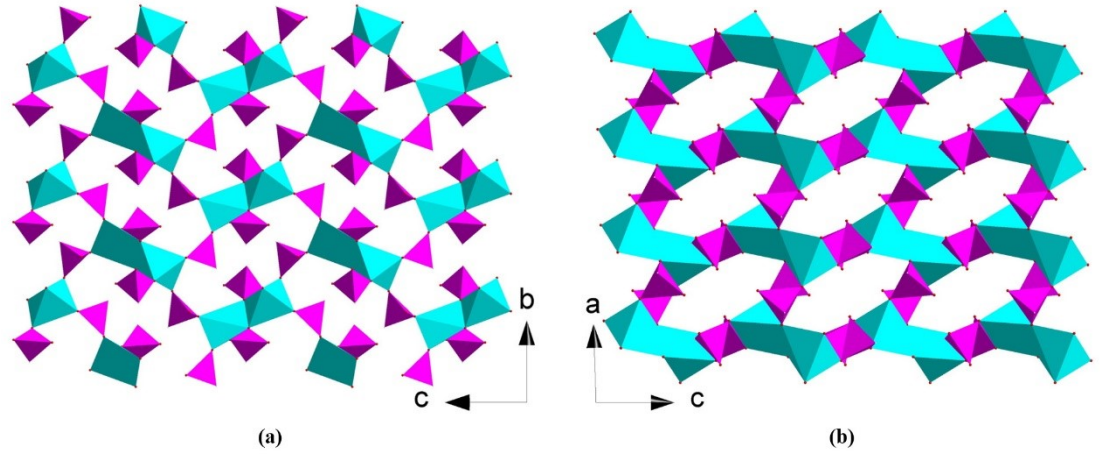

Figure S2. The 1D tunnels of anionic framework along *a*- (a) and *b*- (b) axes.

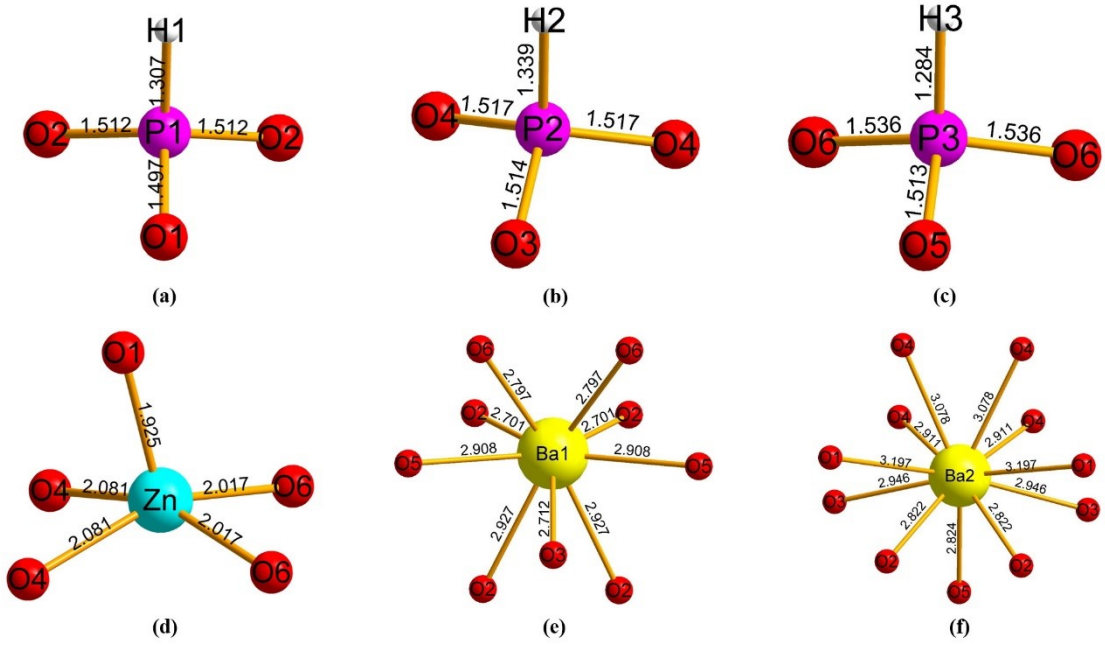

Figure S3. Coordination environments of P(1)(a), P(2)(b), P(3)(c), Zn(d), Ba(1)(e) and Ba(2)(f) with bond lengths marked (Å) in $Ba_2Zn(HPO_3)_3$.

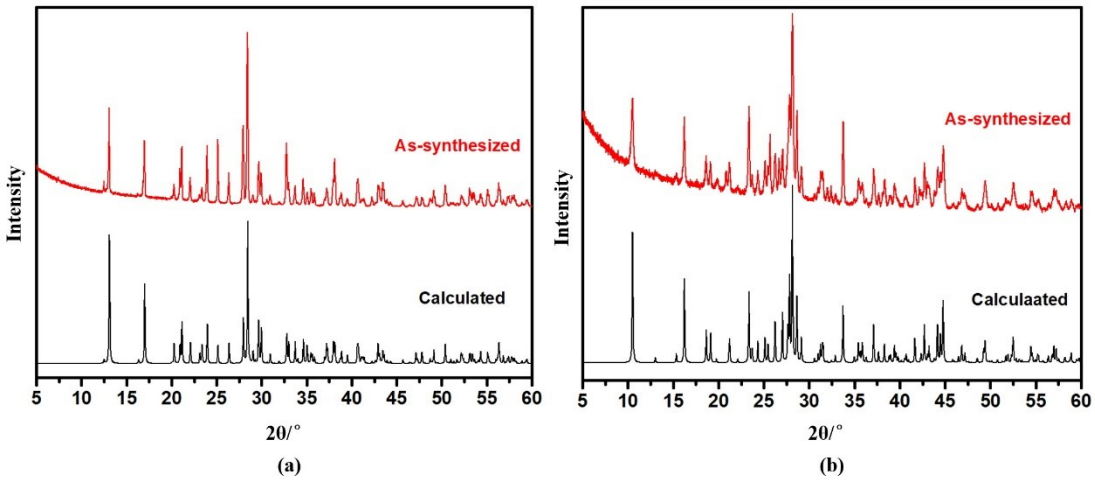

Figure S4. XRD patterns of as-synthesized $CaZn(HPO_3)_2$ (a) and $Ba_2Zn(HPO_3)_3$ (b).

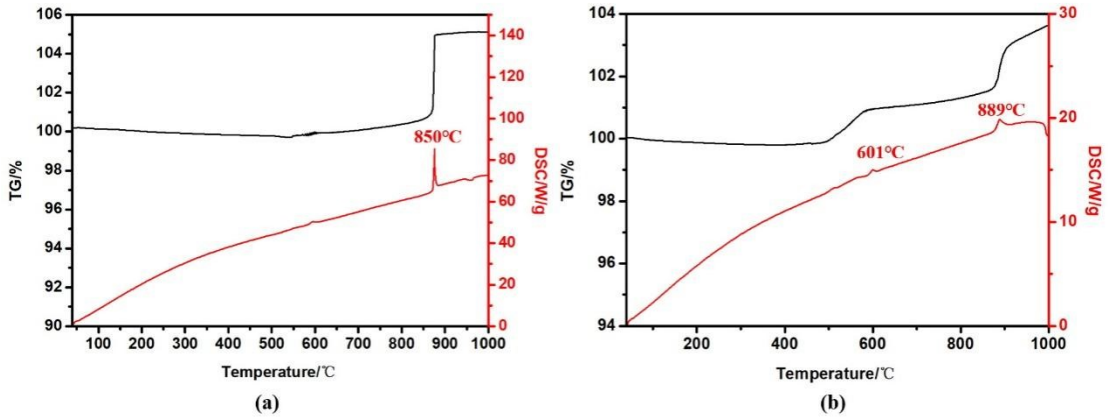

Figure S5. TG-DSC curves of $CaZn(HPO_3)_2$ (a) and $Ba_2Zn(HPO_3)_3$ (b).

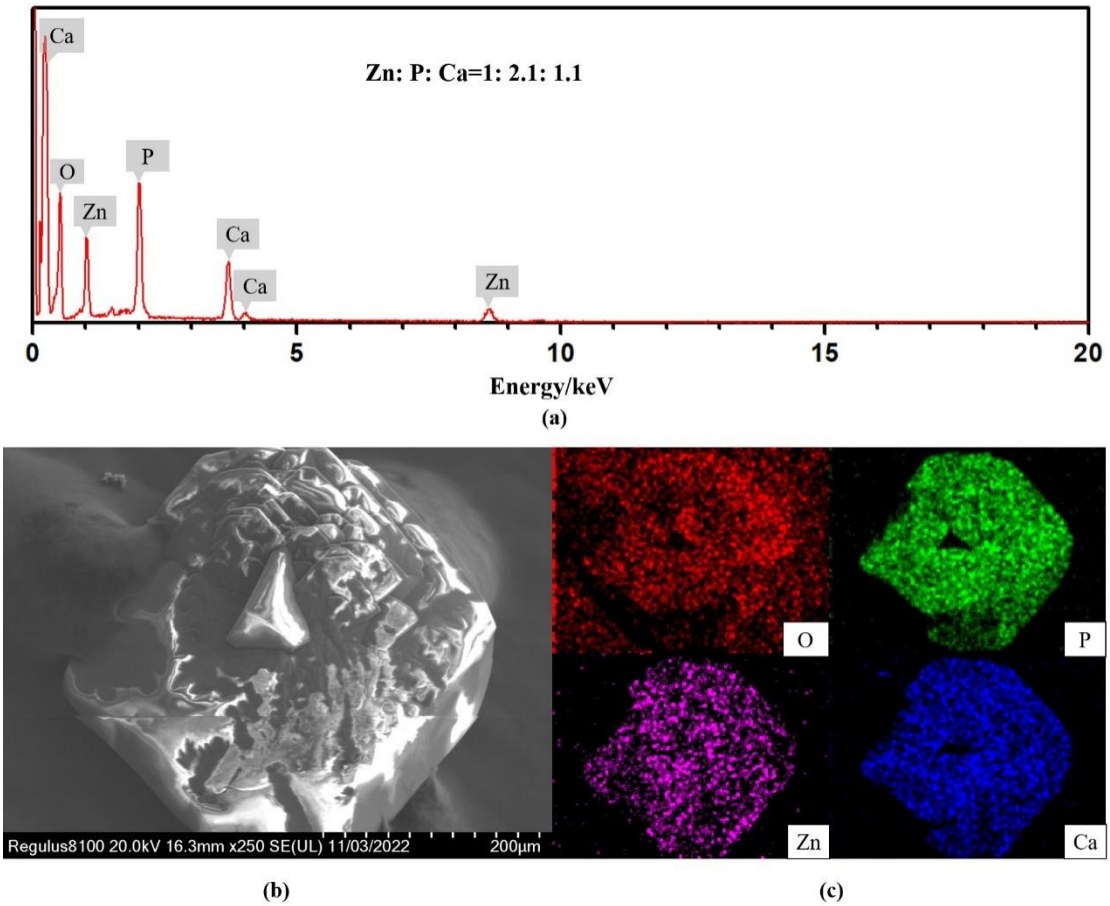

Figure S6. (a)Energy dispersive X-ray spectroscopy element analysis on single crystals of $CaZn(HPO_3)_2$ and scanning electron microscopy characterizations (b) with elemental mapping of O, P, Zn and Ca (c).

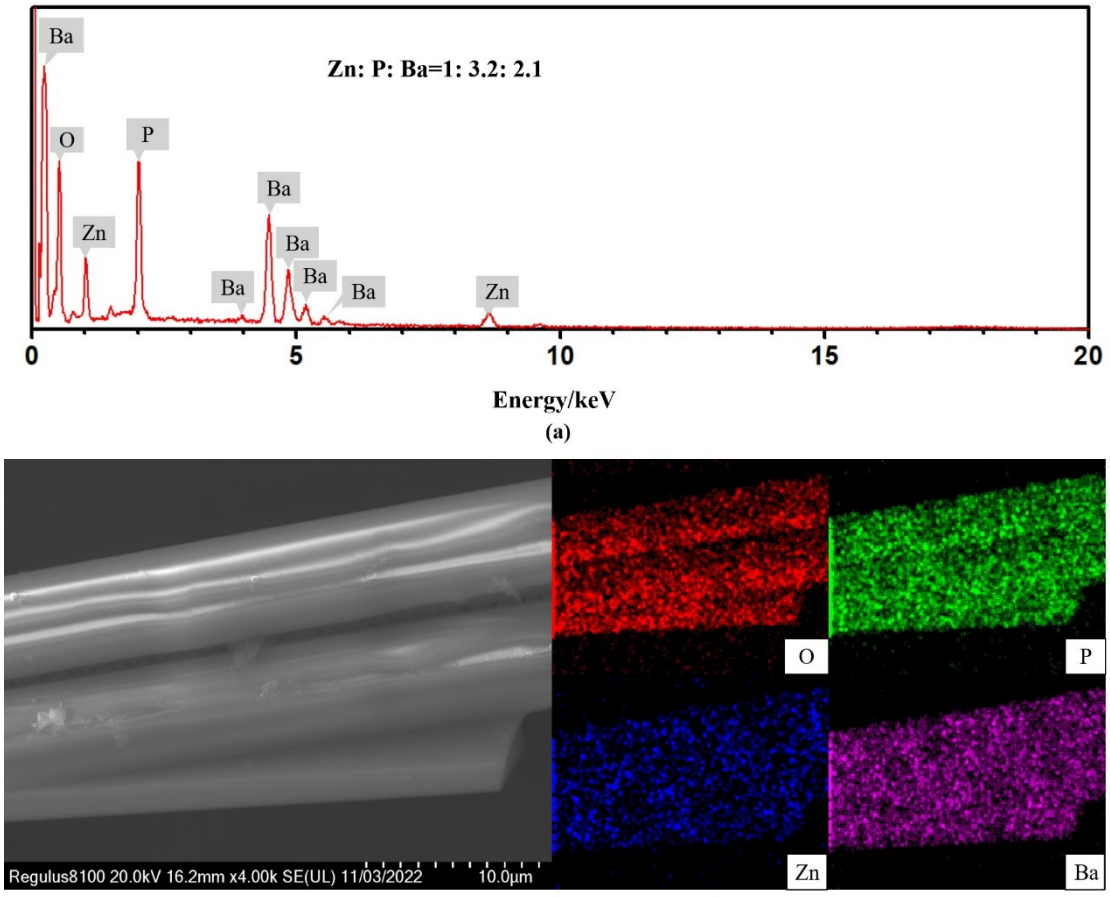

Figure S7. (a) Energy dispersive X-ray spectroscopy element analysis on single crystals of $CaZn(HPO_3)_2$ and scanning electron microscopy characterizations (b) with elemental mapping of O, P, Zn and Ba (c).

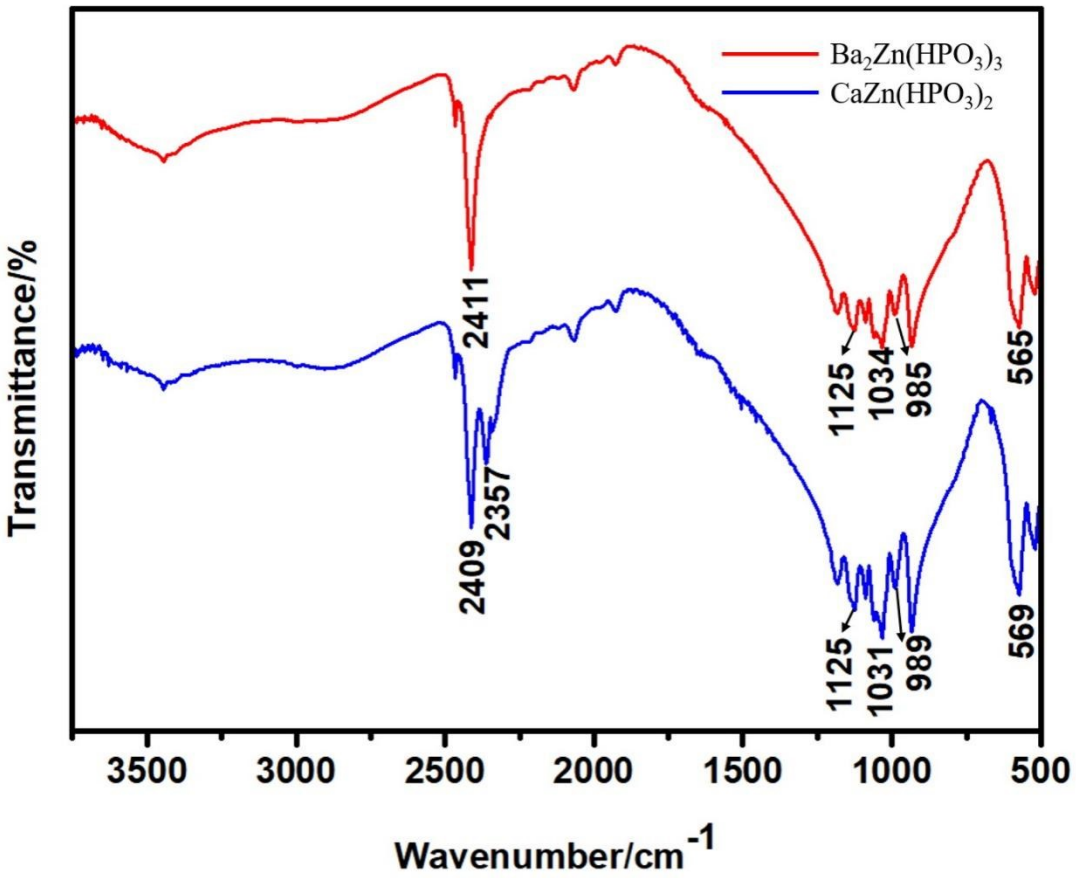

Figure S8. IR spectrum for $CaZn(HPO_3)_2$ (blue) and $Ba_2Zn(HPO_3)_3$ (red).

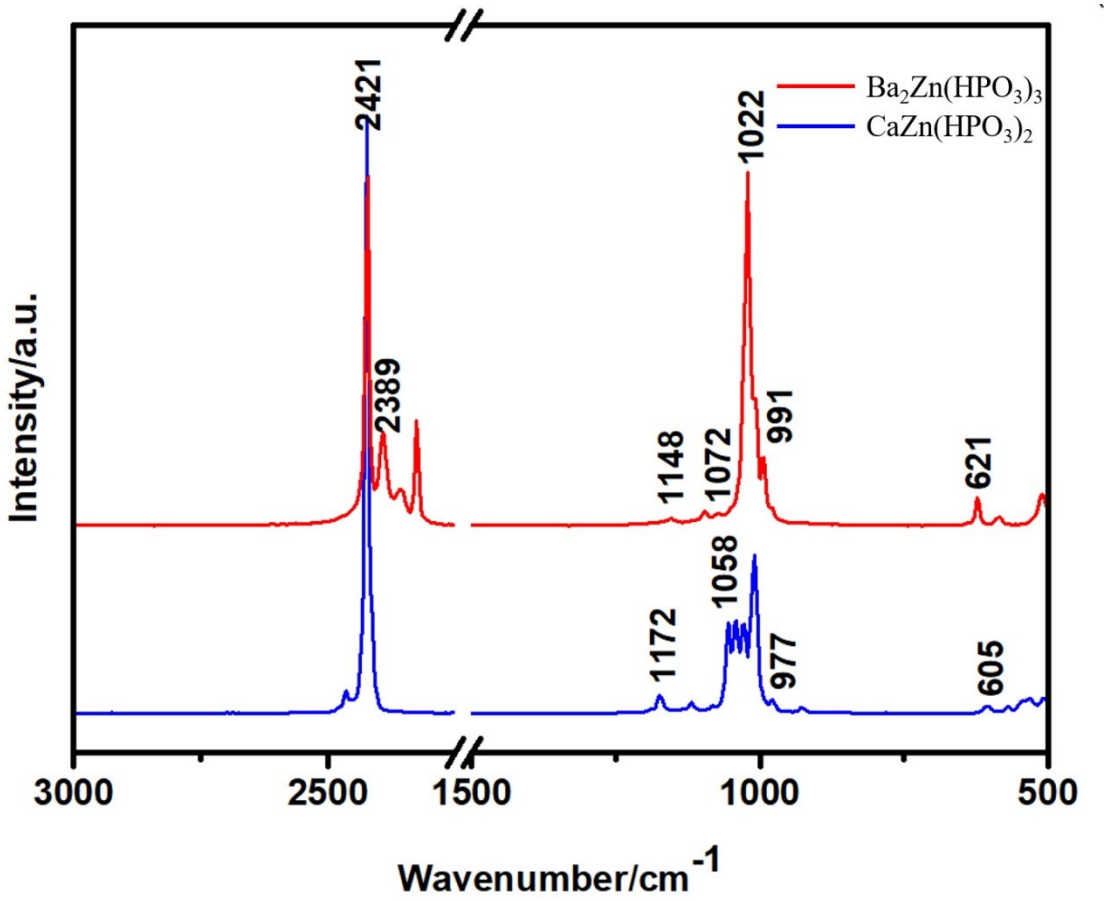

Figure S9. Raman spectrum for $CaZn(HPO_3)_2$ (blue) and $Ba_2Zn(HPO_3)_3$ (red).

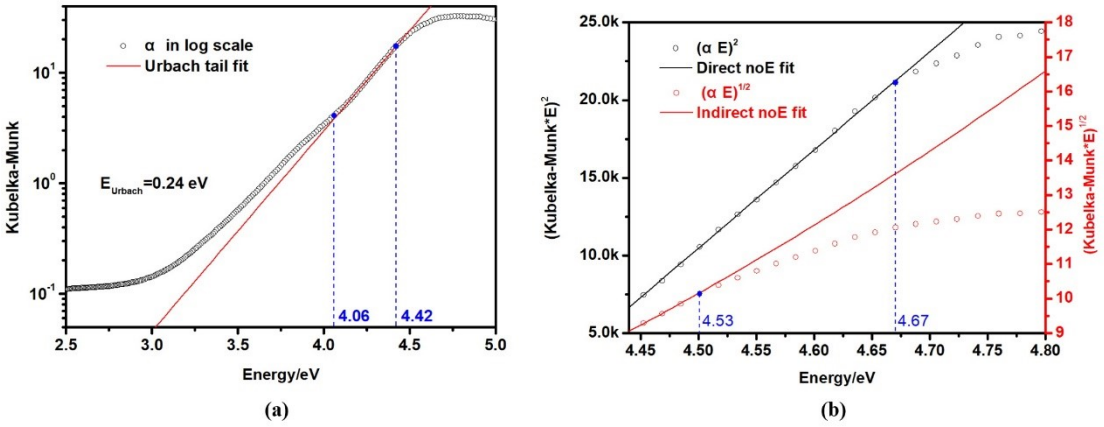

Figure S10. (a)Urbach tail fitting on a log scale KM data of $CaZn(HPO_3)_2$. (b) Direct or indirect bandgap determination by using optical energy above Urbach tail.

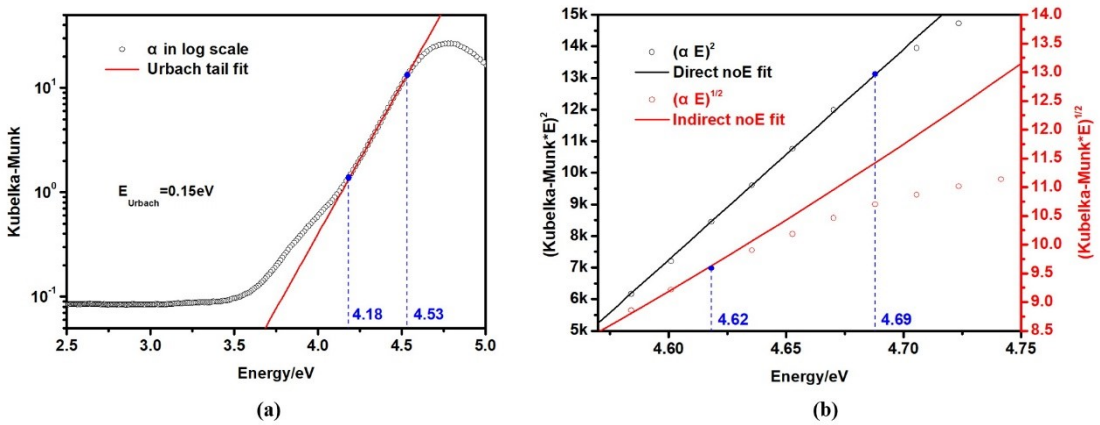

Figure S11. (a)Urbach tail fitting on a log scale KM data of $Ba_2Zn(HPO_3)_3$. (b) Direct or indirect bandgap determination by using optical energy above Urbach tail.

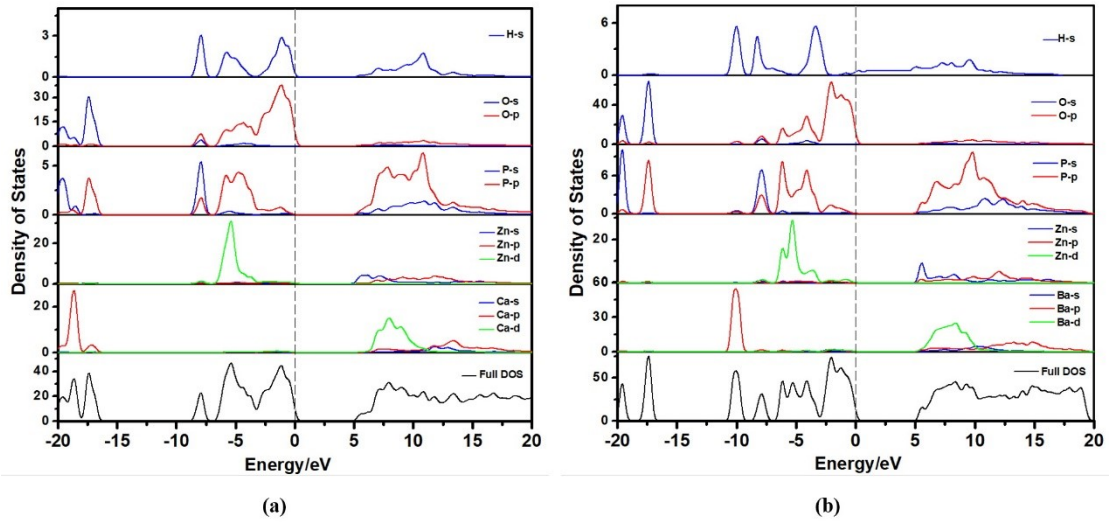

Figure S12. Total and partial DOS of states for $CaZn(HPO_3)_2$ (a) and $Ba_2Zn(HPO_3)_3$ (b); the Fermi level is normalized to 0 eV.