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Neutron powder diffraction study of α-Ti(HPO_4)$_2$.H_2O and α-Hf(HPO_4)$_2$.H_2O; H-atom positions

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Abstract

The complete crystal structures, including H-atom positions, of α-Ti(HPO_4)$_2$.H_2O (α-TiP) and α-Hf(HPO_4)$_2$.H_2O (αHfP) were determined by Rietveld refinement and Fourier synthesis, using constant-wavelength neutron diffraction data. This work is one of few recent examples of the determination of H atoms using neutron powder diffraction with an intense source. The orientation of water molecules in the cavities of α-TiP is similar to that previously found for α-ZrP. For α-HfP, although the hydrogen-bonding scheme is identical, the orientation of water molecules in similar cavities was found to be different.

1. Introduction

The layered phosphates of group IV elements have been synthesized (Llavona, García, Suárez & Rodríguez, 1985; Nakai *et al.*, 1990) and widely investigated due to their practical applications in many fields: ion exchange (Clearfield, 1982), intercalation (Clearfield, 1982; Kijima & Matsui, 1986), proton conduction (Clearfield, 1991), catalysis (Maireles-Torres *et al.*, 1992) *etc.* These compounds are obtained as microcrystalline powders, but the crystals are hardly ever large enough for study with single-crystal techniques.

In order to understand the complete behaviour of these compounds the determination of H-atom positions becomes a fundamental issue (Albertsson, Oskarsson, Tellgren & Thomas, 1977; Rudolf & Clearfield, 1985) and the most appropriate technique is neutron diffraction. The deuteration of samples is the best way to avoid the effect of the large spin-incoherence for hydrogen. Nevertheless, in some cases this technique is not adequate. In fact, a recent study of deuterated α-titanium phosphate (Bruque, Aranda, Losilla, Olivera-Pastor & Maireles-Torres, 1995) has revealed that deuteration leads to less crystalline samples and, more importantly, the presence of hydrogen bonds implies changes in the fine structure when hydrogen is substituted by deuterium.

In spite of the large incoherent contribution, full information about the positions of H atoms can be obtained and this work is one example of the determination of H-atom positions using neutron powder diffraction with an intense source (Harrison, McManus, Kaminsky & Cheetham, 1993; Harrison, Gier, Nicol & Stucky, 1995). The complete crystal structure, including all H-atom positions of α-Ti(HPO_4)$_2$.H_2O (α-TiP) and α-Hf(HPO_4)$_2$.H_2O (α-HfP), have been determined by Rietveld refinement and Fourier synthesis, using constant-wavelength neutron diffraction data.

2. Experimental

The α-TiP was obtained by the method described by Alberti, Cardini-Galli, Constantino & Torracca (1967) using 10 *M* H_3PO_4 and reflux times of 50 h. The α-HfP was synthesized by a similar procedure, using 12 *M* H_3PO_4 and a reflux time of 245 h (Rodríguez, Suárez, García & Rodríguez, 1993).

Powder X-ray diffraction patterns were recorded on a Philips diffractometer using graphite-monochromated Cu $K\alpha$ radiation operating in Bragg–Brentano ($\theta/2\theta$) geometry. For the neutron diffraction experiment 5 cm^3 samples were loaded into a cylindrical vanadium can and room-temperature neutron diffraction data were collected using the powder diffractometer D2B, operating in high-intensity mode at the Institut Laue–Langevin (Grenoble, France). Data were collected over the range 5–159°, with a step size of 0.05°; wavelength 1.59 Å. No absorption correction was made.

Rietveld refinements on X-ray and neutron data were carried out using the program *FULLPROF* (Rodríguez-Carvajal, 1990). The input model for X-ray refinement of α-TiP (Salvadó & García-Granda, 1992) was the structure of α-Zr(HPO_4)$_2$.2H_2O [α-ZrP (Clearfield & Smith, 1969)]. X-ray refinement of α-HfP was carried out using coordinates of α-TiP from this previous study. For the neutron refinement of both structures the starting atomic model, with all non-H atomic positions, was the previous result from the powder X-ray study.

A difference-Fourier synthesis was made on α-TiP using *SHELXL*93 (Sheldrick, 1993) and 'observed' F^2 from neutron refinement, showing the positions of all H atoms as the deepest holes. In the α-HfP case, successive difference-Fourier syntheses combined with Rietveld refinements were necessary to locate the four H atoms. After that the completed structure including hydrogen positions and isotropic temperature factors were refined. The temperature factors of each discrete atom type were constrained to have the same value except O9, which was refined independently. Final refinement yields good agreement factors and minimal profile differences.† All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray Group VAX computers. The crystallographic plots were obtained using *EUCLID* (Spek, 1982).

3. Results and discussion

Details of the refinement parameters are given in Table 1. The final difference plots of the neutron Rietveld refinement are shown in Figs. 1 and 2, while the atomic parameters are contained in Tables 2 and 3. All thermal parameters range within normal values.

This study brings further proof that the positions of the H atoms can be obtained from powder neutron diffraction data

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† Lists of atomic coordinates, complete geometry and neutron powder data have been deposited with the IUCr (Reference: AN0530). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

without previous deuteration. The strong background due to incoherent scattering of hydrogen nuclei is not a limiting factor for the Rietveld method, because all background contributions are included either by interpolation or polynomial refinement. The coherent scattering contribution from H atoms is enough to obtain information on the positions of the protons. This fact becomes evident observing Fig. 1(*b*), which shows the status of refinement of α-TiP without hydrogen and Fig. 1(*a*) with final refinement.

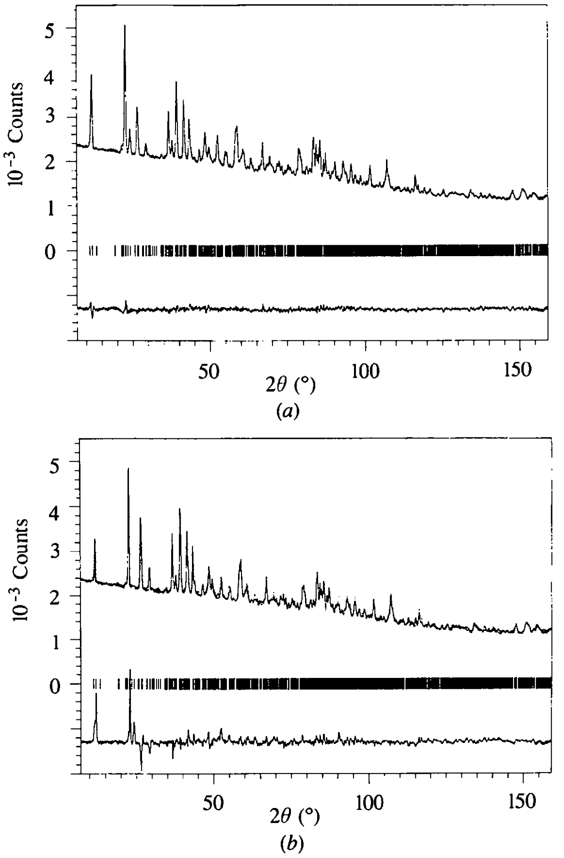

Fig. 1. Neutron diffraction patterns of (*a*) α-Ti$(HPO_4)_2$.H_2O and (*b*) α-Ti$(HPO_4)_2$.H_2O, without H atoms. Points correspond to observed data; the solid line is the calculated profile. Tick marks show the positions of allowed reflections and a difference curve, in the same scale, is plotted at the bottom of the pattern.

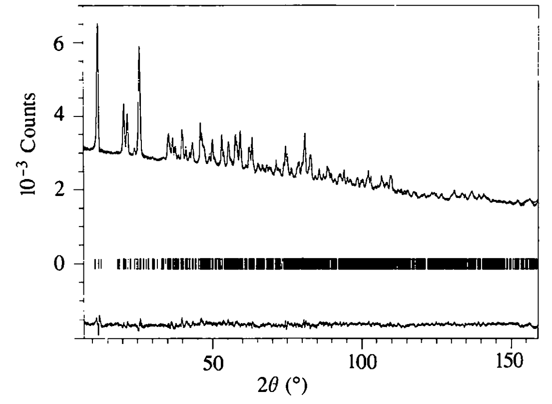

Fig. 2. Neutron diffraction pattern of α-Hf$(HPO_4)_2$.H_2O.

Table 1. *Structural parameters for α-Ti$(HPO_4)_2$.H_2O and α-Hf$(HPO_4)_2$.H_2O*

Empirical formula	$TiP_2O_9H_4$	$HfP_2O_9H_4$
Formula weight	257.87	388.46
Cell setting	Monoclinic	Monoclinic
a (Å)	8.6110 (3)	8.9955 (5)
b (Å)	4.9933 (2)	5.2439 (3)
c (Å)	16.1507 (7)	16.224 (1)
β (°)	110.206 (3)	111.234 (4)
V (Å³)	651.70 (5)	713.37 (8)
Z	4	4
Space group	$P2_1/c$	$P2_1/c$
No. of parameters	71	71
R_{wp}*	1.67	1.66
R_{exp}†	1.05	0.90
R_F‡	4.45	4.38
χ^2§	2.54	3.43

* $R_{wp} = \{[\sum_i w_1(y_{i,\mathrm{obs}} - y_{i,\mathrm{calc}})^2]/[\sum_i w_i(y_{i,\mathrm{obs}})^2]\}^{1/2}$. † $R_F = [\sum_K |(I_{K,\mathrm{obs}})^{1/2} - (I_{K,\mathrm{calc}})^{1/2}|]/[\sum_K (I_{K',\mathrm{obs'}})^{1/2}]$ ‡ $R_{exp} = R_{wp}/(\chi^2)^{1/2}$. § $\chi^2 = \sum_i\{[w_i(y_{\mathrm{obs}} - y_{\mathrm{calc}})^2]/(N_{\mathrm{obs}} - N_{\mathrm{var}})\}$, where N_{obs} and N_{var} = number of observations and variables.

Table 2. *Fractional atomic coordinates and isotropic displacement parameters (Å²) for α-TiP*

	x	*y*	*z*	U_{iso}
Ti1	0.7588 (13)	0.243 (3)	0.5103 (7)	0.0045 (15)
P1	−0.0001 (9)	0.746 (2)	0.6090 (4)	0.0074 (9)
P2	0.4680 (8)	0.236 (2)	0.6014 (4)	0.0074 (9)
O1	0.1149 (9)	0.8320 (15)	0.5580 (4)	0.0127 (4)
O2	−0.0657 (8)	0.4656 (15)	0.5903 (4)	0.0127 (4)
O3	−0.1452 (9)	0.9502 (16)	0.5906 (5)	0.0127 (4)
O4	0.0962 (7)	0.7610 (19)	0.7105 (3)	0.0127 (4)
O5	0.3223 (9)	0.4344 (14)	0.5537 (5)	0.0127 (4)
O6	0.4220 (9)	−0.0463 (16)	0.5648 (5)	0.0127 (4)
O7	0.6332 (10)	0.3299 (15)	0.5875 (5)	0.0127 (4)
O8	0.5117 (7)	0.2529 (19)	0.7033 (4)	0.0127 (4)
O9	0.2553 (9)	0.2240 (14)	0.7617 (5)	0.0156 (14)

Table 3. *Fractional atomic coordinates and isotropic displacement parameters (Å²) for α-HfP*

	x	*y*	*z*	U_{iso}
Hf1	0.7373 (8)	0.2519 (19)	0.4853 (4)	0.0021 (11)
P1	−0.0238 (11)	0.753 (3)	0.6095 (5)	0.0078 (12)
P2	0.4976 (12)	0.234 (2)	0.6129 (5)	0.0078 (12)
O1	0.1231 (12)	0.813 (2)	0.5968 (6)	0.0122 (6)
O2	−0.0830 (11)	0.472 (2)	0.5713 (6)	0.0122 (6)
O3	−0.1661 (12)	0.939 (2)	0.5610 (7)	0.0122 (6)
O4	0.0120 (9)	0.746 (2)	0.7067 (5)	0.0122 (6)
O5	0.3639 (12)	0.447 (2)	0.5901 (7)	0.0122 (6)
O6	0.4287 (14)	−0.017 (2)	0.5955 (7)	0.0122 (6)
O7	0.5981 (10)	0.303 (2)	0.5571 (6)	0.0122 (6)
O8	0.6004 (10)	0.259 (2)	0.7110 (5)	0.0122 (6)
O9	0.2370 (15)	0.222 (2)	0.7406 (7)	0.029 (2)

Once the structures are known it is interesting to compare the forms of the two *zeolitic* cavities, since the active centres (H atoms) of the materials are located in the cavities. Fig. 3 illustrates the geometry of the cavities in α-TiP and α-HfP structures and Table 4 contains the geometry of the water molecule and the hydrogen bonds. The forms of the two cavities resemble each other, except for minor differences.

Comparison of α-TiP H-atom positions with those refined previously in α-ZrP (Albertsson, Oskarsson, Tellgren & Thomas, 1977) reveals a similar disposition. Although α-HfP was refined from α-TiP because it was assumed that they are isostructural, small displacements of O4 and O8 atoms make similar cavities translated in the structure. In fact, when we try to refine H-atom positions from α-TiP in the structure of α-HfP, the refinement does not progress correctly. Furthermore, for similar cavities the orientation of the water molecule is different in both compounds. In spite of this effect, the topological distribution of hydrogen bonding is similar in both cases.

We are in the process of applying this technique to the γ-forms of the metal(IV) phosphates: γ-$M(H_2PO_4)(PO_4).2H_2O$ (M = Ti, Zr).

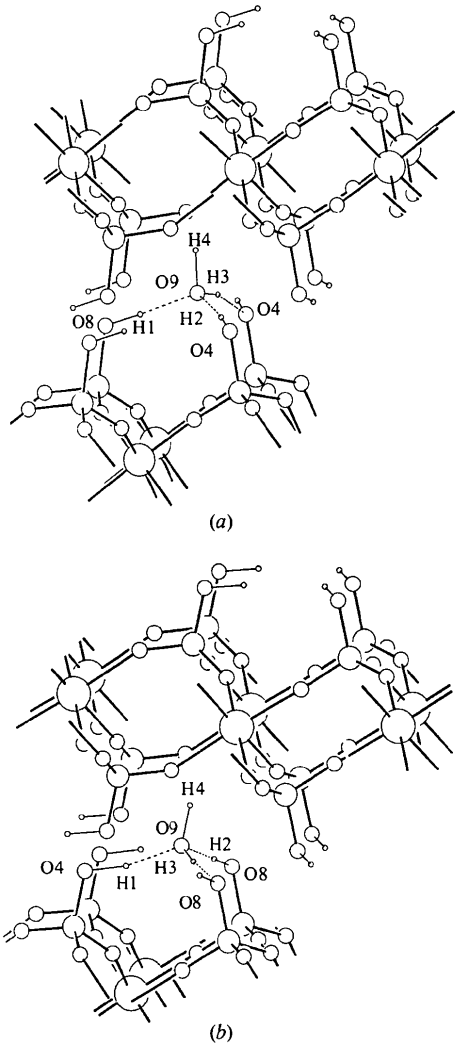

Fig. 3. Cavities in the structure of (*a*) α-$Ti(HPO_4)_2.H_2O$ and (*b*) α-$Hf(HPO_4)_2.H_2O$.

Table 4. *Hydrogen-bond geometry (Å,°)**

	α-TiP	α-HfP
O8[O4]—H1	1.01 (2)	1.13 (3)
O8···O9	2.69 (1)	2.67 (2)
H1···O9	1.68 (2)	1.69 (3)
O8[O4]—H1···O9	177 (1)	143 (2)
O9—H3	0.97 (2)	0.90 (2)
O9···O4[O8]	2.99 (1)	2.79 (2)
H3···O4[O8]	2.06 (2)	1.90 (2)
O9—H3···O4[O8]	163 (1)	170 (2)
O4[O8]—H2	1.00 (2)	1.08 (2)
O4[O8]···O9	2.67 (1)	3.14 (2)
H2···O9	1.68 (2)	2.06 (2)
O4[O8]—H2···O9	170 (1)	178 (2)
O9—H4	1.12 (1)	1.11 (2)
H3—O9—H4	96 (1)	107 (2)

* The O atoms between square brackets are for α-HfP.

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References

Alberti, G., Cardini-Galli, P., Constantino, U. & Torracca, E. (1967). *J. Inorg. Nucl. Chem.* **29**, 571–578.

Albertsson, J., Oskarsson, Å., Tellgren, R. & Thomas, J. O. (1977). *J. Phys. Chem.* **81**, 1574–1578.

Bruque, S., Aranda, M. A. G., Losilla, E. R., Olivera-Pastor, P. & Maireles-Torres, P. (1995). *Inorg. Chem.* **34**, 893–899.

Clearfield, A. (1982). Editor. *Inorganic Ion Exchange Materials*. Boca Raton, Florida: CRC Press.

Clearfield, A. (1991). *Solid State Ion.* **46**, 35–43.

Clearfield, A. & Smith, G. D. (1969). *Inorg. Chem.* **8**, 431–436.

Harrison, W. T. A., Gier, T. E., Nicol, J. M. & Stucky, G. D. (1995). *J. Solid State Chem.* **114**, 249–257.

Harrison, W. T. A., McManus, A. V. P., Kaminsky, M. P. & Cheetham, A. K. (1993). *Chem. Mater.* **5**, 1631–1635.

Kijima, T. & Matsui, Y. (1986). *Nature*, **322**, 533–534.

Llavona, R., García, J. R., Suárez, M. & Rodríguez, J. (1985). *Thermochim. Acta*, **86**, 281–289.

Maireles-Torres, P., Jiménez-López, A., Oliveira-Pastor, P., Rodríguez-Ramos, I., Guerrero-Ruiz, A. & García-Fierro, J. L. (1992). *Appl. Catal.* **92**, 81–92.

Nakai, I., Imai, K., Kawashima, T., Ohsumi, K., Izumi, F. & Tomita, I. (1990). *Anal. Sci.* **6**, 689–693.

Rodríguez, M. L., Suárez, M., García, J. R. & Rodríguez, J. (1993). *Solid State Ion.* **63**, 488–493.

Rodríguez-Carvajal, J. (1990). *FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis.* Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, p. 127. Toulouse: France.

Rudolf, P. R. & Clearfield, A. (1985). *Inorg. Chem.* **24**, 3714–3715.

Salvadó, M. A. & García-Granda, S. (1992). Internal Report. X-ray Laboratory. University of Oviedo, Spain (in Spanish).

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.