X-Ray Powder Structure and Rietveld Refinement of γ-Zirconium Phosphate, $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$

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A highly crystalline sample of γ-zirconium phosphate $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ has been prepared by hydrothermal methods and its structure solved by X-ray powder diffractometry: monoclinic, space group $P2_1$, a = 5.3825(2), b = 6.6337(1), c = 12.4102(4) Å, β = 98.687(2)° and Z = 2. The final agreement factors are: R_{wp} = 0.105, R_p = 0.079 and R_F = 0.041. In the structure the metal atoms and one of the phosphate groups are located nearly in a plane. The octahedral co-ordination of the metal atom is completed by four oxygen atoms of the phosphate group and two oxygen atoms of the dihydrogenphosphate group. The remaining two oxygens of the dihydrogenphosphate group bind to protons and project into the interlayer space. These hydroxyl groups are hydrogen bonded to the water molecules. The water molecules reside in the pockets of these hydroxyl groups and are hydrogen bonded to each other to form a zigzag chain along the b axis.

Clearfield and his co-workers first prepared layered zirconium phosphate compounds with compositions $Zr(HPO_4)_2\cdot H_2O$ (α-ZrP)[1] and $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ (γ-ZrP).[2] The structure of α-ZrP was solved by single-crystal methods[3,4] while only structural models have been reported so far, for γ-ZrP. The earliest model was based on X-ray and electron diffraction data from which Yamanaka and Tanaka[5] deduced that the structure of γ-ZrP is related to that of the α phase but with more densely packed metal phosphate groups in the layers. However, Clayden[6] utilized ^{31}P magic angle spinning (MAS) NMR data to show that γ-ZrP contains equal amounts of phosphate and dihydrogenphosphate groups whereas α-ZrP contains only monohydrogenphosphate species. Subsequently, Christensen *et al.*[7] investigated the structure of the isostructural titanium analogue, $Ti(PO_4)(H_2PO_4)\cdot 2H_2O$ (γ-TiP) and derived a model for the arrangement of the layers in the structure which is consistent with the NMR results. The model was refined in two possible space groups and also they were not able to locate the water molecules in the lattice. Recently we have determined the structure of the ammonium salt of γ-ZrP[8] which confirmed the above model for γ-TiP. In the meantime we were able to obtain a highly crystalline sample of the parent γ-ZrP the structure of which is reported in this paper.

Experimental

Synthesis.—The starting zirconium phosphate gel was prepared according to the reported procedure.[9] The salt $NaH_2PO_4\cdot H_2O$ (677 g, 4.91 mol) was dissolved in a solution consisting of distilled water (376 cm^3) and 85% H_3PO_4 (182.6 g, 1.58 mol) and the solution was refluxed for 30 min. To this was added a 1 mol dm^{-3} solution (238 cm^3) of $ZrOCl_2\cdot 8H_2O$ (76 g) and the resultant gel was refluxed for 72 h. It was then transferred to a hydrothermal bomb and heated at 190 °C for 120 h. The white precipitate was filtered off, washed with 4 mol dm^{-3} HCl to remove sodium ions, with 0.2 mol dm^{-3} H_3PO_4 to remove chloride ions and finally with deionized water. The sample was dried in a desiccator at room temperature before data collection.

Data Collection, Structure Solution and Refinement.—Step-scanned X-ray powder data for the finely ground sample (packed on a flat aluminium sample holder) were collected by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data were collected between 2θ 3 and 80° with a step size of 0.01° and a count time of 10 s per step. They were mathematically stripped of the Kα2 contribution and the pattern was indexed by Ito methods.[10] The indexed reflections showed systematic absences of the type $0k0$, $k = 2n + 1$ indicating that the space group is either $P2_1$ or $P2_1/m$.

The initial structural model for the zirconium phosphate layer was taken from the structure of $\gamma\text{-}Zr(PO_4)(NH_4HPO_4)$.[8] Full pattern refinement[11] was started in the centric space group $P2_1/m$. After the initial refinement of the scale, background and the profile parameters, the atomic positions were refined using soft constraints. A Fourier difference map computed at this stage revealed the positions of the water oxygens. Among them one is very close to a special position (mirror plane) and the other is on a general position. The atom at the general position is at short contact from its symmetry equivalent indicating that it is disordered over two positions each with 50% occupancy. This is in agreement with the chemical analysis data which clearly show that the compound contains only two water molecules for each zirconium atom. The disorder of the water molecule together with some distortion in the geometry of the dihydrogenphosphate group suggested the non-centric space group $P2_1$ for the structure. Accordingly, the symmetry-related atoms were generated and the refinement was switched to the space group $P2_1$. The two water oxygens were included with full occupancies and were refined without any soft constraints. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard deviations. No corrections were made for anomalous dispersion, absorption or preferred orientation. The strong (001) reflection, which is asymmetric and affected by preferred orientation effects, was not included in the final Rietveld difference plot. This reflection however was used in the calculation of the R_F factor.

Results and Discussion

Crystallographic data are given in Table 1, final positional parameters in Table 2, and bond lengths and angles in Table 3. The Rietveld refinement plot is shown in Fig. 1. Fig. 2 is a projection of the structure down the a axis.

Table 1 Crystallographic data for $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$

Formula	$H_6O_{10}P_2Zr$
M	319.21
Space group	$P2_1$ (no. 4)
a/Å	5.3825(2)
b/Å	6.6337(1)
c/Å	12.4102(4)
β/°	98.687(2)
Z	2
D_c/Mg m^{-3}	2.417
Pattern range (2θ)/°	14–80
Step scan increment (2θ)/°	0.01
Step scan time/s	10
No. of contributing reflections	607
No. geometric observations	25
P–O distances and tolerance/Å	1.53(2)
Zr–O distances and tolerance/Å	2.03(3)
O ··· O distances for PO_4/Å	2.55(2)
O ··· O distances for ZrO_6 (*cis*)/Å	2.90(2)
No. structural parameters	51
No. profile parameters	11
Statistically expected R_{wp}	0.035
R_{wp}	0.105
R_p	0.079
R_F	0.041

$R_{wp} = [\Sigma w(I_o - I_c)^2/\Sigma(wI_o^2)]^{\frac{1}{2}}$, $R_p = (\Sigma|I_o - I_c|/\Sigma I_c)$, $R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$; expected $R_{wp} = R_{wp}/(\chi^2)^{\frac{1}{2}}$; $\chi^2 = \Sigma w(I_o - I_c)^2/(N_{obs} - N_{var})$, where N_{obs}, N_{var} = number of observations and variables.

Table 2 Positional parameters for $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$

Atom	x	y	z
Zr	0.7969(5)	0.25	0.1255(2)
P(1)	0.2383(10)	0.2528(15)	0.9395(5)
P(2)	0.3530(12)	0.1877(13)	0.3048(6)
O(1)	0.0857(17)	0.2454(21)	0.0378(7)
O(2)	0.1895(17)	0.0602(12)	0.8722(7)
O(3)	0.1735(24)	0.4456(12)	0.8735(9)
O(4)	0.5202(12)	0.2607(23)	0.9946(7)
O(5)	0.0809(15)	0.2515(22)	0.2600(8)
O(6)	0.5329(17)	0.2491(21)	0.2245(8)
O(7)	0.3584(25)	0.9501(14)	0.3192(12)
O(8)	0.4351(24)	0.2912(25)	0.4160(8)
O(W1)	0.1936(22)	0.2128(26)	0.6308(11)
O(W2)	0.1214(27)	0.5678(20)	0.5355(14)

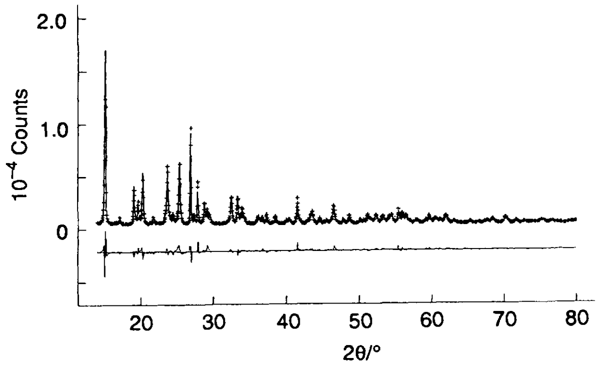

Fig. 1 Observed (+) and calculated (−) profiles (X-ray intensity *versus* 2θ) for the Rietveld refinement. The bottom curve is the difference plot on the same intensity scale

Table 3 Bond lengths (Å) and angles (°) for $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$

Zr–O(1)	2.028(7)	Zr–O(4)	2.032(7)
Zr–O(2)	2.059(8)	Zr–O(5)	2.086(9)
Zr–O(3)	2.026(8)	Zr–O(6)	2.014(7)
P(1)–O(1)	1.571(7)	P(2)–O(5)	1.545(7)
P(1)–O(2)	1.527(8)	P(2)–O(6)	1.545(7)
P(1)–O(3)	1.531(8)	P(2)–O(7)	1.586(7)
P(1)–O(4)	1.568(7)	P(2)–O(8)	1.545(8)
O(1)–Zr–O(2)	89.7(5)	O(2)–Zr–O(6)	91.2(4)
O(1)–Zr–O(3)	85.6(6)	O(3)–Zr–O(4)	95.0(7)
O(1)–Zr–O(4)	95.8(5)	O(3)–Zr–O(5)	87.3(5)
O(1)–Zr–O(5)	84.3(5)	O(3)–Zr–O(6)	93.2(4)
O(1)–Zr–O(6)	174.8(5)	O(4)–Zr–O(5)	177.7(6)
O(2)–Zr–O(3)	173.5(4)	O(4)–Zr–O(6)	89.3(4)
O(2)–Zr–O(4)	89.8(5)	O(5)–Zr–O(6)	90.6(3)
O(2)–Zr–O(5)	87.9(4)		
O(1)–P(1)–O(2)	109.4(7)	O(5)–P(2)–O(6)	110.4(6)
O(1)–P(1)–O(3)	109.8(6)	O(5)–P(2)–O(7)	108.2(6)
O(1)–P(1)–O(4)	104.3(5)	O(5)–P(2)–O(8)	109.1(6)
O(2)–P(1)–O(3)	113.5(5)	O(6)–P(2)–O(7)	109.4(6)
O(2)–P(1)–O(4)	110.0(7)	O(6)–P(2)–O(8)	109.6(6)
O(3)–P(1)–O(4)	109.4(6)	O(7)–P(2)–O(8)	110.0(6)
Zr–O(1)–P(1)	161.7(8)	Zr–O(4)–P(2)	153.1(6)
Zr–O(2)–P(1)	145.6(6)	Zr–O(5)–P(2)	145.8(8)
Zr–O(3)–P(1)	144.9(8)	Zr–O(6)–P(2)	164.3(9)
O(W1) ··· O(7)	2.87(2)	O(W2) ··· O(8′)	2.80(2)
O(W1) ··· O(8)	3.18(2)	O(W2) ··· O(8)	3.03(2)
O(W1) ··· O(W2)	2.65(2)	O(W2) ··· O(7)	3.19(2)
O(W1) ··· O(W2)	2.64(1)		

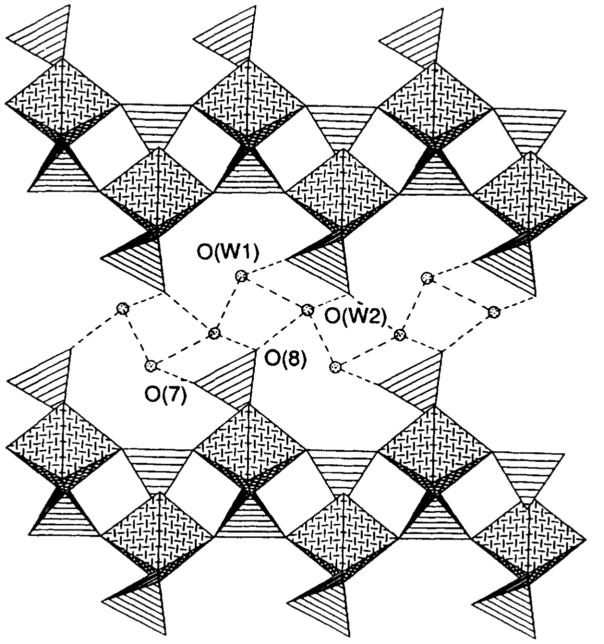

Fig. 2 Polyhedral presentation of the structure down the *a* axis. Hydrogen bonds involving the water molecules and hydroxyl groups are marked. The *c* axis is vertical and the *b* axis is horizontal

The zirconium atom is octahedrally co-ordinated by four oxygen atoms of the phosphate group and two oxygen atoms of the dihydrogenphosphate group. The metal atoms and the phosphate group are located nearly in a plane at $z = 0$ and the dihydrogenphosphate group is shifted on either side of this plane as shown in Fig. 2. A full description of the layer arrangement is presented in an earlier publication which describes the structure of the ammonium intercalate of γ-ZrP, $Zr(PO_4)(NH_4PO_4)$.[8] The intercalate structure, however, was refined in the centric space group $P2_1/m$ where the metal, the phosphate groups and even the nitrogen of the ammonium ion are located on a mirror plane. The ammonium ion is located between adjacent dihydrogenphosphate groups of a layer. In addition to hydrogen bonding to the hydroxyls of these phosphate groups, the ammonium ions also link the neighbouring layers through hydrogen bonds with the same hydroxyl groups. Thus, the nitrogen atom is in a symmetrical environment relative to both the hydroxyl groups of the H_2PO_4 group, which allows the groups to reside on a mirror plane. The parent γ-ZrP, on the other hand, could not be refined in the same space group. The refined positions of the metal atom and the phosphate group, in the present structure, indicate that they are located very close to the mirror symmetry as in the ammonium intercalate. The major deviation from the mirror symmetry is found for the dihydrogenphosphate group. This feature can be seen in Fig. 2 where the P(2) tetrahedron is inclined to the *a* axis. The shifting of this phosphate group from the mirror plane which resulted in the lower symmetry ($P2_1$) for the parent γ-ZrP is attributed to the presence of two lattice water molecules and the associated interactions which are discussed below.

The water molecule, O(W1), is located in the pockets formed by the adjacent H_2PO_4 groups of a layer in such a way that it is closer to one of the hydroxyl groups [O(W1) ··· O(7) 2.87(2) Å]. The oxygen of the other OH group is at 3.54 Å from O(W1). Water molecule O(W2) is located nearly at the centre of the layers and links the adjacent layers through hydrogen bonding to two symmetry-related O(8) atoms [O(W2) ··· O(8) 3.03(2), O(W2) ··· O(8′) 2.80(2) Å]. Additionally, O(W1) is hydrogen bonded to two O(W2) water molecules and each O(W2) in turn is bonded to two O(W1) water molecules [O(W1) ··· O(W2) 2.65(2), 2.64(1) Å]. This arrangement leads to a zigzag chain of water molecules which runs between the dihydrogenphosphate groups as shown in Fig. 2. The bonding scheme described above creates loose four-membered rings in the interlayer space. One such ring involves O(7), O(8), O(W1) and O(W2) while the other consists of O(8), O(W2), O(W1) and O(W2). These rings alternate along the *b* axis (Fig. 2). In the former four-membered ring O(7) is 3.19(2) Å from O(W2) and O(8) is 3.18(2) Å from O(W1).

The interaction between the water molecules and the POH groups in this structure is different from that observed in α-ZrP which contains only one water molecule in the lattice. This water molecule interacts with the POH groups entirely from a single layer. The layers are, therefore, held together only by weak van der Waals forces. This difference in these two structures may very well be due to the way these two layer structures are formed. The interlayer separation is 7.55 Å in α-ZrP as compared to 12.2 Å in γ-ZrP. This difference is basically due to the thickness of the layers which in turn is related to the arrangement of metal phosphate polyhedra in these two structures. The γ structure consists of a central phosphate tetrahedron sandwiched between the metal octahedra. The dihydrogenphosphate groups are linked axially to the metal atoms which further increases the thickness of the layer. In α-ZrP the metal atoms are located nearly in a plane and the bridging HPO_4^{2-} groups are situated slightly above and below this plane. Three oxygens of each of these phosphate groups are bonded to three different Zr atoms arranged in the form of an equilateral triangle. The fourth oxygen which constitutes the hydroxyl group is pointing into the interlayer space. The neighbouring phosphate groups containing this hydroxyl group are separated by ≈ 5.3 Å both along *a* and *b* axes which leads to nearly symmetrical cavities on either side of the layer. In the case of γ-ZrP the adjacent $H_2PO_4^-$ groups are separated by ≈ 5.4 Å along the *a* axis and ≈ 6.63 Å along the *b* axis. This larger separation of 6.63 Å, however, is required to accommodate two hydroxyl groups which are displaced along the *b* axis (Fig. 2).

In Fig. 2 it appears that the dihydrogenphosphate group of one layer projects into the cavity formed by two such groups in the adjacent layer. The relative orientation of the dihydrogenphosphate groups in this case is similar to that observed in the ammonium-exchanged phase.[8] This feature may also be visualised by comparing the value of the monoclinic angles (β) which are similar in these two structures. In the case of α-type structures,[12] however, the value of β varies over a wide range. This result indicates that the layers in α-ZrP can easily be moved relative to one another as required by the size, charge and nature of interaction of the sorbed ions or guest molecules. More structural data on the γ-type structures, however, are needed for a complete understanding of their layer properties.

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