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Structural transformation and thermochromic behavior of Co^{2+}-doped $Zn_3(PO_4)_3.4H_2O$ hopeites

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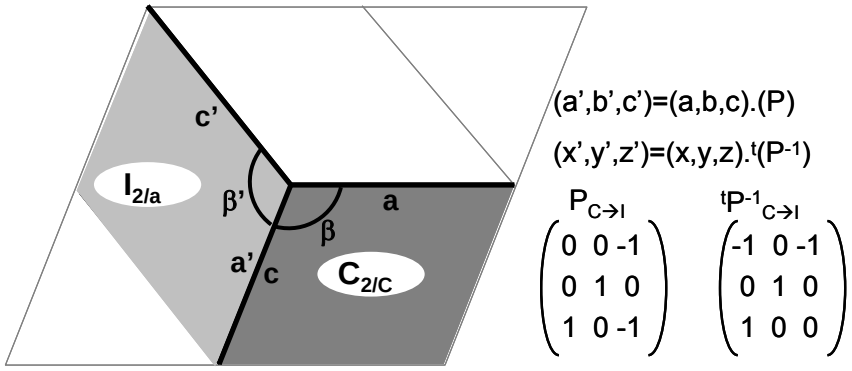

Figure S1. Cell transposition from *C2/c* to *I2/a* space groups. Pathway matrixes used for the cell parameters and the atomic positions.

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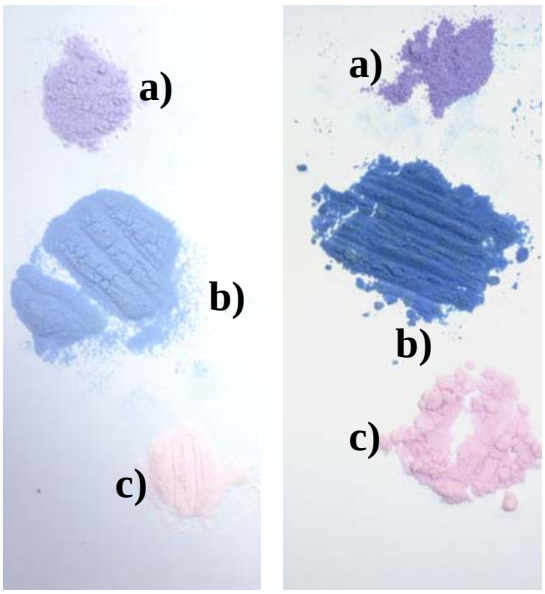

Figure S2. Photographs of HP-2% (left) and HP-9% (right) compounds after no calcination (a), calcination at 300°C (b) and calcination at 900°C (c).

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Table S1. Single crystal structure determination of $Zn_{2.74}Co_{0.26}(PO_4)_2.4H_2O$ (measured by ICP-OES)

Crystal Data	
Empirical formula	$Zn_{2.68}Co_{0.32}(PO_4)_2.4H_2O$
Formula weight	456.05 $g.mol^{-1}$
Temperature	293(2) K
Crystal system	Orthorhombic
Space group	Pbnm
a (Å)	5.0309(2)
b (Å)	10.6075(7)
c (Å)	18.3074(11)
Volume ($Å^3$)	976.98(10)
Z	4
Density (calculated)	3.101 $g.cm^{-3}$
Refinement	
Absorption coefficient	7.453 mm^{-1}
F(000)	892
Theta range for data collection	3.84 to 29.03°.
Index ranges	$-6\leq h\leq 6$, $-14\leq k\leq 14$, $-20\leq l\leq 24$
Reflections collected	7174
Independent reflections	1337 [R(int) = 0.0740]
Data / restraints / parameters	1337 / 10 / 102
Goodness-of-fit on F^2	0.995
Final R indices [$I>2\sigma(I)$]	R1 = 0.0318, wR2 = 0.0595
R indices (all data)	R1 = 0.0630, wR2 = 0.0686
Largest diff. peak and hole	1.052 and -0.759 $e.Å^{-3}$

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Table S2. Atomic coordinates and equivalent isotropic displacement parameters extracted from the single crystal refinement. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atoms	**x/a**	**y/b**	**z/c**	**Ueq(Å^2)**
Zn1	0.7925(1)	0.1428(1)	0.9993(1)	0.015(1)
Zn2	0.4288(1)	0.2370(1)	0.2500	0.017(1)
Co2	0.4288(1)	0.2370(1)	0. 2500	0.017(1)
P1	0.2746(2)	0.1028(1)	0.943(1)	0.014(1)
O1	0.1439(5)	-0.247(2)	0.782(2)	0.023(1)
O2	0.1413(5)	0.1981(2)	0.400(2)	0.018(1)
O3	0.5716(5)	0.1002(3)	0.796(2)	0.030(1)
O4	0.2154(5)	0.1401(3)	0.1725(2)	0.022(1)
O5	0.7432(7)	0.1062(4)	0.2500	0.024(1)
O6	0.1503(8)	0.3856(4)	0.2500	0.030(1)
O7	0.6650(6)	0.3362(3)	0.1691(2)	0.028(1)
H51	0.8570(100)	0.1060(60)	0.2900(20)	0.0110(30)
H61	0.1200(300)	0.4730(30)	0.2500	0.0240(80)
H62	-0.100(300)	0.3360(190)	0.2500	0.0360(120)
H71	0.5840(130)	0.4020(50)	0.1430(40)	0.0110(30)
H72	0.7400(200)	0.3270(120)	0.1220(30)	0.0220(50)

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Table S3. Anisotropic displacement parameters ($Å^2$) extracted from the single crystal refinement. The anisotropic displacement factor exponent takes the form:

$-2\pi^2[\ h^2a^{*2}U_{11} + ... + 2hka^*b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	0.014(1)	0.014(1)	0.017(1)	0.000(1)	0.001(1)	0.000(1)
Zn2	0.015(1)	0.015(1)	0.020(1)	0	0	-0.001(1)
Co2	0.015(1)	0.015(1)	0.020(1)	0	0	-0.001(1)
P1	0.014(1)	0.016(1)	0.012(1)	0.001(1)	0.001(1)	0.000(1)
O1	0.036(2)	0.015(1)	0.018(2)	-0.001(1)	0.005(1)	-0.003(1)
O2	0.016(1)	0.016(1)	0.022(2)	0.003(1)	-0.005(1)	-0.003(1)
O3	0.015(1)	0.053(2)	0.021(2)	0.009(1)	0.002(1)	0.005(1)
O4	0.019(1)	0.031(2)	0.016(2)	-0.004(1)	0.001(1)	-0.007(1)
O5	0.022(2)	0.020(2)	0.028(3)	0	0	0.001(2)
O6	0.028(2)	0.018(2)	0.043(3)	0	0	0.007(2)
O7	0.034(2)	0.024(2)	0.026(2)	0.006(1)	-0.004(1)	-0.003(1)

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Table S4. Bond distances (Å) extracted from the single crystal refinement.

Zn1-O3[a]	1.898(3)	O3[a]-Zn1-O1[b]	120.98(13)	O7[e]-Zn2-O7	86.01(16)
Zn1-O1[b]	1.919(3)	O3[a]-Zn1-O2[c]	105.01(11)	O4-P1-O3	111.45(15)
Zn1-O2[c]	1.986(3)	O1[b]-Zn1-O2[c]	110.53(11)	O4-P1-O1	109.16(15)
Zn1-O2[d]	1.995(2)	O3[a]-Zn1-O2[d]	107.20(11)	O3-P1-O1	111.82(17)
Zn2-O4[e]	2.055(3)	O1[b]-Zn1-O2[d]	108.74(11)	O4-P1-O2	110.29(16)
Zn2-O4	2.055(3)	O2[c]-Zn1-O2[d]	102.86(7)	O3-P1-O2	108.69(15)
Zn2-O5	2.104(4)	O4[e]-Zn2-O4	87.35(15)	O1-P1-O2	105.25(15)
Zn2-O6	2.110(4)	O4[e]-Zn2-O5	93.62(11)	P1-O1-Zn1[b]	130.31(17)
Zn2-O7[e]	2.171(3)	O4-Zn2-O5	93.62(11)	P1-O2-Zn1[f]	127.84(14)
Zn2-O7	2.171(3)	O4[e]-Zn2-O6	91.53(12)	P1-O2-Zn1[g]	115.08(14)
P1-O4	1.515(3)	O4-Zn2-O6	91.53(12)	P1-O3-Zn1[h]	135.15(17)
P1-O3	1.518(3)	O5-Zn2-O6	172.87(17)	P1-O4-Zn2	132.88(15)
P1-O1	1.533(3)	O4[e]-Zn2-O7[e]	93.30(11)	Zn2-O5-H51	118(4)
P1-O2	1.568(3)	O4-Zn2-O7[e]	178.28(12)	Zn2-O6-H61	149(10)
O5-H51	0.931(18)	O5-Zn2-O7[e]	84.75(11)	Zn2-O6-H62	98(10)
O6-H61	0.945(18)	O6-Zn2-O7[e]	90.05(12)	Zn2-O7-H71	118(5)
O6-H62	0.947(19)	O4[e]-Zn2-O7	178.28(12)	Zn2-O7-H72	142(7)
O7-H71	0.943(18)	O4-Zn2-O7	93.30(11)	H71-O7-H72	77(7)
O7-H72	0.941(18)	O5-Zn2-O7	84.75(11)	H61-O6-H62	113(10)
		O6-Zn2-O7	90.05(12)	Zn1[f]-O2-Zn1[g]	116.82(12)

[a]x,y,z+1 [b]-x+1,-y,-z+1 [c]x+1/2,-y+1/2,-z+1 [d]x+1,y,z+1 [e]x,y,-z+1/2 [f] x-1/2,-y+1/2,-z+1 [g]x-1,y,z-1 [h]x,y,z-1

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Table S5. Cell parameters, atomic positions for the *C2/c* cells proposed from Idler,[xx-xx] for α-$Zn_3(PO_4)_2$ and δ-$Zn_3([P/V]O_4)_2$ and for the *I2/a* cell for δ-$Zn_3([P/V]O_4)_2$ after transposition.

α-$Zn_3(PO_4)_2$			
Space-group	***C 1 2/c 1*** (15)		
Cell parameters	a=8.14 Å b=5.63 Å c=15.04 Å β=108.13°		
Cell ratio	a/b=1.4458 b/c=0.3743 c/a=1.8477		
Cell volume	655.04 Å^3		
Atom position	*x/a*	*y/b*	*z/c*
Zn1	0	0.7448	1/4
Zn2	0.2678	0.5548	0.0675
P1	0.1592	0.0634	0.1286
O1	0.2929	0.0607	0.2211
O2	0.1197	0.3092	0.0770
O3	0.2129	0.9021	0.0625
O4	0.9935	0.9676	0.1429
δ-$Zn_3([P/V]O_4)_2$			
Space-group	***C 1 2/c 1*** (15)		
Cell parameters	a=15.941Å b=5.314 Å c=8.265 Å β=106.96°		
Cell ratio	a/b=2.9998 b/c=0.6430 c/a=0.5185		
Cell volume	669.68 Å^3		
Atom position	*x/a*	*y/b*	*z/c*
Zn1	0	0.0587	3/4
Zn2	0.18558	0.7929	0.7137
P1	0.1209	0.292	0.5294
O1	0.1209	0.292	0.5294
O2	0.6021	0.672	0.3456
O3	0.6491	0.931	0.0253
O4	0.4601	0.747	0.9089
δ-$Zn_3([P/V]O_4)_3$			
Space-group	***I 1 2/a 1*** (15)		
Cell parameters	a=8.265 Å b=5.314 Å c=15.757 Å β=104.612°		
Cell ratio	a/b=1.5553 b/c=0.3372 c/a=1.9065		
Cell volume	669.67 Å^3		
Atom position	*x/a*	*y/b*	*z/c*
Zn2	0.7210	0.7929	0.4356
Zn1	0	0.5587	1/4
P1	0.3415	0.608	0.3709
O1	0.1988	0.747	0.7899
O2	0.8738	0.669	0.3991
O3	0.5065	0.828	0.3511
O4	0.8031	0.138	0.4536