

Determination of Formation Regions of Titanium Phosphates; Determination of the Crystal Structure of β -Titanium Phosphate, $\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$, from Neutron Powder Data

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The formation region of the various types of layered titanium hydrogen phosphate hydrates was investigated. The materials were prepared by hydrothermal methods, treating amorphous titanium phosphate with phosphoric acid (8 to 16 M) in the temperature range 175 to 250°C. The materials obtained were: α - $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, γ - $\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$, and its anhydrous form β - $\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$. The structure of β - $\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$ has been determined by Rietveld powder refinement of high resolution neutron diffraction data. The structure is refined in the monoclinic space group $P2_1/n$ (No. 14). The unit cell parameters are: $a = 18.9503(4)$ Å, $b = 6.3127(1)$ Å, $c = 5.1391(1)$ Å, $\beta = 105.366(2)^\circ$; $Z = 4$. The final agreement factors were: $R_p = 2.9\%$ and $R_{wp} = 3.8\%$. The structure of β - $\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$ is built from TiO_6 octahedra linked together by tertiary phosphate (PO_4) and dihydrogen phosphate ($(\text{OH})_2\text{PO}_2$) tetrahedra. The layers are held together by hydrogen bonds. © 1998 Academic Press

INTRODUCTION

The chemistry of layered phosphates of tetravalent metals has been studied extensively since the 1960s. The materials can be divided into two structural types: the α -type and γ -type compounds. The structure of α - $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -ZrP) was solved by single-crystal methods by Clearfield *et al.* (1,2). The structures of the other α -type compounds were recently shown to be isostructural with α -ZrP (3).

The existence of the γ -type compounds was first reported by Clearfield *et al.* (4). The hydrated material was named γ -ZrP and the anhydrous form, β -ZrP. For many years the larger interlayer distance (12.2 Å for γ -ZrP and 9.4 Å for

β -ZrP) was attributed to a different stacking of the layers rather than a different arrangement within the layers (4). In 1979 the first papers attributing the difference between the compounds to different intralayer arrangement were published (5,6). It was, however, not until the ^{31}P MAS NMR studies of Clayden (7) in 1987 that a real breakthrough was achieved. Clayden showed that, whereas only one ^{31}P resonance is observed in the α -layered compounds, spectra of the γ -compounds have two ^{31}P resonances of equal integrated intensity. Clayden's conclusion was that γ -ZrP contains tertiary phosphate groups and dihydrogen phosphate groups in equal amounts. The formula should therefore be written: γ - $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$.

In 1990 Christensen *et al.* (8) proposed a structure for γ -TiP from X-ray powder diffraction data. The proposed structure is consistent with the NMR results for γ -ZrP, i.e., it has both tertiary phosphate groups and dihydrogen phosphate groups. However, the positions of the water molecules were not found and there was uncertainty concerning the space group. Recently, Poojary *et al.* (9,10) have published the structures of γ -zirconium phosphate and the monoammonium form: γ - $\text{Zr}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$ from X-ray powder data. These studies confirm the model reported by Christensen *et al.* (8).

The aim of our present work was to determine the structure of the γ -type layers and to study the hydrogen bonds holding the layers together. The anhydrous material, β -TiP, was chosen to avoid the influence of the water of crystallization. Hydrothermal treatment of amorphous titanium phosphate yielded large crystals of β -titanium phosphate using one combination of temperature and concentration of phosphoric acid. These crystals were used in single crystal determinations. However, due to poor mechanical stability of the crystals only a partial model was found. The subsequent structure determinations based on neutron powder diffraction data showed that the structure could be described in a monoclinic unit cell, space group $P2_1/n$.

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EXPERIMENTAL

Preparation

α -, β -, and γ -TiP were prepared by hydrothermal treatment of amorphous titanium phosphate. 0.5 g of amorphous titanium phosphate, prepared as described by Alberti *et al.* (11), was placed in a Teflon-lined autoclave and 10 ml of phosphoric acid was added. After stirring for 24 h the autoclave was sealed and heated in an oven for 48 h. After quenching (in cold water) the solid was isolated by filtration. Pure microcrystalline β -TiP was obtained using phosphoric acid with a concentration higher than 12 M and a temperature higher than 200°C; 10 M phosphoric acid at 250°C yielded large crystals of β -TiP. To avoid hydration the solid was washed with 99.9% ethanol. IR and X-ray diagrams showed no sign of intercalation of ethanol. β -TiP obtained by this method is stable at ambient condition for about 1–2 weeks; thereafter it is gradually transformed to the hydrated form (γ -TiP). If, instead, the solid is washed with water until pH \sim 3.5 the pure hydrated material γ -TiP was obtained.

Only one combination of concentration and temperature (10 M H₃PO₄ and 250°C) yielded large single crystals. These crystals had a size of about 0.5 \times 0.5 \times 0.1 mm; i.e., they were thin and plate-shaped. The crystals were not mechanically stable, tending to fan out like a deck of cards. The formation of large crystals was proven to be reproducible by performing several syntheses.

Characterization

The products were characterized by X-ray powder diffraction using a Siemens D5000 diffractometer equipped with a primary Ge-monochromator. The patterns were recorded from 2 to 90° in 2θ using a step length of 0.02° and a counting time of 10 s per step.

The infrared spectra were recorded on a Fourier Transform IR Spectrometer 170. The spectra were recorded with the potassium bromide technique (1 mg sample in 350 mg KBr).

Data Collection, Structure Solution, and Refinement

X-ray powder diffraction. A powder diffraction data set of β -TiP was recorded using a Siemens D5000 diffractometer, equipped with a primary Ge-monochromator (CuK α ₁-radiation, $\lambda = 1.540598$ Å). The data were collected on a flat sample from 8.5° to 90.0° in 2θ using a step length of 0.02°. In order to obtain the correct intensities of the low-angle reflections, the diffractogram was recorded in two parts. The diffractograms were scaled together using reflections in the overlapping range.

The trial-and-error indexing program TREOR (12) suggested a monoclinic unit cell. The CELLKANT program (13) was used to refine this unit cell from the observed

d -spacings. The refined unit cell dimensions were: $a = 18.952(1)$ Å, $b = 6.312(1)$ Å, $c = 5.142(1)$ Å, $\beta = 105.37(1)^\circ$. The indexed powder pattern is provided in Table 1. The indexed pattern showed systematic absences of the type: $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$), and $0kl$ ($k + l = 2n + 1$), indicating that the possible space group is $P2_1/n$ (No. 14).

Attempts were made to solve the structure using single crystal X-ray diffraction techniques. The unit cell found was orthorhombic with $a = 18.23(2)$, $b = 6.30(2)$, $c = 5.10(3)$ Å. The apparent space group was $Pna2_1$ (No. 33). The orthorhombic unit cell is related to the monoclinic by the transformation,

$$T = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

However, Weissenberg diagrams showed splitting of the $h0l$ reflections, indicating twinning of the single crystal. A partial solution was determined from the single crystal data with direct methods, but it was not possible to refine it satisfactorily.

A total of 480 structure factors were extracted from the X-ray powder diffractogram using the program ALLHKL (14). The positions of titanium and phosphorus atoms found in the orthorhombic single crystal solution were transformed to the monoclinic unit cell. In a subsequent difference Fourier calculation the positions of all eight oxygen atoms were found. The data were refined by the Rietveld method using the program GSAS (general structure analysis system) (15). The final agreement factors were $R_p = 14.8\%$ and $R_{wp} = 19.6\%$. During the refinement it was necessary to include a preferred orientation factor. The crystallites are thin platelets which gives a severe preferred orientation effect. This is probably the reason for the unsatisfactory refinement. To obtain the correct structure a set of high resolution neutron data were recorded.

Neutron powder diffraction. Neutron powder data were recorded at the high resolution neutron powder diffractometer (HRNPD) at beamline H1A of the high flux beam reactor (HFBR) at Brookhaven National Laboratory (BNL) (16). The material (approximately 0.5 g) was contained in a sealed glass vial to avoid hydration. The material was not deuterated because of the small amount of hydrogen in the sample.

The data consisted of 3050 points from 9° to 151° in 2θ in steps of 0.05°. The total counting time was 67 h. The data were refined by the Rietveld method using GSAS (15). The positions from the X-ray powder refinement were used as starting parameters for the refinement. After some initial cycles of refinement, a Fourier difference map was calculated and the hydrogen positions were found as holes

TABLE 1
Indexed Powder Pattern for β -Ti(PO₄)(H₂PO₄)

h	k	l	d _{calc} (Å)	d _{obs} (Å)	int	h	k	l	d _{calc} (Å)	d _{obs} (Å)	int	h	k	l	d _{calc} (Å)	d _{obs} (Å)	int
2	0	0	9.1371	9.1489	100	4	0	2	1.9709	1.9712	3	-12	1	2	1.4454	1.4453	2
1	1	0	5.9675	5.9712	1	-8	0	2	1.9582	1.9590	13	1	2	3	1.4329	1.4331	1
2	1	0	5.1943	5.1962	23	0	2	2	1.9496	1.9487	13	11	1	1	1.4250	1.4249	6
4	0	0	4.5686	4.5712	2	-2	3	1	1.9362	1.9365	1	-13	1	1	1.4202	1.4199	3
1	0	1	4.4934	4.4912	14	9	1	0	1.9330	1.9333	1	10	2	1	1.4157	1.4158	1
-3	0	1	4.4683	4.4691	14	4	3	0	1.9115	1.9121	1	10	3	0	1.3798	1.3798	2
3	1	0	4.3838	4.3863	14	1	3	1	1.9059	1.9066	1	12	2	0	1.3716	1.3718	1
-1	1	1	3.9868	3.9867	7	-8	1	2	1.8703	1.8708	1	9	1	2	1.3663	1.3662	1
0	1	1	3.8993	3.8982	10	-4	3	1	1.8538	1.8524	1	9	3	1	1.3343	1.3344	1
4	1	0	3.7012	3.7037	7	10	0	0	1.8274	1.8277	3	-11	3	1	1.3310	1.3310	1
1	1	1	3.6609	3.6608	4	8	1	1	1.8131	1.8135	1	-3	3	3	1.3289	1.3291	1
3	0	1	3.4263	3.4285	34	-10	1	1	1.8056	1.8057	1	-10	3	2	1.3234	1.3234	1
-5	0	1	3.4041	3.4052	24	-5	3	1	1.7901	1.7910	1	-4	0	4	1.2854	1.2854	1
2	1	1	3.3436	3.3449	1	10	1	0	1.7554	1.7557	10	-12	1	3	1.2784	1.2785	1
-4	1	1	3.3281	3.3287	1	-7	2	2	1.7463	1.7453	1	-7	3	3	1.2743	1.2743	1
0	2	0	3.1568	3.1599	9	-9	2	1	1.7383	1.7383	1	13	0	1	1.2672	1.2669	4
1	2	0	3.1108	3.1120	1	6	3	0	1.7314	1.7317	2	-15	0	1	1.2632	1.2629	1
6	0	0	3.0457	3.0473	1	6	0	2	1.7132	1.7134	2	-11	2	3	1.2541	1.2538	1
3	1	1	3.0114	3.0132	4	-10	0	2	1.7020	1.7022	2	-6	1	4	1.2467	1.2465	1
-5	1	1	2.9963	2.9967	5	4	2	2	1.6718	1.6720	1	13	1	1	1.2424	1.2422	3
2	2	0	2.9838	2.9820	1	9	1	1	1.6644	1.6644	1	-15	1	1	1.2387	1.2385	1
3	2	0	2.8028	2.8026	1	-11	1	1	1.6580	1.6582	1	-7	1	4	1.2319	1.2318	1
6	1	0	2.7432	2.7442	2	6	1	2	1.6534	1.6535	2	-8	4	2	1.2289	1.2288	1
-6	1	1	2.6873	2.6881	1	-10	1	2	1.6434	1.6432	3	8	3	2	1.2183	1.2183	1
5	0	1	2.6280	2.6292	1	-7	3	1	1.6390	1.6393	2	1	5	1	1.2156	1.2156	1
4	2	0	2.5971	2.5973	1	-2	3	2	1.6285	1.6284	1	-12	3	2	1.2133	1.2132	1
-2	0	2	2.5707	2.5729	2	1	0	3	1.6081	1.6079	2	11	3	1	1.2011	1.2009	2
-7	1	1	2.4144	2.4145	10	-7	0	3	1.6012	1.6013	1	-13	3	1	1.1982	1.1983	1
-1	1	2	2.3628	2.3623	1	0	4	0	1.5784	1.5791	1	8	1	3	1.1758	1.1758	1
3	2	1	2.3216	2.3219	1	1	4	0	1.5726	1.5728	1	-14	1	3	1.1684	1.1685	1
-4	1	2	2.3006	2.3027	1	2	4	0	1.5554	1.5560	1	14	1	1	1.1668	1.1668	1
8	0	0	2.2843	2.2848	19	8	3	0	1.5478	1.5477	1	4	5	1	1.1631	1.1629	1
1	1	2	2.2221	2.2228	1	10	1	1	1.5363	1.5364	1	-1	4	3	1.1524	1.1524	1
6	1	1	2.1891	2.1903	2	-6	3	2	1.5319	1.5318	1	-5	4	3	1.1511	1.1511	1
-8	1	1	2.1790	2.1784	1	12	0	0	1.5229	1.5228	4	-16	1	2	1.1417	1.1418	1
4	2	1	2.1701	2.1717	1	6	2	2	1.5057	1.5058	1	9	1	3	1.1239	1.1237	2
8	1	0	2.1480	2.1482	1	3	0	3	1.4978	1.4979	1	15	0	1	1.1165	1.1166	1
2	1	2	2.1167	2.1169	1	1	4	1	1.4892	1.4888	1	-8	5	1	1.1093	1.1089	1
7	0	1	2.0926	2.0934	1	-5	2	3	1.4848	1.4848	1	4	1	4	1.1060	1.1057	1
-9	0	1	2.0825	2.0829	9	-9	3	1	1.4803	1.4803	1	15	1	1	1.0995	1.0994	1
2	3	0	2.0509	2.0510	2	11	2	0	1.4702	1.4699	1	12	4	0	1.0959	1.0959	1
5	2	1	2.0197	2.0200	1	11	0	1	1.4628	1.4628	1						
-7	2	1	2.0129	2.0132	1	3	1	3	1.4574	1.4572	1						
3	1	2	2.0005	2.0019	1	8	1	2	1.4539	1.4538	1						
-7	1	2	1.9895	1.9907	1	-9	1	3	1.4496	1.4496	1						

Note. The indexing is based on a monoclinic unit cell with the dimensions: $a = 18.952(1)$ Å, $b = 6.312(1)$ Å, $c = 5.142(1)$ Å, $\beta = 105.37(1)^\circ$.

(negative density) in the map. After including the hydrogen positions the refinement converged with final agreement factors $R_p = 2.9\%$ and $R_{wp} = 3.7\%$. During the refinement soft constraints were imposed on the Ti–O (1.97 Å), the P–O (1.54 Å), and the P–OH (1.65 Å) bond lengths. The soft constraints were gradually released. It was not necessary to make corrections for preferred orientation. All the atoms were refined isotropically. The diffraction pattern has a con-

tribution to the background due to incoherent scattering from the hydrogen present in the sample. Scattering from the amorphous glass container also contributes, giving rise to the modulated structure in the background. The background was fitted with a Chebyshev function with 30 parameters. In Fig. 1 the observed, calculated, and difference powder diffraction patterns are shown. Some discrepancies between the observed and calculated intensities are

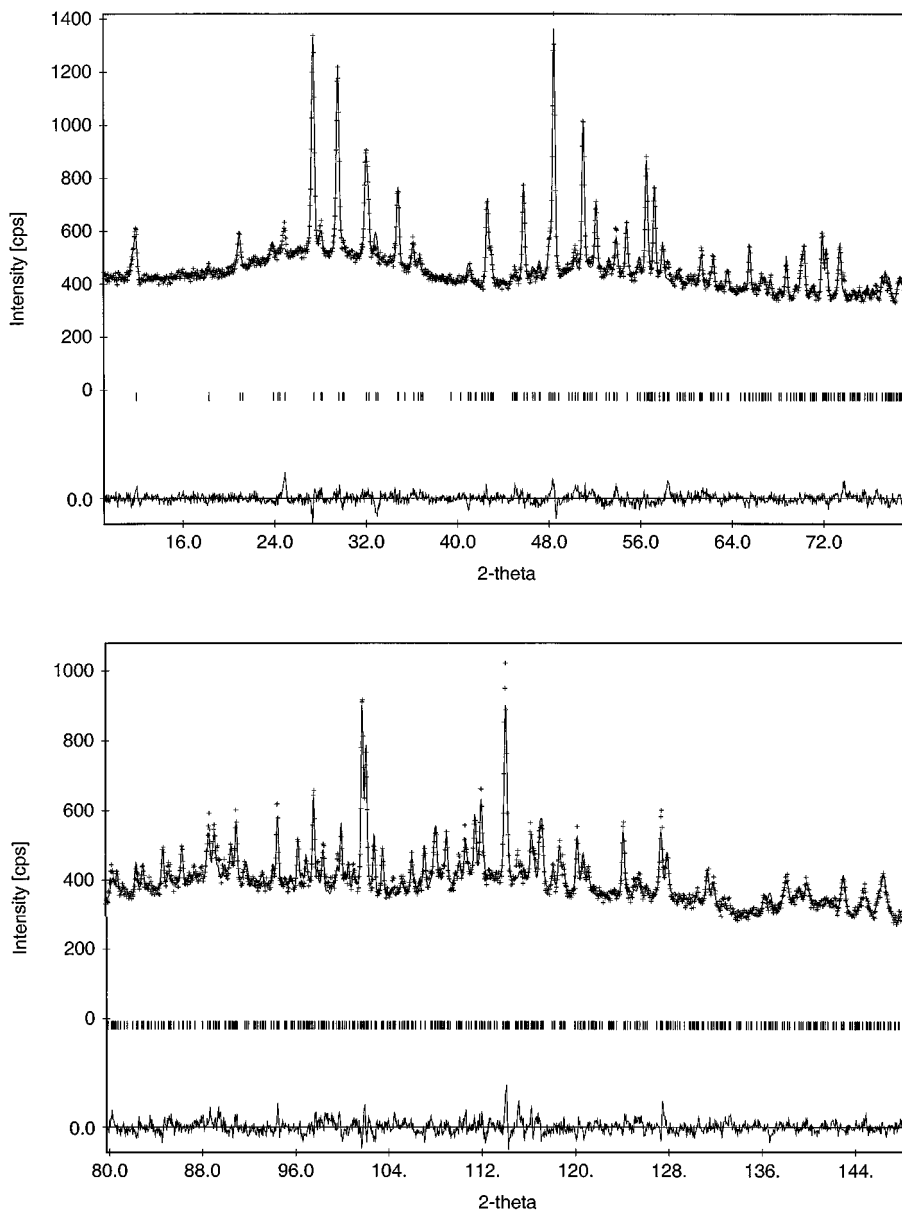


FIG. 1. Observed (+) and calculated (-) profiles for the Rietveld refinement of β -Ti(PO₄)(H₂PO₄). The bottom curve is the difference plot.

observed, e.g. at $2\theta = 25^\circ, 33^\circ, 60^\circ$. This is not due to preferred orientation, but it may be related to small amounts of residual water in the structure, which it was not possible to locate. Another possibility is disorder on the hydrogen positions. However, when the populations of the hydrogen atoms were allowed to refine, values close to 1 were obtained.

RESULTS AND DISCUSSION

Determination of the Formation Region of α - and γ -TiP

The preparations were carried out at temperatures between 175°C and 250°C with concentrations of phosphoric acid in the range from 8 M to 16 M. The formation regions

are shown in Fig. 2. The figure shows the final products of autoclave synthesis when washed with water (i.e., no distinction is made between the anhydrous material β -Ti(PO₄)(H₂PO₄) and the hydrated material γ -Ti(PO₄)(H₂PO₄)·2H₂O).

As can be seen in Fig. 2 nearly all combinations of concentration and temperature give microcrystalline solids (α -Ti(HPO₄)₂·H₂O (α -TiP) or γ -Ti(PO₄)(H₂PO₄)·2H₂O (γ -TiP)). Quenching of the autoclave is important in order to avoid formation of α -TiP. Mixtures of α -TiP and γ -TiP have been obtained when the autoclave was not quenched. The results are in accordance with the formation regions reported by Kobayashi and Yamazaki (17).

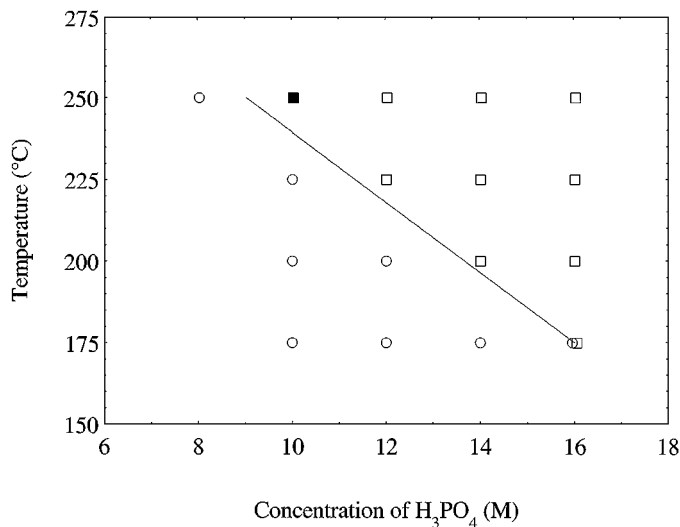


FIG. 2. Formation region of α - and β/γ -titanium hydrogen phosphate. The figure shows the final products from hydrothermal syntheses, when washed with water (i.e., no distinction is made between β - and γ -titanium hydrogen phosphate): \circ , α -Ti(HPO₄)₂·H₂O, microcrystalline powder; \square , γ -Ti(PO₄)(H₂PO₄)·2H₂O, microcrystalline powder; \blacksquare , γ -Ti(PO₄)(H₂PO₄)·2H₂O, large crystals.

Discussion of the Structure

Physical and crystallographic data for β -titanium hydrogen phosphate are given in Table 2, the refined atomic

TABLE 2
Physical and Crystallographic Data for β -Ti(PO₄)(H₂PO₄)

<i>Crystal data</i>	
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å)	18.9502(4)
b (Å)	6.3126(1)
c (Å)	5.1392(1)
β (°)	105.366(2)
V (Å ³)	592.80
Z	4
Molecular weight	240.04
D_{calc} (g/cm ³)	2.69
<i>Data collection</i>	
Temperature (°C)	20
Wavelength (Å)	1.8857
Pattern Range (° 2θ)	9–151
Step Size (° 2θ)	0.05
<i>Structure refinement</i>	
Total no. Reflections	697
No. Profile Points	2819
No. Parameters Refined	93
No. Atoms Refined	13
R_p (%)	2.9
R_{wp} (%)	3.8
χ^2	3.3

Note. $R_p = [\sum (y_i(\text{obs}) - y_i(\text{calc})) / \sum y_i(\text{obs})]$; $R_{wp} = [\sum w_i (y_i(\text{obs}) - y_i(\text{calc}))^2 / \sum w_i (y_i(\text{obs}))^2]^{1/2}$; $\chi^2 = [\sum w_i (y_i(\text{obs}) - y_i(\text{calc}))^2 / (N_{\text{obs}} - N_{\text{var}})]$.

TABLE 3
Atomic Coordinates for β -Ti(PO₄)(H₂PO₄) with Esd's in Parentheses

	x	y	z	U_{iso}^a
Ti	0.1664(5)	0.7380(18)	0.930(2)	1.7(3)
P(1)	0.0573(5)	0.6610(12)	0.2911(19)	0.9(3)
P(2)	0.2137(4)	0.2369(16)	0.9435(15)	0.3(2)
O(1)	0.1693(6)	0.0403(11)	0.922(2)	0.8(2)
O(2)	0.7482(5)	0.251(2)	0.2112(18)	2.6(3)
O(3)	0.6601(7)	0.0708(13)	0.443(3)	1.8(3)
O(4)	0.2716(4)	0.2704(18)	0.2065(14)	0.9(2)
O(5)	0.9196(4)	0.2478(19)	0.9397(16)	0.6(2)
O(6)	0.3991(4)	0.2552(20)	0.9272(14)	0.7(2)
O(7)	0.5690(6)	0.0900(15)	0.821(3)	3.3(3)
O(8)	0.5242(5)	0.236(3)	0.199(2)	2.6(2)
H(1)	−0.0658(13)	0.642(4)	0.541(6)	8.1(8)
H(2)	−0.0626(11)	0.657(3)	0.125(4)	4.3(6)

^a U_{iso} has been multiplied by 100.

coordinates are in Table 3, and the interatomic distances and angles in Table 4. Figures 3 and 4 show polyhedral representations of the structure along [010] and [001], respectively.

The refinements of β -TiP show that the structure of the layer is similar to that found by Christensen *et al.* (8) for γ -TiP and by Poojary *et al.* (9) for γ -ZrP. The structure is built from TiO₆ octahedra and phosphate tetrahedra (PO₄ and (OH)₂PO₂). All four oxygen atoms of the tertiary phosphate group (P2) bind to titanium. In the dihydrogen phosphate group (P1) two oxygen atoms bind to titanium while the other two oxygen atoms point toward the interlamellar space as hydroxyl groups. A very efficient packing of the layers is obtained by a staggered arrangement of the dihydrogen phosphate groups along 001 as seen from Fig. 3.

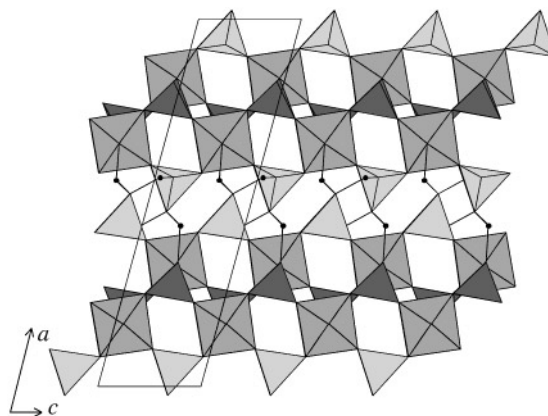


FIG. 3. Polyhedral representation of the crystal structure of β -Ti(PO₄)(H₂PO₄) projected along [010]. Octahedra represent TiO₆; dark grey tetrahedra represent tertiary phosphate groups (PO₄); light grey tetrahedra represent dihydrogen phosphate groups ((OH)₂PO₂); black circles represent hydrogen atoms.

TABLE 4
Bond Lengths (Å) and Angles (°) for β -Ti(PO₄)(H₂PO₄) with
Esd's in Parentheses

Ti-O1	1.910(12)	Ti-O4	1.938(12)
Ti-O2	1.942(12)	Ti-O5	1.921(11)
Ti-O3	1.956(12)	Ti-O6	1.926(12)
O1-Ti-O2	85.6(7)	O2-Ti-O6	92.9(6)
O1-Ti-O3	177.9(8)	O3-Ti-O4	95.6(7)
O1-Ti-O4	84.4(7)	O3-Ti-O5	88.3(7)
O1-Ti-O5	89.6(6)	O3-Ti-O6	93.4(7)
O1-Ti-O6	86.4(7)	O4-Ti-O5	90.7(6)
O2-Ti-O3	96.5(7)	O4-Ti-O6	170.4(8)
O2-Ti-O4	90.2(6)	O5-Ti-O6	86.4(5)
O2-Ti-O5	175.0(9)		
P2-O1	1.487(11)	P1-O5	1.485(11)
P2-O2	1.508(10)	P1-O6	1.580(11)
P2-O3	1.582(11)	P1-O7	1.601(11)
P2-O4	1.512(9)	P1-O8	1.629(11)
O1-P2-O2	109.8(8)	O5-P1-O6	113.1(8)
O1-P2-O3	106.8(6)	O5-P1-O7	113.4(9)
O1-P2-O4	116.5(8)	O5-P1-O8	113.1(8)
O2-P2-O3	111.8(9)	O6-P1-O7	105.1(9)
O2-P2-O4	109.7(6)	O6-P1-O8	97.6(7)
O3-P2-O4	101.9(8)	O7-P1-O8	113.2(9)
Ti-O1-P2	148.3(8)	Ti-O4-P2	163.4(8)
Ti-O2-P2	150.8(8)	Ti-O5-P1	135.8(8)
Ti-O3-P2	136.1(9)	Ti-O6-P1	154.1(9)
H1-O7	0.80(4)	H2-O8	1.12(3)
H1-O8	1.74(3)	H2-O3	1.87(3)
O7-O8	2.499(20)	O8-O3	2.754(16)
O7-H1-O8	137.4(15)	O3-H2-O8	133.1(16)
P1-O7-H1	116.9(18)	P1-O8-H2	105.4(13)
P1-O8-H1	122.3(12)	P1-O3-H2	112.4(8)

The layers are held together by hydrogen bonds. The dihydrogen phosphate groups are hydrogen bonded pairwise in an edge-sharing manner, seen most clearly in Fig. 4. The strongest bond is between O7 and O8 (O-O distance 2.5 Å). The refined O7-H1 distance is 0.80 Å and the O7-H1-O8 angle is 137.4°. The second hydrogen bond is longer, O-O distance 2.8 Å, connecting O8 and O3. The refined O8-H2 distance is 1.12 Å and the O8-H2-O3 angle is 133.1°.

The mean P-O distance in β -titanium phosphate is 1.55 Å while the P-OH distances are 1.60 Å and 1.64 Å. This is in accordance with the observation that P-OH bonds generally are longer than P-O bonds in primary and secondary phosphates (18–20). As can be seen from Table 4 the hydrogen bond to O3 causes the P2-O3 bond to be relatively long (1.58 Å). The elongation of the P-OH bonds leads to a distortion of the dihydrogen phosphate tetrahedron, where the tertiary phosphate tetrahedron is relatively regular as can be seen from Table 4.

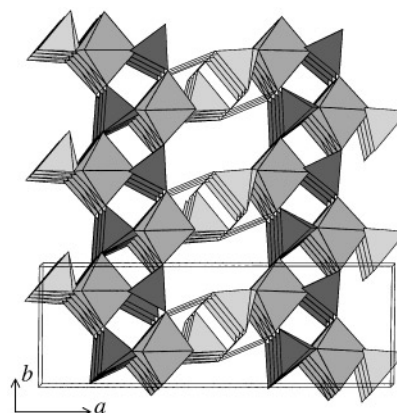


FIG. 4. Polyhedral representation of the crystal structure of β -Ti(PO₄)(H₂PO₄) projected along [001]. Octahedra represent TiO₆; dark grey tetrahedra represent tertiary phosphate groups (PO₄); light grey tetrahedra represent dihydrogen phosphate groups ((OH)₂PO₂).

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