

Characterization of δ -KZnPO₄ by X-ray powder diffractionPeter G. Self , and Mark D. Raven ^{a)}

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The structural parameters of a second low-temperature form of KZnPO₄ have been refined using Rietveld analysis of X-ray powder diffraction (XRPD) data. This form of KZnPO₄ is isostructural with NH₄ZnPO₄I and has previously been denoted as KZnPO₄II. This article uses the notation δ -KZnPO₄, to be consistent with the α , β , and γ notation commonly used for other KZnPO₄ phases. © The Author(s), 2021. Published by Cambridge University Press on behalf of International Centre for Diffraction Data. [doi:10.1017/S0885715621000427]

Key words: δ -KZnPO₄, KZnPO₄II, structure refinement, XRPD, NH₄ZnPO₄I, synthesis

I. INTRODUCTION

Three forms of the stoichiometric compound KZnPO₄ have been well characterized. These forms are generally labeled α , β , and γ . The α form is stable up to a temperature of 691 °C (Wallez *et al.*, 1999) and has a hexagonal crystal structure (space group *P6₃*) (Andratschke *et al.*, 1992). The β and γ forms are high-temperature phases that have orthorhombic crystal structures (space groups *Pna2₁* and *Pnma*, respectively) (Wallez *et al.*, 1999). A second room temperature form of KZnPO₄ is known to exist but has not been well characterized. This second form was first reported by Barbou des Courières and Simonot-Grange (1979) as a transformation product of KZn₂H(PO₄)₂(H₂O)_{2.5} in slightly alkaline aqueous KCl solutions. Barbou des Courières and Simonot-Grange (1979) used the notation KZnPO₄II for this second room temperature variant while using the notation KZnPO₄I for α -KZnPO₄. Barbou des Courières and Simonot-Grange (1979) noted that the X-ray diffraction (XRD) powder pattern of KZnPO₄II is similar to the XRD powder pattern of NH₄ZnPO₄I, the monoclinic form of NH₄ZnPO₄ (Averbuch-Pouchot and Durif, 1968). Barbou des Courières and Simonot-Grange (1979) showed that KZnPO₄II is one end member of the isostructural series K_x(NH₄)_{1-x}ZnPO₄ with NH₄ZnPO₄I being the other end member.

The aim of our study is to characterize KZnPO₄II using XRD and Rietveld refinement (Rietveld, 1967). Rather than use the notation KZnPO₄II, the notation δ -KZnPO₄ will be used in this article so as to be more consistent with the more widely used α , β , and γ notation for KZnPO₄ phases.

II. EXPERIMENTAL

A. Synthesis of δ -KZnPO₄

According to studies by Frazier *et al.* (1966) and Barbou des Courières and Simonot-Grange (1979), the form of potassium zinc phosphate that precipitates from aqueous solutions of potassium phosphates and zinc salts is dependent on the

pH of the solution. In solutions with a pH of around 4 or less, KZn₂H(PO₄)₂(H₂O)_{2.5} forms. If left in solution, this phase slowly dehydrates in solution to the anhydrous form. At pH values between 5 and 7, α -KZnPO₄ forms. At pH values of 7 and above, δ -KZnPO₄ forms. Consequently, methods for synthesizing δ -KZnPO₄ begin with an aqueous solution of the weak base K₂HPO₄. For the present study, two methods of synthesizing δ -KZnPO₄ were used.

The first synthesis method is the method of Salutsky and Steiger (1964). For this method, 92 g of K₂HPO₄(H₂O)₃ was dissolved in 200 ml of high-purity water held at a temperature of 70 °C. The beaker of K₂HPO₄ solution was transferred to a water bath set to a temperature of 65 °C. A second solution consisting of 3.5 g of ZnCl₂ in 100 ml of high-purity water was slowly added and stirred into the K₂HPO₄ solution. The beaker of combined solution was left in the water bath (65 °C) for 3 days. The precipitated material in the solution was recovered using centrifugation and then washed three times using high-purity water. The washed precipitate was dried overnight in air at room temperature (approximately 20 °C). In order for this method of synthesis to produce a pure δ -KZnPO₄ product, the amount of K₂HPO₄ used must be sufficiently high to maintain the solution at a pH of 7 or higher when the ZnCl₂ solution is added and the potassium zinc phosphate phase precipitates. If insufficient K₂HPO₄ is used or too much ZnCl₂ is used, the solution pH will drop below 7 and the precipitated material will be α -KZnPO₄ or a mixture of α -KZnPO₄ and δ -KZnPO₄.

The second synthesis method follows the method of Barbou des Courières and Simonot-Grange (1979) and uses KOH to control the pH of the solution and allows smaller amounts of K₂HPO₄ and larger amounts of ZnCl₂ to be used relative to the method of Salutsky and Steiger (1964). For the second method of synthesis, 13.0 g of K₂HPO₄(H₂O)₃ and 10.0 g of KCl were dissolved in 500 ml of high-purity water. A second solution consisting of 5.0 g of ZnCl₂ in high-purity water was slowly added to the K₂HPO₄/KCl solution while stirring. The pH of the mixture was immediately adjusted to 8.5 by the drop-wise addition of 1M KOH solution. Over the following 2 h, the pH of the mixture was monitored and the solution pH maintained close to 8.5 by the addition of drops of 1M KOH solution

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as required. The mixture was left stirring for 3 days at room temperature after which time the precipitate was recovered as per the first synthesis method. It was found that the concentration of the K_2HPO_4/KCl solution was not critical and less than 500 ml of water could be used in preparing this solution. However, if too little water was used (approximately 200 ml), the addition of the $ZnCl_2$ solution to the K_2HPO_4/KCl solution caused the solution to gel.

B. XRD data collection and structure refinement

XRD powder patterns were recorded with a PANalytical X'Pert Pro multi-purpose diffractometer using Fe filtered $CoK\alpha$ radiation (40 kV, 55 mA), automatic divergence slit, fixed illuminated area, 2° anti-scatter slit, and a fast X'Celerator Si strip detector. For structure refinement, an XRD powder pattern was recorded from 4° to $80^\circ 2\theta$ with a recording interval of $0.017^\circ 2\theta$ and an overall counting time of a little over 9 h. Structure refinement was carried out on the $CoK\alpha$ radiation data using the TOPAS version 5 software suite from Bruker-AXS. A Rigaku SmartLab diffractometer was used to collect powder patterns using $CuK\alpha$ radiation (40 kV, 200 mA), fixed 2° divergence slit, 0.01° step size, and a D/tex Ultra 250 Si strip detector.

Elemental concentrations of samples were determined using a PANalytical Axios, wavelength-dispersive, X-ray fluorescence (XRF) spectrometer in conjunction with the PANalytical SuperQ software package. For XRF analysis AR-grade ZnO , KH_2PO_4 and a mixture of ZnO and KH_2PO_4 were used to check the calibration of the XRF software for the elements K, Zn, and P.

III. RESULTS AND DISCUSSION

Multiple batches of potassium zinc phosphate were made using the two synthesis methods. XRD showed that the precipitates produced were the same as the material called $KZnPO_4II$ by Barbou des Courières and Simonot-Grange (1979). Furthermore, XRF analysis showed that the composition of the precipitates to be consistent with the formula $KZnPO_4$. Both synthesis methods were found to be equally effective in producing pure δ - $KZnPO_4$ although in one of the batches made using the synthesis method based on the method of Barbou des Courières and Simonot-Grange (1979), a significant amount of $KZnPO_4(H_2O)_{0.8}$ (Broach *et al.*, 1999) was formed along with δ - $KZnPO_4$. Both synthesis methods have a recovery rate of close to 100% based on the amount of $ZnCl_2$ used.

Based on the observed peak widths from the X-ray powder diffraction (XRPD) data of the synthesized materials, the synthesis method based on the method of Barbou des Courières and Simonot-Grange (1979), in general terms, gave δ - $KZnPO_4$ material with slightly higher crystallinity than the method of Salutsky and Steiger (1964) and so δ - $KZnPO_4$ synthesized using the former method was used for structure refinement. An attempt was made to improve the crystallinity of the δ - $KZnPO_4$ by heating the synthesized material at a range of temperatures. Heating did not significantly improve the crystallinity of the synthesized material, but it was found that after heating for 12 h at $350^\circ C$, the δ - $KZnPO_4$ had partially converted to α - $KZnPO_4$. Heating

for 12 h at $400^\circ C$ completely converted the δ - $KZnPO_4$ to α - $KZnPO_4$.

Barbou des Courières and Simonot-Grange (1979) demonstrated that δ - $KZnPO_4$ is isostructural with NH_4ZnPO_4I . The NH_4ZnPO_4I is described as having a tridymite derivative structure (Averbuch-Pouchot and Durif, 1968) or an ABW zeolite topology (Bu *et al.*, 1997). The structure of NH_4ZnPO_4I consists of corner-sharing ZnO_4 and PO_4 tetrahedra (Averbuch-Pouchot and Durif, 1968; Bu *et al.*, 1997). The NH_4 entities lie in a network of channels that lie parallel to the a and b crystallographic directions. As a starting point for the structure refinement of δ - $KZnPO_4$ from the observed XRPD data (Table I) the atomic coordinates for NH_4ZnPO_4I determined by Bu *et al.* (1997) with K replacing NH_4 were used for the δ - $KZnPO_4$ structure and the unit cell of δ - $KZnPO_4$ refined (Table II). The unit cell dimensions of δ - $KZnPO_4$ are all smaller than the unit cell dimensions of NH_4ZnPO_4I . The unit cell volume of δ - $KZnPO_4$ is approximately 6% smaller than the unit cell volume of NH_4ZnPO_4I .

The calculated XRPD pattern generated by using the atomic coordinates of NH_4ZnPO_4I with K substituted for NH_4 gave quite a good fit to the measured XRPD pattern of δ - $KZnPO_4$. However, the smaller unit cell size of δ - $KZnPO_4$ relative to NH_4ZnPO_4I means that the bond lengths of the ZnO_4 and PO_4 tetrahedra become unrealistically small. Rietveld refinement of the δ - $KZnPO_4$ structure while allowing the atomic coordinates of all, but the y coordinate of one of the atoms in the structure to vary gave an extremely good fit to the measured XRD pattern of δ - $KZnPO_4$. The requirement to keep the y coordinate of one atom fixed is dictated by the $P12_11$ space group symmetry that does not have an inversion center in the y -direction. Although the fit from this refinement was very good, the atoms in the refined structure had moved to positions where the ZnO_4 and PO_4 tetrahedra were very distorted and had unrealistic bond lengths.

In order to constrain the rearrangement of the ZnO_4 and PO_4 tetrahedra during Rietveld refinement, bond distances, and angles of the ZnO_4 and PO_4 tetrahedra that were determined from the NH_4ZnPO_4I structure were used as constrained parameters in the software package DLS-76 (Baerlocher *et al.*, 1978). In this way, the ZnO_4 and PO_4 tetrahedra are free to move about their shared corners, but the geometry of the tetrahedra is maintained. The atomic coordinates generated for Zn, P, and O atoms by DLS-76 are, therefore, a set of coordinates that satisfy the unit cell geometry of δ - $KZnPO_4$ while maintaining realistic Zn–O and P–O bond lengths and angles.

The atomic coordinates for the Zn, P, and O atoms generated by DLS-76 along with the thermal parameters for the corresponding atoms in the NH_4ZnPO_4I structure of Bu *et al.* (1997) were used in Rietveld refinements of the δ - $KZnPO_4$ structure. The atomic coordinates of the K atoms in the δ - $KZnPO_4$ structure were refined by allowing their coordinates to change in an unconstrained manner while holding the atomic coordinates and thermal parameters of the Zn, P, and O atoms fixed. The final step in the refinement was to refine the thermal parameters of the K atoms while holding all other structural parameters fixed.

The structural parameters for the refined structure of δ - $KZnPO_4$ are given in Tables II and III, and the XRD pattern and the difference between the measured XRD pattern and the calculated XRD pattern are shown in Figure 1. The R_{wp} and

TABLE I. X-ray powder diffraction data of δ -KZnPO₄.

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	I_{obs}	h	k	l	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	I_{cal}	$\Delta 2\theta$ (°)
10.124	8.7301	52	0	0	1	10.117	8.7364	49	0.007
14.383	6.1529	413	-1	0	1	14.403	6.1445	439	-0.020
14.530	6.0912	321	1	0	1	14.534	6.0893	325	-0.005
19.353	4.5827	478	0	1	1	19.344	4.5849	453	0.009
20.318	4.3672	256	0	0	2	20.313	4.3682	256	0.005
20.726	4.2821	461	2	0	0	20.720	4.2834	542	0.006
21.938	4.0482	28	1	-1	-1	21.926	4.0504	55	0.012
22.025	4.0324	51	1	1	1	22.014	4.0344	110	0.011
22.706	3.9130	10	-1	0	2	22.748	3.9058	17	-0.043
22.929	3.8754	63	1	0	2	22.917	3.8774	78	0.012
23.187	3.8328	48	-2	0	1	23.023	3.8598	49	0.164
23.187	3.8328		2	0	1	23.190	3.8323		-0.003
26.250	3.3922	37	0	1	2	26.246	3.3927	43	0.004
26.572	3.3518	126	2	1	0	26.566	3.3525	170	0.006
28.204	3.1614	779	1	-1	-2	28.199	3.1620	802	0.005
28.356	3.1448	847	1	1	2	28.338	3.1468	683	0.018
28.423	3.1376	581	2	-1	-1	28.425	3.1374	786	-0.002
28.577	3.1210	719	2	1	1	28.562	3.1226	796	0.015
29.030	3.0734	341	-2	0	2	29.040	3.0723	355	-0.011
29.316	3.0440	354	2	0	2	29.310	3.0447	367	0.006
30.679	2.9118	198	0	0	3	30.675	2.9121	159	0.004
32.347	2.7654	71	-1	0	3	32.354	2.7648	78	-0.007
32.544	2.7490	66	1	0	3	32.537	2.7496	64	0.007
32.877	2.7219	377	-3	0	1	32.882	2.7215	382	-0.005
33.078	2.7059	288	3	0	1	33.063	2.7071	312	0.014
33.252	2.6921	1000	0	2	0	33.239	2.6931	1000	0.012
33.778	2.6514	52	2	1	2	33.790	2.6505	50	-0.012
35.015	2.5605	682	0	1	3	34.998	2.5617	822	0.017
35.483	2.5278	16	3	1	0	35.554	2.5230	1	-0.071
36.426	2.4645	128	1	-2	-1	36.394	2.4666	172	0.032
36.426	2.4645		1	2	1	36.449	2.4630		-0.023
37.126	2.4196	96	3	1	1	37.140	2.4188	117	-0.013
37.126	2.4196		-2	0	3	37.145	2.4184		-0.018
37.441	2.4000	31	-3	0	2	37.439	2.4001	52	0.002
37.441	2.4000		2	0	3	37.469	2.3982		-0.028
40.778	2.2109	70	1	2	2	40.759	2.2119	153	0.019
40.880	2.2057	56	2	-1	-3	40.869	2.2063	90	0.011
41.172	2.1907	156	3	-1	-2	41.140	2.1923	141	0.032
41.172	2.1907		2	1	3	41.169	2.1909		0.003
41.449	2.1767	50	3	1	2	41.439	2.1772	72	0.010
42.168	2.1412	61	4	0	0	42.159	2.1417	77	0.009
42.796	2.1113	51	1	0	4	42.783	2.1119	72	0.012
43.569	2.0756	16	4	0	1	43.565	2.0758	25	0.004
44.177	2.0484	28	-3	0	3	44.182	2.0482	23	-0.005
44.624	2.0289	16	3	0	3	44.604	2.0298	34	0.020
44.729	2.0244	72	2	-2	-2	44.711	2.0252	80	0.018
44.729	2.0244		0	1	4	44.738	2.0240		-0.009
44.929	2.0159	26	2	2	2	44.897	2.0172	53	0.032
45.542	1.9901	48	4	1	0	45.542	1.9901	79	0.000
45.886	1.9760	28	0	2	3	45.856	1.9772	38	0.030
46.309	1.9589	8	3	2	0	46.302	1.9592	21	0.007
46.684	1.9441	76	4	-1	-1	46.687	1.9440	72	-0.003
46.874	1.9366	47	4	1	1	46.867	1.9369	33	0.007
47.064	1.9293	57	-4	0	2	47.048	1.9299	57	0.016
47.064	1.9293		1	-2	-3	47.066	1.9292		-0.002
47.218	1.9233	42	1	2	3	47.201	1.9240	45	0.017
47.457	1.9142	245	3	-2	-1	47.455	1.9143	298	0.003
47.609	1.9085	202	3	2	1	47.588	1.9092	250	0.020
49.609	1.8361	63	2	-1	-4	49.613	1.8360	36	-0.004
50.005	1.8225	4	2	1	4	49.956	1.8241	6	0.049
50.161	1.8172	11	4	-1	-2	50.172	1.8168	22	-0.012
50.659	1.8005	15	2	-2	-3	50.691	1.7994	31	-0.032
50.959	1.7906	30	2	2	3	50.945	1.7910	45	0.014
51.975	1.7579	25	0	3	1	51.952	1.7587	27	0.023
52.391	1.7449	11	0	0	5	52.315	1.7473	9	0.076
52.777	1.7331	14	-4	0	3	52.786	1.7328	31	-0.009

Continued

TABLE I. Continued

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	I_{obs}	h	k	l	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	I_{cal}	$\Delta 2\theta$ (°)
53.015	1.7259	14	1	-3	-1	53.098	1.7234	18	-0.083
53.143	1.7220	1	1	3	1	53.139	1.7221	44	0.004
53.383	1.7148	36	-1	0	5	53.375	1.7151	42	0.008
53.588	1.7088	32	1	0	5	53.579	1.7090	36	0.009
54.037	1.6956	45	0	2	4	54.011	1.6964	53	0.026
54.448	1.6838	19	-5	0	1	54.434	1.6842	31	0.014
55.363	1.6581	226	3	-1	-4	55.372	1.6579	291	-0.009
55.893	1.6436	159	3	1	4	55.849	1.6448	230	0.044
55.893	1.6436		4	2	1	55.876	1.6441		0.017
56.483	1.6278	198	2	-3	-1	56.481	1.6279	153	0.002
56.483	1.6278		2	3	1	56.559	1.6258		-0.076
56.765	1.6204	23	3	2	3	56.745	1.6209	20	0.020
57.281	1.6070	24	5	-1	-1	57.266	1.6075	43	0.016
57.480	1.6020	33	5	1	1	57.460	1.6025	42	0.019
58.656	1.5726	16	2	2	4	58.623	1.5734	26	0.032
58.805	1.5690	30	4	-2	-2	58.817	1.5687	40	-0.012
60.288	1.5339	47	5	-1	-2	60.295	1.5337	90	-0.007
60.553	1.5278	136	0	3	3	60.531	1.5283	192	0.021
60.702	1.5244	129	5	1	2	60.672	1.5251	175	0.031
61.944	1.4968	13	-3	0	5	61.960	1.4964	48	-0.017
61.944	1.4968		3	3	1	61.970	1.4962		-0.026
62.587	1.4830	26	3	0	5	62.516	1.4845	27	0.070
63.199	1.4701	4	5	0	3	62.605	1.4826	4	0.594
63.533	1.4631	10	3	-2	-4	63.542	1.4629	5	-0.010
63.880	1.4560	18	4	-2	-3	63.821	1.4572	19	0.059
64.187	1.4498	18	4	2	3	64.258	1.4484	13	-0.071
64.358	1.4464	32	1	-2	-5	64.344	1.4466	49	0.014
64.358	1.4464		5	2	0	64.396	1.4456		-0.038
64.595	1.4416	72	3	-1	-5	64.584	1.4418	60	0.010
64.595	1.4416		2	-3	-3	64.597	1.4416		-0.002
64.838	1.4368	38	3	-3	-2	64.794	1.4377	45	0.043
65.316	1.4274	98	6	0	0	65.298	1.4278	70	0.018
65.486	1.4241	8	5	2	1	65.470	1.4245	57	0.016
66.498	1.4049	11	0	1	6	66.460	1.4056	21	0.038

The data are for a fixed divergence slit of 2° and CuK α radiation. RIR = 0.53.

R_{exp} for the refined structure were 1.91% and 0.48%, respectively (GOF = 3.97). Refining the thermal parameters for the K atoms had virtually no effect on the R -factor of the refinement and so the values for these parameters given in Table III must be considered to have a reasonable degree of uncertainty.

The examination of the refined structures of δ -KZnPO $_4$ (Figure 2) and NH $_4$ ZnPO $_4$ I shows that the difference between these structures is rotations of the Zn–O and P–O tetrahedra around their shared corners. These rotations allow the constituent atoms of the δ -KZnPO $_4$ structure to be accommodated in the smaller unit cell of δ -KZnPO $_4$ relative to the unit cell of

TABLE II. Unit cell data for δ -KZnPO $_4$ and NH $_4$ ZnPO $_4$ I.

	δ -KZnPO $_4$	NH $_4$ ZnPO $_4$ I
System	Monoclinic	Monoclinic
Space group	$P12_11$ (4)	$P12_11$ (4)
Z	4	4
d_{calc} (g cm $^{-3}$)	3.29	2.75
a (Å)	8.5673(3)	8.8039(2)
b (Å)	5.3868(2)	5.4477(1)
c (Å)	8.7370(3)	8.9812(1)
β (°)	90.515(2)	90.092(2)
V (Å 3)	403.28	430.75

NH $_4$ ZnPO $_4$ I parameters from Bu *et al.* (1997).

NH $_4$ ZnPO $_4$ I. The K atoms of δ -KZnPO $_4$ fill the cavities between the Zn–O and P–O tetrahedra in the same way that NH $_4$ entities fill the cavities in the NH $_4$ ZnPO $_4$ I structure.

Although the methodology used in the refinement of the atomic positions of δ -KZnPO $_4$ should not be regarded as

TABLE III. Structural parameters for δ -KZnPO $_4$.

Atom	x	y	z	B_{eq} (Å 2)
Zn1	0.3203	0.0910	0.4038	1.03
Zn2	0.8236	0.0659	0.0725	1.03
P1	0.1963	0.0700	0.0715	0.87
P2	0.6986	0.0875	0.4030	0.79
K1	-0.0069	0.0707	0.6848	1.4
K2	0.5028	0.5944	0.1874	2.0
O1	0.7300	0.3656	0.4299	1.50
O2	0.1803	0.0000	0.2384	1.97
O3	0.5344	0.0482	0.3361	1.82
O4	0.2821	0.4438	0.4459	1.42
O5	0.1815	0.4900	0.7113	1.42
O6	0.0343	0.0951	-0.0030	1.34
O7	0.7117	0.3676	0.0162	1.50
O8	0.2848	0.3163	0.0533	1.42

Thermal parameters for Zn, P, and O atoms from Bu *et al.* (1997). Fractional coordinates for Zn, P, and O atoms refined using the DLS-76 software (Baerlocher *et al.*, 1978). Average uncertainty values in the x , y and z coordinates are 0.0009, 0.0024 and 0.0009 respectively.

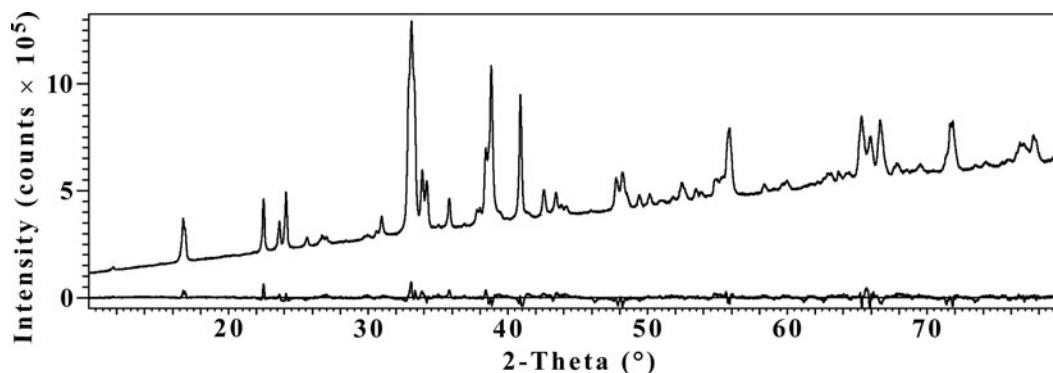


Figure 1. Measured XRD pattern of δ -KZnPO₄ (upper pattern) and the difference between the measured and calculated XRD patterns (lower pattern). (CoK α radiation.)

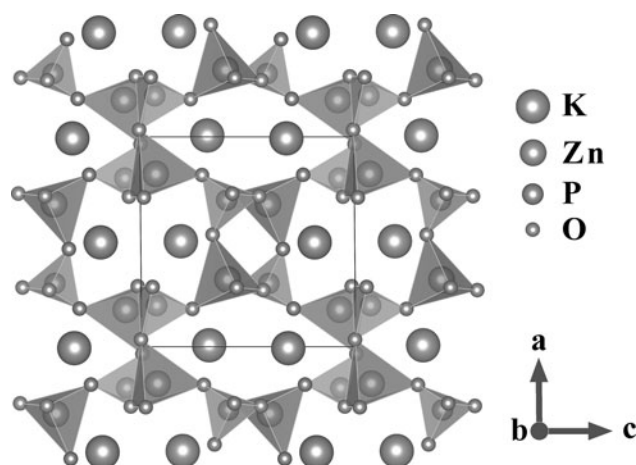


Figure 2. Structure of δ -KZnPO₄ projected along the b -axis and showing Zn–O and P–O tetrahedra. Graphic generated using VESTA 3 (Momma and Izumi, 2011).

giving a complete characterization of the δ -KZnPO₄ structure, it has been found that the derived crystallographic parameters are adequate for quantitative XRD analyses of mixtures containing δ -KZnPO₄.

IV. DEPOSITED DATA

Files containing the raw diffraction data for δ -KZnPO₄ using CoK α radiation and CuK α radiation along with a file containing the refined structural parameters for δ -KZnPO₄ were deposited with the ICDD. The data can be requested at info@icdd.com.

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- Andratschke, M., Range, K.-J., Haase, H., and Klement, U. (1992). "Die kristallstruktur von α -KZnPO₄," *Z. Naturforsch.* **47b**, 1249–1254.
- Averbuch-Pouchot, M. T. and Durif, A. (1968). "Donnees cristallographiques sur les deux varietes du phosphate ammoniac-zincique: ZnNH₄PO₄," *Mater. Res. Bull.* **3**, 719–722.
- Baerlocher, C., Hepp, A., and Meier, W. M. (1978). *DLS-76: A Program for the Simulation of Crystal Structures by Geometric Refinement* (Institute of Crystallography and Petrography – ETH, Zürich).
- Barbou des Courières, T. and Simonot-Grange, M.-H. (1979). "KZn₂H(PO₄)₂·2.5H₂O. II. Instability. Characterization of new, mixed zinc and potassium phosphates," *Mater. Res. Bull.* **14**, 1419–1424.
- Broach, R. W., Bedard, R. L., and Song, S. G. (1999). "Synthesis and characterization of ZP-4 (KZnPO₄·0.8H₂O) a new zincophosphate microporous material: structure solution from a 2.5 × 2.5 × 8 μ m single crystal using a third generation synchrotron X-ray source," *Chem. Mater.* **11**, 2076–2080.
- Bu, X., Feng, P., Gier, T. E., and Stucky, G. D. (1997). "Structural and chemical studies of zeolite ABW type phases: syntheses and characterizations of an ammonium zincophosphate and an ammonium beryllophosphate zeolite ABW structure," *Zeolites* **19**, 200–208.
- Frazier, A. W., Smith, J. P., and Lehr, J. R. (1966). "Precipitated impurities in fertilizers prepared from wet-process phosphoric acid," *J. Agric. Food Chem.* **14**, 522–529.
- Momma, K. and Izumi, F. (2011). "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *J. Appl. Crystallogr.* **44**, 1272–1276.
- Rietveld, H. M. (1967). "Line profiles of neutron powder-diffraction peaks for structure refinement," *Acta Crystallogr.* **22**, 151–152.
- Salutsky, M. L. and Steiger, R. P. (1964). "Metal potassium phosphates," *J. Agric. Food Chem.* **12**, 486–491.
- Wallez, G., Lucas, F., Souron, J.-P., and Querton, M. (1999). "Potassium-zinc monophosphate: an original polymorphic tridymite derivative," *Mater. Res. Bull.* **34**, 1251–1261.