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Synthesis and Structural Study of a Novel Mixed Phosphate: $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$

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Abstract

Single crystals of the new phosphate $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ were successfully grown hydrothermally and structurally determined by single crystal X-ray diffraction data. This new phase is isotypic with the Hopeite and crystallizes in the orthorhombic space group *Pnma* with the cell parameters a = 10.6592(9) Å, b = 18.408(2) Å and c = 5.0565(4) Å. This crystal structure contains seven independent fully occupied cationic sites. The first six, that is located in 4c (.m.) Wycokoff positions, accommodate Cd(1)/Zn(1), four sites are filled by Zn(2) and three hydrogen, while the remaining site is entirely occupied by one P atom. This crystal structure can be described in terms of a net framework built up from a slightly distorted $(Cd(1)/Zn(1))O_2(OH_2)_4$ octahedra and regular $Zn(2)O_4/PO_4$ tetrahedra units. In the structure, two $Zn_2(2)O_7$ dimers are held together by means of PO_4 groups in such way to form zigzag chains of corner-sharing. Adjacent chains are connected with the apical corners resulting in a complex layer of three- and four-membered sequential rings extending along [001]. The stacked layers are bridged by $(Cd(1)/Zn(1))O_2(OH_2)_4$ octahedra that stabilizes the structure.

Keywords

Hydrothermal synthesis, X-ray diffraction, Phosphate, Crystal structure

Introduction

Over the past decades, several transition metal phosphates have been widely synthesized and structurally investigated [1]. Among these phases are those with open structures that offer a considerable number of interesting geometries resulting in valuable physical properties [2]. In such compounds, the presence of orthophosphate groups stabilizes various cationic oxidation states and coordination numbers, providing a high level of stability for the anionic building units [3]. Furthermore, due to their flexibility, these structures allow a wide range of metal substitutions leading to outstanding behaviors. For instance, gradually increasing of Metal/P ratio leads to denser and more rigid structures (e.g., CAS, ABW, BIK, and ANA zeotypes families) [4] and improves the capacity, lifetime, and throughput capability of $Li_{0.98}Al_{0.02}FePO_4/C$ mixed cathode [5]. In addition, one interesting approach for developing new nonlinear optical materials is the inclusion of specific d^{10} transition metal cations, such as Zn^{2+} and Cd^{2+}, that are sensitive to high polarization into metal phosphate matrix. These ions can also exhibit a number of coordination polyhedra, like ZnO_n (n = 4, 5, and 6) and CdO_m (m = 6, 7, and 8), that will offer options for predicting and designing new open frameworks. Net frameworks comprising interstitial voids are of considerable interest particularly in phosphate-based divalent cations, due to their promising applications in different fields such oxygen electrocatalysis [7], luminescence [8], anticorrosive pigments [9], biomedical sector [10], ceramics [11], lithium-ion

batteries [12], and automotive industry [13]. In the course of our research, we were able to synthesize and structurally characterize several hydrated phosphates based on transition metals, namely $Co_{2.39}Cu_{0.61}(PO_4)_2.H_2O$ [14], $Co_2Pb(HPO_4)(PO_4)OH.H_2O$ [15], $Mn_2Zn(PO_4)_2.H_2O$ [16], $Ni_2Sr(PO_4)_2.2H_2O$ [17] and $Mg_{1-x}Cu_x(PO_4)_2.H_2O$ where (x = 1.26 [18] or 1.35 [19]). The present paper reports the hydrothermal synthesis and structural study using single-crystal X-ray diffraction of the novel phosphate $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ belonging to the Hopeite family.

Experimentation

Single crystals of $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ were provided hydrothermally using an optimal reaction mixture of $Cd(NO_3)_2.4H_2O$, ZnO, and H_3PO_4 (85% by weight), adjusted in agreement with the molar ratios of Cd:Zn:P = 1:3:3. The hydrothermal process was carried out over two days at 473 K in a suitable autoclave reactor using a 23 ml PTFE-lined container that was only halfway filled with deionized water. The reaction mixture was filtered, washed with distillate water, and air dried at room temperature. The colorless crystals obtained in parallelepiped shape correspond to this newly formed phase. The structure is determined at nanometric scale.

Results and Discussion

Structure determination

To collect X-ray diffraction data, a proper single crystal was picked using a polarizing microscope and mounted on a Bruker X8 APEX-II diffractometer. The observed data were gathered at 296 K utilizing the X-ray Mokα radiation (λ = 0.71073 Å) and the φ-ω scanning procedure on the whole sphere of reciprocal space. Integration, scaling, filtering, reflections merging, and correction of Lorentz-polarisation effects were carried out with the SAINT program [20]. Supplementary empirical absorption corrections using the SADABS program were also undertaken [21]. At this stage a total of 13878 intensities, of which 2418 are independent and 2049 meets the I > 2(I) condition were obtained successfully. The structural elucidation of the title phosphate was carried out using the WinGX suite [22]. The current crystal structure was solved by Direct Methods with the SHELXT 2014/7 program [23] and then refined by SHELXL2018/3 program [24]. As a result of the structural resolution the Zn, Co, and P atoms were located first in the asymmetric unit, while the remaining oxygen and hydrogen atoms were positioned after numerous repetitive refinements and Fourier-difference analysis. During the refinement, hydrogen atoms were introduced in a riding model, with $U_{iso}(H)$ fixed at 1.5 $U_{iso}(O)$ and O-H bond length limited to 0.82 Å. The anisotropic and isotropic refinements carried out on the H and non-hydrogen atom coordinates, respectively lead to the given structural model. The last refining cycle yields the following residual electron densities $\Delta\rho_{min}$ = -0.81 e.Å^{-3} at 0.41 Å from H7B and $\Delta\rho_{max}$ = 0.72 e.Å^{-3} at 0.65 Å from Zn1. Table 1 contains the crystal characteristics, data collection, and structural refinement results.

Atomic positions and their corresponding displacement parameters are reported in table 2 and table 3. The number of inter-atomic bond lengths and bond valence sum (BVS) are given in table 4 and the number characteristics of the hydrogen bond are given in table 5. Structural representations were done using Vesta-3 [25] and Ortep-3 [26].

Table 1: Crystal details, X-ray data collecting, and structural refinement results for $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$.

Crystal details	
Chemical formula	$Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$
M_r	481.63
System, space group	Orthorhombic, *Pnma*
T (K)	296
a, *b*, *c* (Å)	10.6592 (9), 18.408 (2), 5.0565 (4)
V (Å^3)	992.2 (2)
Z	4
Mo Kα	λ = 0.71073 Å
μ (mm^{-1})	7.44
Data acquisition	
θ_{min}, θ_{max} (°)	3.8, 36.2
Miller indices	-16 ≤ h ≤ 17, -29 ≤ k ≤ 29, -8 ≤ l ≤ 8
Measured reflections	13878
Independent reflections	2418
Reflections with $I > 2\sigma(I)$	2049
R_{int}	0.037
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.832
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.024, 0.056, 1.06
Number of variables	82
$\Delta\rho_{max/min}$ (e Å^{-3})	0.72, -0.81

Crystal structure description

T'This new phosphate's crystal structure may be defined as a net framework made up of significantly deformed (Cd(1)/Zn(1))$O_2(H_2O)_4$ octahedra and two regular Zn(2)O_4 and P(1)O_4 tetrahedra (Figure 1).

In the structure, Zn(2)O_4 units are held together by means of the connecting PO_4 groups in a manner as to create zigzag chains of corner-sharing. Adjacent chains are connected with

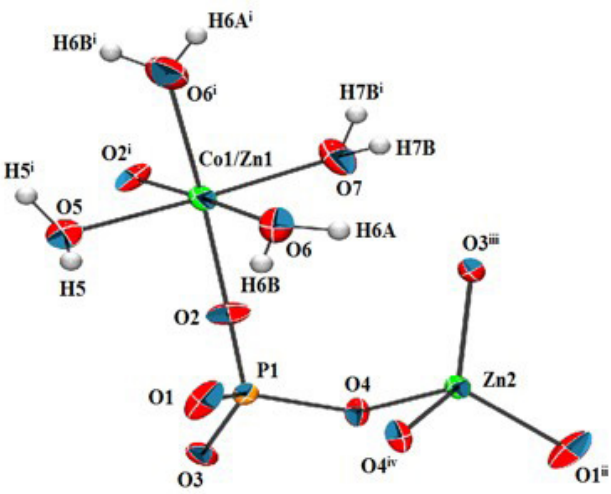

Figure 1: Polyhedral arrangement in $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$. Displacement ellipsoids were plotted with a 50% probability.

Table 2: Atomic positions and isotropic or equivalent thermal parameters (Å²) in $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$.

Atom	Site	*x*	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cd1	4c	0.74199 (2)	0.250000	0.06018 (4)	0.01788 (5)	0.5
Zn1	4c	0.74199 (2)	0.250000	0.06018 (4)	0.01788 (5)	0.5
Zn2	8d	0.85628 (2)	0.49930 (2)	0.20851 (4)	0.01380 (5)	
P1	8d	0.60241 (4)	0.40739 (2)	0.22589 (8)	0.01312 (8)	
O1	8d	0.6005 (2)	0.42161 (8)	-0.0695 (2)	0.0300 (3)	
O2	8d	0.6391 (2)	0.32968 (8)	0.2856 (3)	0.0241 (3)	
O3	8d	0.4749 (2)	0.42295 (7)	0.3548 (3)	0.0223 (3)	
O4	8d	0.6973 (2)	0.46105 (7)	0.3593 (2)	0.0176 (2)	
O5	4c	0.6055 (2)	0.250000	-0.2601 (4)	0.0239 (4)	
H5	8d	0.609538	0.285875	-0.355887	0.036*	
O6	8d	0.8416 (2)	0.33439 (9)	-0.1831 (4)	0.0350 (4)	
H6A	8d	0.895348	0.359095	-0.109756	0.053*	
H6B	8d	0.808139	0.366201	-0.272047	0.053*	
O7	4c	0.8929 (2)	0.250000	0.3517 (5)	0.0349 (5)	
H7B	8d	0.957906	0.268204	0.295741	0.052*	

Table 3: Atomic displacement parameters (Å²) in $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01534 (9)	0.0228 (2)	0.01555 (9)	0.000	0.00001 (7)	0.000
Zn1	0.01534 (9)	0.0228 (2)	0.01555 (9)	0.000	0.00001 (7)	0.000
Zn2	0.01250 (9)	0.0179 (2)	0.01104 (8)	-0.00018 (6)	-0.00029 (6)	-0.00093 (6)
P1	0.0162 (2)	0.0121 (2)	0.0112 (2)	-0.0013 (2)	-0.0002 (2)	0.0016 (2)
O1	0.058 (2)	0.0208 (7)	0.0118 (5)	-0.0113 (6)	-0.0064 (6)	0.0036 (4)
O2	0.0354 (7)	0.0158 (6)	0.0210 (6)	0.0068 (5)	0.0085 (5)	0.0049 (4)
O3	0.0128 (5)	0.0193 (6)	0.0346 (7)	0.0003 (4)	0.0016 (5)	0.0066 (5)
O4	0.0144 (5)	0.0244 (6)	0.0139 (5)	-0.0052 (4)	0.0023 (4)	-0.0039 (4)
O5	0.0258 (9)	0.025 (1)	0.0210 (9)	0.000	0.0022 (7)	0.000
O6	0.0274 (7)	0.0320 (8)	0.046 (2)	-0.0047 (6)	-0.0041 (7)	-0.0077 (7)
O7	0.0208 (9)	0.054 (2)	0.03 (2)	0.000	0.0003 (8)	0.000

Table 4: Selection of bond lengths and cationic bond valence sum in the crystal structure of $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$.

Bond	Length (Å)	Bond	Length (Å)
Cd1/Zn1—O2	2.157 (2)	Zn2—O4	1.987 (2)
Cd1/Zn1—O2	2.157(2)	Zn2—O4	1.994 (2)
Cd1/Zn1—O5	2.177 (2)	**<Zn2—O> = 1.9484 Å**	
Cd1/Zn1—O7	2.182 (2)	**BVS(Zn2) = 2.08 v.u**	
Cd1/Zn1—O6	2.248 (2)	P1—O2	1.514 (2)
Cd1/Zn1—O6	2.248 (2)	P1—O1	1.516 (2)
<Cd1/Zn1—O> = 2.1948 Å		P1—O3	1.535 (2)
BVS(Cd1/Zn1) = 2.17 v.u		P1—O4	1.567 (2)
Zn2—O1	1.895 (2)	**<P1—O> = 1.5329 Å**	
Zn2—O3	1.917 (2)	**BVS(P1) = 5.02 v.u**	

Table 5: Hydrogen-bonding geometry in $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ crystal structure.

D—H···*A* (°)	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O5—H5···O1	0.82	2.89	3.3033 (16)	114
O5—H5···O2	0.82	2.01	2.749 (2)	150
O5—H5···O3	0.82	3.25	3.9833 (17)	150
O6—H6*A*···O1	0.82	2.96	3.429 (2)	119
O6—H6*A*···O2	0.82	3.12	3.756 (2)	136
O6—H6*A*···O3	0.82	1.94	2.726 (2)	160
O6—H6*B*···O1	0.82	2.64	3.085 (2)	115
O6—H6*B*···O2	0.82	2.95	3.447 (2)	121
O6—H6*B*···O4	0.82	2.81	3.627 (2)	172
O6—H6*B*···O4	0.82	3.25	3.794 (2)	127
O7—H7*B*···O2	0.82	2.28	3.086 (2)	169
O7—H7*B*···O2	0.82	2.67	3.086 (2)	113
O7—H7*B*···O3	0.82	2.95	3.4623 (16)	122

the apical corners resulting in a complex layer of three- and four-membered sequential rings running parallel to [001] (Figure 2). The stacked layers are bridged by (Cd(1)/Zn(1)) $O_2(OH_2)_4$ octahedra that stabilizes the structure by means of two oxygen atoms positioned in cis- configuration. The existence of water molecules in the resulting interstitial space also enhances cohesiveness between the neighboring layers through the hydrogen bonds (Figure 3).

Conclusion

Single crystals of $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ were successfully obtained hydrothermally and their structure was established by single crystal X-ray diffraction analysis. This newly identified phase is isotypic with Hopeite and crystallizes in the orthorhombic space group Pnma with cell parameters

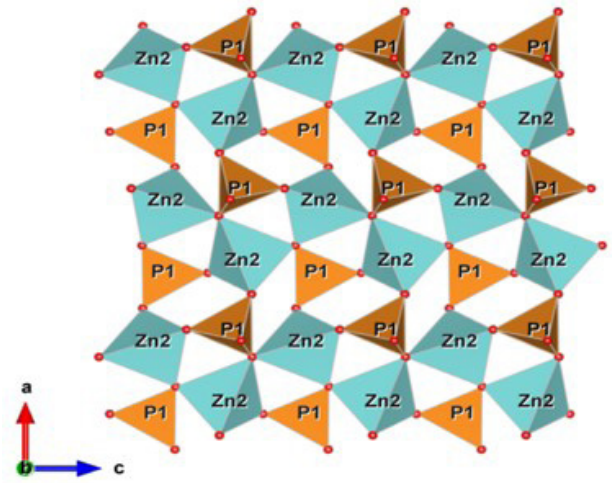

Figure 2: A perpendicular layer to [010] resulting from the corner junction between the $Zn(2)O_4$ and $P(1)O_4$ tetrahedra.

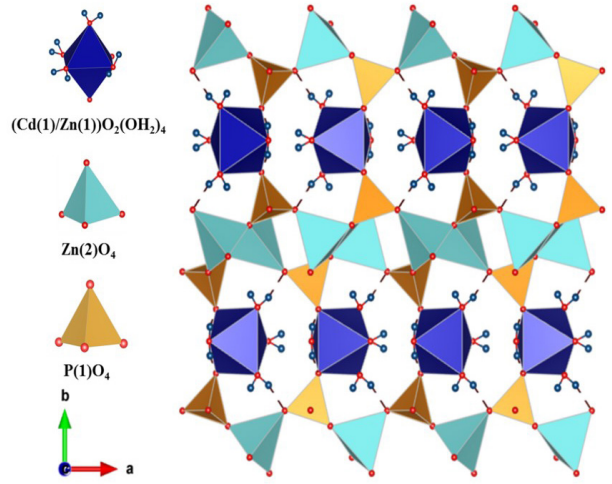

Figure 3: Projection of the $Cd_{0.5}Zn_{2.5}(PO_4)_2.4H_2O$ crystal structure along the c-axis.

a = 10.6592(9) Å, b = 18.408(2) Å, and c = 5.0565(4) Å. The crystal structure of this phase is describable in terms of a net framework made up of slightly distorted $(Cd(1)/Zn(1))O_2(OH_2)_4$ octahedra and two regular $Zn(2)O_4/PO_4$ tetrahedra units. In the structure, $Zn(2)O_4$ groups are linked to each other by means of PO_4 units to form zigzag chains by corner-sharing. Neighboring chains are connected by apical corners, yielding a complex layer of three- and four-membered consecutive rings running along [001]. The Stacking layers are bounded by $(Cd(1)/Zn(1))O_2(OH_2)_4$ octahedra that stabilize the structure.

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Conflict of Interest

None.

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