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# Preparation and Characterization of a New 3-Dimensional Zirconium Hydrogen Phosphate, τ-Zr(HPO$_4$)$_2$. Determination of the Complete Crystal Structure Combining Synchrotron X-ray Single-Crystal Diffraction and Neutron Powder Diffraction

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A new 3-dimensional zirconium hydrogen phosphate, $\tau$-Zr(HPO$_4$)$_2$, was prepared by hydrothermal syntheses. The preparation, characterization, and determination of the crystal structure of this new material are reported. The structure was solved from single-crystal synchrotron diffraction on a $25 \times 25 \times 50$ $\mu$m crystal. The position of the hydrogen atom was found using high-resolution neutron powder diffraction data. The unit cell is tetragonal, space group $I4_1cd$ (No. 110), with lattice parameters $a = 11.259(1)$ Å, $c = 10.764(1)$ Å, and $Z = 8$. The structure can be described as a 3-dimensional framework built from ZrO$_6$ octahedra bound together by hydrogen phosphate groups (PO$_3$(OH)). The OH groups form a hydrogen-bonded spiral along the 4$_1$ axes, with each hydrogen phosphate both donating and accepting hydrogen bonds. The thermal transformations of $\tau$-Zr(HPO$_4$)$_2$ were studied using in-situ temperature-resolved powder diffraction experiments. Hereby the existence of two new phases was discovered. The new phases have been indexed and the unit cell parameters are as follows. Intermediate I: $a = 8.172(1)$, $b = 7.691(1)$, and $c = 10.794(2)$ Å. Intermediate II: $a = 8.283(2)$, $b = 6.620(2)$, and $c = 10.643(2)$ Å.

## Introduction

Insoluble acid salts of tetravalent metals with layered structure have been studied extensively over the last 40 years because of their ion-exchange, intercalation, and ion conductivity properties. Two different types of crystalline layered phosphates have been characterized: the α-type compounds with the general formula α-M$^{IV}$(HPO$_4$)$_2$·H$_2$O (M$^{IV}$ = Zr, Ti, Sn, Pb, etc.) and the $\gamma$-type compounds with the general formula $\gamma$-M$^{IV}$(PO$_4$)(H$_2$PO$_4$)·2H$_2$O (M$^{IV}$ = Zr, Ti).

The α-type layers consist of octahedrally coordinated metal atoms bound together by hydrogen phosphate groups. Three oxygen atoms of each phosphate group are bonded to three different metal atoms. The OH group points away from the layer. The water molecules are situated in cavities in the interlayer region, and hydrogen bonds are present between the OH group and the water molecule.[1]

The $\gamma$-type layers consist of octahedrally coordinated metal atoms linked together by tertiary phosphate groups (PO$_4^{3-}$) and dihydrogen phosphate groups (PO$_2$(OH)$_2^-$). The PO$_4$ tetrahedra are sandwiched between two layers of metal octahedra, so that all four oxygen atoms bind to zirconium atoms. In the dihydrogen phosphate groups two oxygen atoms bind to zirconium atoms and the two remaining oxygen atoms form OH groups which point toward the interlayer space.[2]

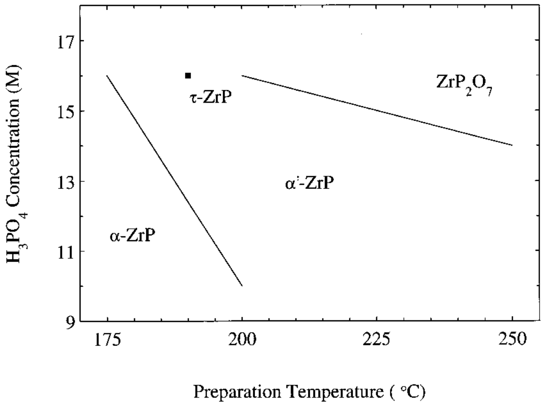

**Figure 1.** Sketch of the formation region of zirconium hydrogen phosphates.

During studies on the hydrothermal synthesis of α- and $\gamma$-zirconium phosphate we have discovered a new zirconium hydrogen phosphate phase.[3] The new phase ($\tau$-ZrP) has a very narrow window of formation, and it forms under conditions very close to those for cubic zirconium pyrophosphate, ZrP$_2$O$_7$. The composition of the new phase is identical with that of anhydrous α-ZrP (*i.e.* Zr(HPO$_4$)$_2$), and the powder pattern resembles the powder patterns of a phase with unknown structure described

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**Table 1.** Indexed X-ray Powder Diffraction Pattern for τ-$Zr(HPO_4)_2$[a]

| *h* | *k* | *l* | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ | *h* | *k* | *l* | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 0 | 0 | 5.6294 | 5.6334 | 100 | 6 | 4 | 2 | 1.4995 | 1.4996 | 1 |
| 2 | 1 | 1 | 4.5608 | 4.5583 | 13 | 6 | 2 | 4 | 1.4847 | 1.4848 | 4 |
| 1 | 1 | 2 | 4.4586 | 4.4590 | 29 | 7 | 3 | 0 | 1.4784 | 1.4788 | 1 |
| 2 | 2 | 0 | 3.9806 | 3.9815 | 7 | 2 | 1 | 7 | 1.4706 | 1.4707 | 1 |
| 2 | 0 | 2 | 3.8901 | 3.8887 | 39 | 4 | 2 | 6 | 1.4610 | 1.4614 | 1 |
| 3 | 1 | 0 | 3.5604 | 3.5606 | 31 | 7 | 3 | 2 | 1.4256 | 1.4256 | 4 |
| 3 | 2 | 1 | 2.9990 | 2.9993 | 2 | 7 | 2 | 3 | 1.4202 | 1.4201 | 1 |
| 3 | 1 | 2 | 2.9694 | 2.9696 | 79 | 8 | 0 | 0 | 1.4074 | 1.4074 | 1 |
| 2 | 1 | 3 | 2.9219 | 2.9224 | 2 | 6 | 1 | 5 | 1.4035 | 1.4035 | 1 |
| 4 | 0 | 0 | 2.8147 | 2.8149 | 37 | 5 | 1 | 6 | 1.3923 | 1.3925 | 1 |
| 0 | 0 | 4 | 2.6909 | 2.6908 | 6 | 7 | 4 | 1 | 1.3849 | 1.3852 | 1 |
| 4 | 1 | 1 | 2.6468 | 2.6465 | 3 | 5 | 5 | 4 | 1.3703 | 1.3706 | 1 |
| 4 | 2 | 0 | 2.5176 | 2.5169 | 4 | 8 | 2 | 0 | 1.3653 | 1.3651 | 3 |
| 4 | 0 | 2 | 2.4942 | 2.4935 | 1 | 8 | 0 | 2 | 1.3616 | 1.3614 | 1 |
| 2 | 0 | 4 | 2.4278 | 2.4272 | 2 | 6 | 4 | 4 | 1.3505 | 1.3504 | 6 |
| 3 | 3 | 2 | 2.3801 | 2.3804 | 1 | 0 | 0 | 8 | 1.3454 | 1.3456 | 1 |
| 3 | 2 | 3 | 2.3555 | 2.3556 | 1 | 6 | 5 | 3 | 1.3376 | 1.3379 | 1 |
| 4 | 2 | 2 | 2.2804 | 2.2806 | 1 | 6 | 6 | 0 | 1.3269 | 1.3267 | 2 |
| 2 | 2 | 4 | 2.2293 | 2.2290 | 2 | 8 | 2 | 2 | 1.3234 | 1.3234 | 1 |
| 4 | 3 | 1 | 2.2041 | 2.2054 | 1 | 5 | 3 | 6 | 1.3143 | 1.3143 | 2 |
| 4 | 1 | 3 | 2.1729 | 2.1727 | 1 | 7 | 5 | 0 | 1.3088 | 1.3088 | 1 |
| 3 | 1 | 4 | 2.1467 | 2.1467 | 2 | 7 | 4 | 3 | 1.3014 | 1.3014 | 1 |
| 5 | 2 | 1 | 2.0524 | 2.0525 | 1 | 7 | 3 | 4 | 1.2957 | 1.2956 | 1 |
| 5 | 1 | 2 | 2.0428 | 2.0430 | 13 | 7 | 5 | 2 | 1.2718 | 1.2716 | 5 |
| 4 | 4 | 0 | 1.9903 | 1.9898 | 1 | 6 | 2 | 6 | 1.2636 | 1.2634 | 1 |
| 2 | 1 | 5 | 1.9794 | 1.9795 | 1 | 9 | 1 | 0 | 1.2433 | 1.2435 | 1 |
| 4 | 0 | 4 | 1.9451 | 1.9447 | 12 | 8 | 3 | 3 | 1.2370 | 1.2368 | 1 |
| 4 | 3 | 3 | 1.9073 | 1.9072 | 1 | 8 | 2 | 4 | 1.2176 | 1.2176 | 1 |
| 6 | 0 | 0 | 1.8765 | 1.8764 | 20 | 7 | 6 | 1 | 1.2134 | 1.2138 | 1 |
| 4 | 2 | 4 | 1.8384 | 1.8379 | 12 | 9 | 1 | 2 | 1.2114 | 1.2114 | 3 |
| 6 | 1 | 1 | 1.8242 | 1.8238 | 2 | 6 | 5 | 5 | 1.1978 | 1.1972 | 1 |
| 5 | 3 | 2 | 1.8175 | 1.8174 | 16 | 5 | 5 | 6 | 1.1908 | 1.1907 | 4 |
| 6 | 2 | 0 | 1.7802 | 1.7798 | 9 | 7 | 5 | 4 | 1.1770 | 1.1770 | 1 |
| 1 | 1 | 6 | 1.7500 | 1.7504 | 2 | 7 | 4 | 5 | 1.1716 | 1.1715 | 1 |
| 5 | 4 | 1 | 1.7353 | 1.7355 | 1 | 9 | 3 | 2 | 1.1589 | 1.1589 | 2 |
| 5 | 1 | 4 | 1.7069 | 1.7068 | 3 | 7 | 6 | 3 | 1.1561 | 1.1561 | 1 |
| 6 | 2 | 2 | 1.6901 | 1.6902 | 3 | 8 | 4 | 4 | 1.1402 | 1.1407 | 2 |
| 6 | 3 | 1 | 1.6583 | 1.6581 | 1 | 9 | 4 | 1 | 1.1368 | 1.1368 | 1 |
| 6 | 1 | 3 | 1.6450 | 1.6451 | 1 | 8 | 6 | 0 | 1.1259 | 1.1260 | 3 |
| 4 | 4 | 4 | 1.6002 | 1.6009 | 6 | 7 | 7 | 2 | 1.1127 | 1.1128 | 1 |
| 5 | 4 | 3 | 1.5789 | 1.5790 | 1 | 8 | 0 | 6 | 1.1073 | 1.1069 | 1 |
| 6 | 4 | 0 | 1.5613 | 1.5615 | 5 | 10 | 2 | 0 | 1.1040 | 1.1039 | 3 |
| 6 | 0 | 4 | 1.5392 | 1.5391 | 4 | 8 | 6 | 2 | 1.1020 | 1.1019 | 1 |
| 5 | 5 | 2 | 1.5268 | 1.5266 | 14 |  |  |  |  |  |  |

[a] Indexing based on a tetragonal unit cell: $a = b = 11.259(1)$ Å, $c = 10.764(1)$ Å. Unit cell volume = 1364.42 Å$^3$.

**Table 2.** Chemical and Crystallographic Data for τ-$Zr(HPO_4)_2$[a]

|  | X-ray data | neutron data |
|---|---|---|
| $a$ (Å) | 11.255(2) | 11.2611(1) |
| $c$ (Å) | 10.750(2) | 10.7688(1) |
| $V$ (Å$^3$) | 1361.8(4) | 1365.62 |
| $\lambda$ (Å) | 0.9542 | 1.8857 |
| R1 | 3.5 |  |
| wR2 | 9.3 |  |
| GooF | 0.796 |  |
| $R_p$ |  | 3.0 |
| $R_{wp}$ |  | 4.0 |
| $\chi^2$ |  | 4.23 |

[a] Fw = 286 g/mol; $d_{obsd} = 2.78$ g/cm$^3$; space group $I4_1cd$ (No. 110); $Z = 8$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$. $GooF = S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{\frac{1}{2}}$. $R_p = \Sigma(y_i(obs) - y_i(calc))/\Sigma y_i(obs)$. $R_{wp} = [\Sigma w_i(y_i(obs) - y_i(calc))^2/\Sigma w_i(y_i(obs))^2]^{\frac{1}{2}}$. $\chi^2 = [\Sigma w_i(y_i(obs) - y_i(calc))^2/(N_{obs} - N_{var})]$.

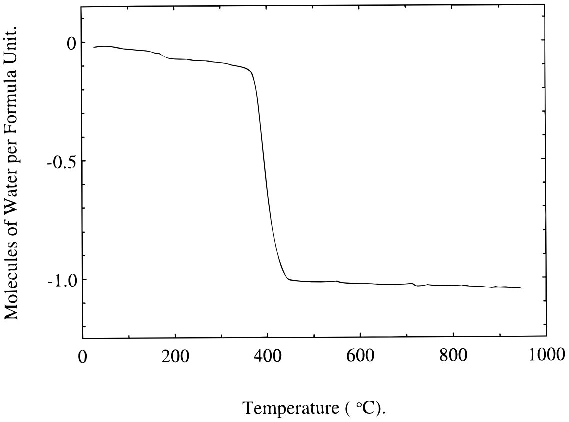

**Figure 2.** TGA curve for τ-$Zr(HPO_4)_2$.

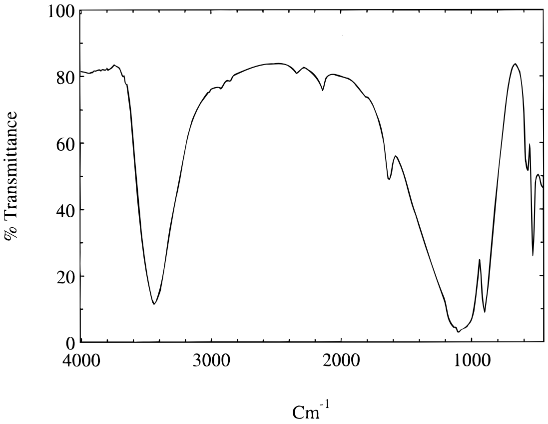

**Figure 3.** IR Spectrum for τ-$Zr(HPO_4)_2$.

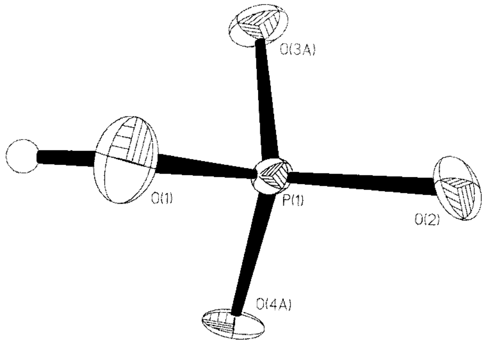

**Figure 4.** ORTEP plot of the $HPO_4$ tetrahedron. The probability level is 50%.

by Clearfield *et al.*[4] and Segawa *et al.*[5] Contrary to the known phases of zirconium phosphate, this material proved to have a 3-dimensional framework structure built from $ZrO_6$ octahedra bound together by $HPO_4$ tetrahedra. The prefix τ was chosen to distinguish the new 3-dimensional framework structure from the bidimensional, layered phosphates.

## Experimental Section

**Preparation.** The chemicals used in the preparation were $ZrCl_4$ (Fluka, >98%), orthophosphoric acid (Fluka, 89%), and hydrochloric acid (37%).

τ-ZrP was prepared by autoclave synthesis. The starting material, amorphous zirconium phosphate, was prepared by dissolving 30.7 g of $ZrCl_4$ in 430 mL of 2 M HCl. This solution was then added to 400 mL of 1.25 M $H_3PO_4$. The resulting solid was allowed to stand overnight and was then separated by filtration, washed with water, and air-dried.

In the preparations of τ-ZrP 1.5 g of amorphous zirconium phosphate was stirred with 10 mL of 89% $H_3PO_4$ for 48 h. The resulting gel was then transferred to a Teflon-lined autoclave which was placed in an oven and slowly heated to 190 °C and kept at this temperature for 4−6 days. After cooling, the product was separated from the liquid,

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**Table 3.** Atomic Positions and Thermal Parameters (with Esd's in Parentheses) for $\tau$-Zr(HPO$_4$)$_2$ with Values from Refinement of the Neutron Powder Diffraction Data in Brackets

| | $x$ | $y$ | $z$ | $U_{eq}{}^{a}$ [$U_{iso}$] (Å$^2$) |
|---|---|---|---|---|
| Zr | 0 | 0 | 0$^b$ | 0.18(4) [1.26(7)] |
| P | 0.1953(1) [0.1961(3)] | 0.0392(1) [0.0393(3)] | −0.2488(11) [−0.2463(11)] | 1.11(4) [1.40(9)] |
| O(1) | 0.2066(5) [0.2095(4)] | 0.1788(4) [0.1789(3)] | −0.2547(13) [−0.2533(11)] | 2.72(13) [3.07(10)] |
| O(2) | 0.1289(8) [0.1340(7)] | 0.0146(5) [0.0138(5)] | −0.1299(13) [−0.1273(10)] | 2.25(18) [3.4(2)] |
| O(3) | −0.0144(4) [−0.0146(4)] | 0.1818(3) [0.1839(3)] | 0.006(1) [0.0019(12)] | 2.09(12) [2.21(19)] |
| O(4) | −0.1295(8) [−0.1283(6)] | −0.0047(4) [−0.0037(4)] | 0.1386(13) [0.1427(11)] | 1.79(20) [1.28(13)] |
| H | 0.241(9) [0.2290(10)] | 0.1979(6) [0.2023(9)] | −0.319(5) [−0.3275(13)] | 3$^c$ [7.4(3)] |

[a] $U_{eq} = (^1/_3\Sigma_i\Sigma_j U_{ij} a_i{}^* a_j{}^* a_i a_j) \times 100$. [b] $z$ (Zr) fixed in order to define origin. [c] The value was restrained during refinement.

**Table 4.** Bond Lengths (Å) and Angles (deg) for $\tau$-Zr(HPO$_4$)$_2$ with Esd's in Parentheses

| | X-ray data | neutron data | | X-ray data | neutron data |
|---|---|---|---|---|---|
| Zr−O(2) | 2.020(12) × 2 | 2.044(9) × 2 | O(2)−Zr−O(2) | 91.4(7) | 95.8(5) |
| Zr−O(3) | 2.054(4) × 2 | 2.078(3) × 2 | O(2)−Zr−O(3) | 89.4(2) × 2 | 89.4(3) × 2 |
| Zr−O(4) | 2.085(12) × 2 | 2.110(9) × 2 | O(2)−Zr−O(3) | 92.1(5) × 2 | 91.4(4) × 2 |
| | | | O(2)−Zr−O(4) | 176.8(2) × 2 | 174.4(4) × 2 |
| $V_i a$ | 4.29 | 4.02 | O(2)−Zr−O(4) | 89.4(2) × 2 | 89.0(1) × 2 |
| | | | O(3)−Zr−O(3) | 178.1(14) | 178.9(7) |
| | | | O(3)−Zr−O(4) | 91.1(6) × 2 | 91.6(3) × 2 |
| | | | O(3)−Zr−O(4) | 87.6(5) × 2 | 87.6(3) × 2 |
| | | | O(4)−Zr−O(4) | 89.9(7) | 86.5(5) |
| P−O(1) | 1.577(4) | 1.580(5) | O(1)−P−O(2) | 105.0(4) | 106.1(4) |
| P−O(2) | 1.506(10) | 1.489(10) | O(1)−P−O(3) | 109.0(3) | 108.7(3) |
| P−O(3) | 1.510(4) | 1.481(5) | O(1)−P−O(4) | 109.4(4) | 109.4(4) |
| P−O(4) | 1.503(11) | 1.499(9) | O(2)−P−O(3) | 111.1(10) | 111.1(5) |
| | | | O(2)−P−O(4) | 112.3(3) | 112.6(3) |
| $V_i{}^a$ | 5.16 | 5.34 | O(3)−P−O(4) | 109.8(9) | 108.8(4) |
| | | | Zr−O(2)−P | 163.9(7) | 159.9(5) |
| | | | Zr−O(3)−P | 151.7(3) | 151.2(3) |
| | | | Zr−O(4)−P | 155.4(4) | 157.4(4) |
| H(1)−O(1) | 0.820$^b$ | 0.870(13) | P−O(1)−H(1) | 109.5(3) | 111.7(8) |
| H(1)−O(1) | 2.19(7) | 2.160(13) | O(1)−H(1)−O(1) | 166(3) | 159.7(10) |

[a] The bond valencies have been calculated according to ref 23. The values for the oxygen atoms are in the range 2.02−2.30 for the X-ray data and 1.99−2.14 for the neutron data. [b] The O(1)−H(1) distance was restrained to 0.820 Å.

washed with water, and air-dried. The materials obtained from these preparations were microcrystalline powders, but in one preparation very small single crystals (about 25 × 25 × 50 $\mu$m) were obtained.

Figure 1 shows a sketch of the formation region of the various zirconium phosphates as a function of the molarity of the phosphoric acid and the preparation temperature.[3] The materials obtained were α-ZrP, α′-ZrP (a form with lower water content, probably the hemihydrate, Zr(HPO$_4$)$_2$·0.5H$_2$O[6]), zirconium pyrophosphate, and $\tau$-ZrP. The window of formation of $\tau$-ZrP is very narrow, and $\tau$-ZrP is produced under conditions very near those for the formation of zirconium pyrophosphate. It is therefore difficult to obtain samples of $\tau$-ZrP without zirconium pyrophosphate.

**Characterization.** X-ray powder diffraction data for determining and refining unit cell parameters were recorded using a Siemens D5000 diffractometer equipped with a primary Ge monochromator (Cu K$\alpha_1$ radiation, $\lambda = 1.540\,598$ Å). The data were recorded using a flat sample from 5 to 90° in 2$\theta$ with a steplength of 0.02° and a counting time of 12 s per step. The trial-and-error indexing program TREOR[7] suggested a tetragonal unit cell. Unit cell refinements using the program CELLKANT[8] confirmed the tetragonal symmetry. The unit cell parameters are $a = b = 11.259(1)$ Å and $c = 10.764(1)$ Å, and the unit cell volume is 1364.4 Å$^3$. Systematic extinctions suggested an *I*-centered cell. The indexed powder pattern is provided in Table 1. From the indexing the following systematic extinctions were suggested: $hkl$ ($h + k + l = 2n + 1$), $h00$ ($h = 2n + 1$), $00l$ ($l = 2n + 1$), $hk0$ ($h + k = 2n + 1$), and $h0l$ ($h + l = 2n + 1$). This gives the following possibilities in the choice of space groups $I4_1md$, $I\bar{4}2d$, and $I4_1cd$. Preliminary structural investigations from X-ray powder data indicated that the true space group was $I4_1cd$ (No. 110).[9]

The density of $\tau$-Zr(HPO$_4$)$_2$ was determined pycnometrically, using ultrasound to eliminate air bubbles. The density was found to be 2.78 g/cm$^3$ (the density of α-ZrP has been reported[1] to be 2.72 g/cm$^3$). Using this information and knowing the unit cell volume allows the molecular weight of $\tau$-ZrP to be calculated as 286 g/mol. The molecular weight for H$_2$ZrP$_2$O$_8$ is 283 g/mol. This molecular formula can be interpreted as two monohydrogen phosphate groups, Zr(HPO$_4$)$_2$, or as one dihydrogen phosphate group and one tertiary phosphate group, Zr(PO$_4$)(H$_2$PO$_4$). To determine the correct formula, $^{31}$P MAS NMR experiments were performed.

A $^{31}$P MAS NMR spectrum was recorded on a Varian UNITY-500 spectrometer (11.7 T, $\nu$($^{31}$P) = 202.3 mHz), using a Jakobsen MAS probe.[10] The sample was placed in a cylindrical rotor (Si$_3$N$_4$, 3 mm o.d., volume 220 $\mu$L). The FID was recorded with a spinning speed of 7.8 kHz and the resulting spectrum had a spectral resolution of 5 Hz. An 85% H$_3$PO$_4$ solution (Fluka, puriss, pa) was used as external standard. The spectrum showed only one $^{31}$P resonance situated at −23.7 ppm. Investigations of α-zirconium phosphate (α-Zr(HPO$_4$)$_2$·H$_2$O; α-ZrP) and $\gamma$-zirconium phosphate ($\gamma$-Zr(PO$_4$)(H$_2$PO$_4$)·2H$_2$O; $\gamma$-ZrP) by $^{31}$P MAS NMR have been published by Clayden.[11] He showed that where α-ZrP has only one $^{31}$P resonance (−18.7 ppm) $\gamma$-ZrP has two $^{31}$P resonances (−9.4 and −27.4 ppm) of equal integrated intensity. Considering these results it was concluded that $\tau$-ZrP, having only one $^{31}$P resonance, contains only monohydrogen phosphate groups, giving the correct formula Zr(HPO$_4$)$_2$.

A thermogravimetric measurement was performed up to 1000 °C using a SETARAM TG92-12 instrument. The heating rate was 5 °C/min, and the measurement was performed in an N$_2$ flow. The curve

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obtained is shown in Figure 2, where the weight loss has been converted to molecules of water. The curve indicates that the compound does not contain any crystal water or zeolitic water, which would have been lost at 50−350 °C. At 400 °C the compound loses one molecule of water per formula unit. This loss corresponds to the condensation of the hydrogen phosphate groups to form cubic zirconium pyrophosphate ($2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$).

An infrared spectrum was recorded on a model 170 Fourier transform IR spectrometer. The spectrum was recorded with the potassium bromide technique (1 mg sample and 350 mg KBr). The spectrum is shown in Figure 3.

The transformations in $\tau$-ZrP upon heating were investigated using in-situ temperature-resolved powder diffraction. The sample was contained in a 0.5 mm quartz capillary and heated to 900 °C using an Enraf-Nonius heatergun. The heating rate was 10 °C/min. The detector used was a translating imaging plate system (TIPS)[9] built especially for time- and temperature-dependent experiments at beamline X7B, NSLS (Brookhaven National Laboratory, BNL). Figure 8 shows a representation of a small range of the powder diffraction patterns as a function of temperature.

**Synchrotron X-ray Single-Crystal Diffraction.** A small transparent single crystal (25 × 25 × 50 $\mu$m) was mounted on a thin (<10 $\mu$m) glass fiber, and imaging plate data were collected using a wavelength of 0.9542 Å at the beamline X7B at the National Synchrotron Light Source, NSLS (BNL). The crystal was indexed and the orientation matrix determined using DENZO[12,13] from an imaging plate collected with a 4° $\phi$ scan. The sample-imaging plate distance (106.6 mm) was determined from a CaF$_2$ standard crystal. Single-crystal diffraction data were collected using $\phi$ scans (a total of 180° with steps of 6°) with the flat imaging plate positioned at an angle of 40° with the incoming beam. To measure the overexposed reflections a second data set was collected with the imaging plate mounted perpendicular to the incoming X-ray beam using a faster scan speed. A total of 130° were collected on 10 imaging plates using 13° $\phi$ scans. The imaging plates (Fuji) were read using a Fuji BAS2000 scanner, and intensities were extracted using the program DENZO. A total of 4102 reflections were extracted from the 40 imaging plates and merged with SCALEPACK assuming $I4_1mm$ symmetry with a resulting agreement factor of 8.9% ($R^2 = \sum(I - \langle I \rangle)^2/\sum I^2$). The absences were analyzed using the XPREP program in the SHELXTL-package,[14] which suggested the space group $I4_1cd$, in agreement with the results from the powder diffraction data. After data reduction a total of 513 unique reflections were used for structure solution and refinement.

The structure was solved by direct methods using the XS program, and least-squares structure refinements were performed using the XL program (both of the SHELXTL package). All the non-hydrogen atoms were found in the direct methods solution, and the refinement rapidly converged. In the last cycles of refinement the hydrogen position found from neutron data was included. Constraints on the O−H bond distance and P−O−H angle were used. In these final cycles the data were limited to $d > 0.75$ Å ($2\theta < 80°$), giving a total of 381 unique reflections. The thermal displacement of the zirconium atom was highly anisotropic, and the thermal parameter $U(33)$ was very small. The other anisotropic thermal parameters were reasonable (see Figure 4). The final agreement factors were R1 = 3.5% and wR2 = 9.3%. There is support for the absolute configuration found in the refinement in the Flack parameter, which was found to be −0.016 with a $\sigma$ of 0.23. The crystallographic parameters are given in Table 2. In Table 3 refined coordinates are given, and in Table 4 interatomic distances and angles are listed.

**High-Resolution Neutron Powder Diffraction.** Neutron powder diffraction data were collected at the high-resolution neutron powder diffractometer (HRNPD) at beamline H1A of the high-flux beam reactor (HFBR) at Brookhaven National Laboratory (BNL). The sample was not deuterated because of the small amount of hydrogen in the material.

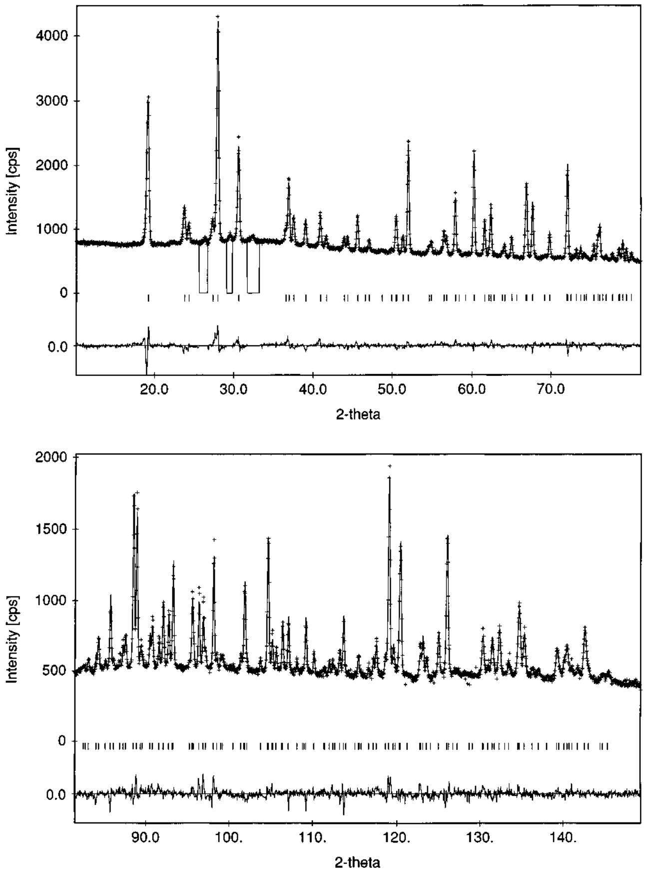

**Figure 5.** Observed (+) and calculated (−) profiles for the Rietveld refinement of $\tau$-Zr(HPO$_4$)$_2$. The bottom curve is the difference plot. Three regions of the pattern were excluded in the refinement, due to a small amount of zirconium pyrophosphate in the sample.

This instrument features a monochromator which is a 30 cm tall vertical focusing array of 24 Ge(115) composites at a takeoff angle of 120°, providing a beam cross-section of 4.5 × 2.5 cm$^2$ and a wavelength of 1.8857 Å. The HRNPD is equipped with a detector bank positioned 99 cm from the specimen and consisting of 64 individual $^3$He detectors which are separated by 2.5°. The entire detector bank was moved in 0.05° steps. For further experimental details see ref 15 .

The data consisted of 2836 points from 5 to 152° in steps of 0.05°. The data were refined by the Rietveld method using the general structure analysis system (GSAS).[16] The atomic positions from the single-crystal refinement were used as starting parameters for the neutron powder refinement. After some initial cycles of refinement, a difference Fourier map was calculated, and the hydrogen positions were easily found as holes (negative density) in the map. After inclusion of the hydrogen atoms, the refinement converged with final agreement factors $R_p$ = 3.0% and $R_{wp}$ = 4.0%. Figure 5 shows the observed, calculated, and difference powder diffraction patterns after refinement. Due to small amounts of zirconium pyrophosphate present in the sample, three regions of the data were excluded.

## Results and Discussion

The refined atomic coordinates from the single-crystal synchrotron X-ray and neutron powder diffraction data are compared in Table 3, and in Table 4 the interatomic distances and angles are listed.

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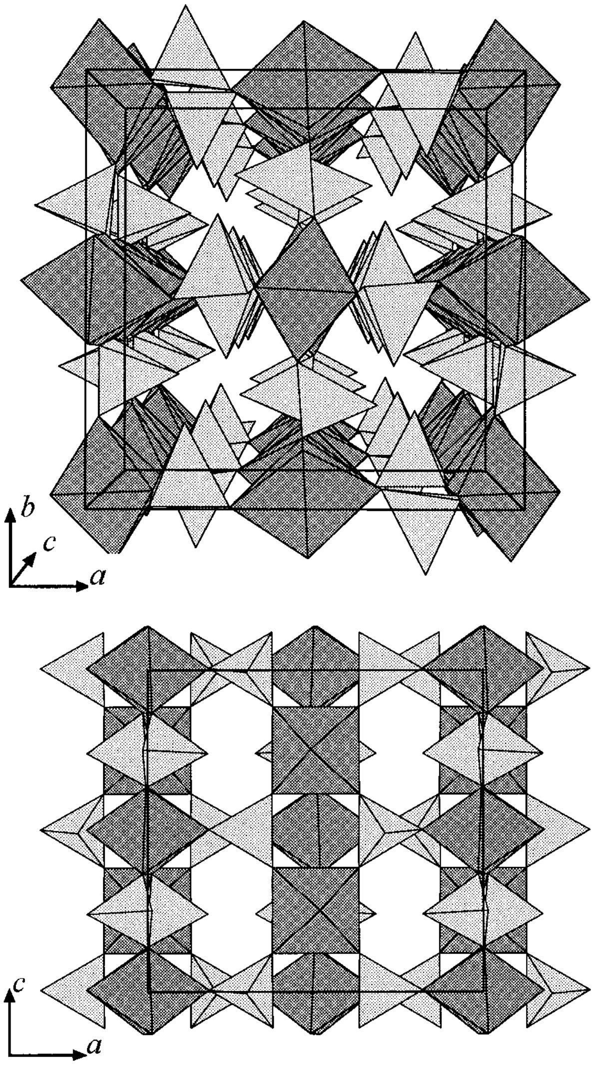

**Figure 6.** Polyhedral representation of the structure in the $a-b$ plane (a, top) and $a-c$ plane (b, bottom). The dark gray octahedra represent $ZrO_6$, and the light gray tetrahedra represent $HPO_4$.

Contrary to the well-known series of layered hydrogen phosphates with tetravalent metal cations, $\tau$-$Zr(HPO_4)_2$ has a three-dimensional framework structure. $ZrO_6$ octahedra are linked together by $HPO_4$ tetrahedra forming an interconnected network with a 4-ring channel extending along the *c*-axis. Figure 6a,b shows polyhedral representations of the structure in the $a-b$ and $a-c$ planes.

The OH groups of the hydrogen phosphates are pointing into the channel and form a hydrogen-bonded spiral along the $4_1$ axis. Each hydrogen phosphate both donates and accepts a hydrogen bond. Figure 7 shows the hydrogen bond arrangement. The hydrogen bonds are long (2.2 Å) compared to the hydrogen bonds of α-ZrP (mean value: 1.85 Å)[17] and to those of $\beta$-TiP ($Ti(PO_4)(H_2PO_4)$) with a mean value of 1.84 Å.[18] This can be understood as the framework structure of $\tau$-$Zr(HPO_4)_2$ is significantly more rigid than its layered counterparts. Thus, the hydrogen bonds are constrained by the structure instead of holding the structure together.

The mean P−O distances in $\tau$-$Zr(HPO_4)_2$ is 1.52 Å, while the P−OH bond distance is 1.57 Å. This is consistent with the general observation that P−OH bonds are longer than P−O bonds in primary and secondary phosphates.[19,20]

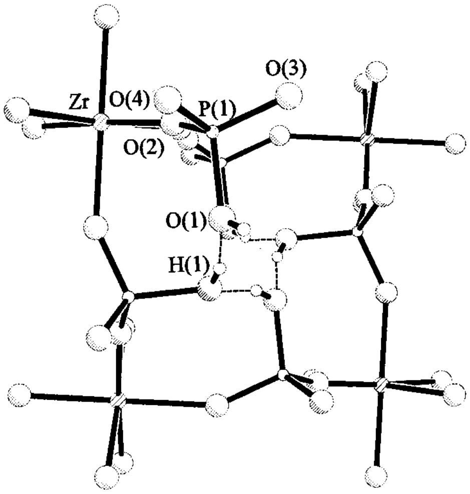

**Figure 7.** Representation of the hydrogen-bonded spiral along the $4_1$ axes.

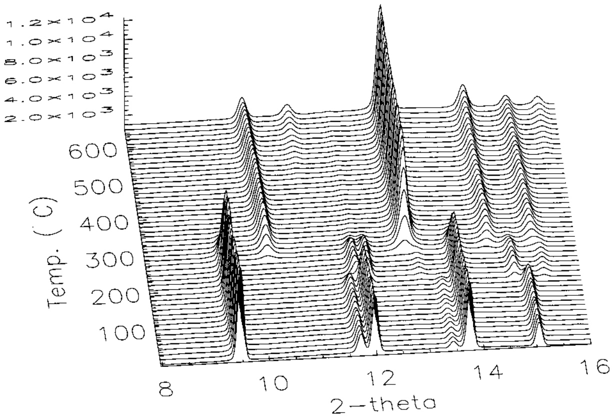

**Figure 8.** Synchrotron powder diffraction patterns showing the thermal transformations of $\tau$-$Zr(HPO_4)_2$.

The proton conductivity of $\tau$-ZrP has been measured. At room temperature and 90% RH it was found to be $3 \times 10^{-6}$ S $cm^{-1}$, a value that corresponds to that of α-ZrP under the same conditions.[21] The conductivity of anhydrous α-ZrP, which has the same molecular formula as $\tau$-ZrP, would be expected to have the same magnitude as that of the monohydrated material, because the materials are surface conductors.[22]

When $\tau$-$Zr(HPO_4)_2$ is heated, several thermal transformations are observed. Figure 8 shows a 3-dimensional representation of a small angular range of the powder diffraction patterns as a function of temperature. In Table 5 the unit cell parameters for the various phases are listed. At 225 °C a reversible transformation to the first intermediate phase is observed. Indexing of a powder pattern of the pure phase gives an orthorhombic cell, with the unit cell parameters $a = 8.172(1)$, $b = 7.691(1)$, and $c = 10.794(2)$ Å. The indexed powder pattern is given in Table 6. This transformation takes place below the temperature where the dehydroxylation occurs, which indicates

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**Table 5.** Unit Cell Parameters (with Esd's in Parentheses) for $\tau$-ZrP and the Intermediate Phases Formed by Heating

| | $\tau$-ZrP | intermediate I (Zr(HPO$_4$)$_2$) | intermediate II (ZrP$_2$O$_7$) | ZrP$_2$O$_7$ |
|---|---|---|---|---|
| $a$ (Å) | 11.259(1) | 8.172(1) | 8.283(2) | 8.317(1) |
| $b$ (Å) | | 7.691(1) | 6.620(2) | |
| $c$ (Å) | 10.764(1) | 10.794(2) | 10.643(2) | |
| $\alpha = \beta = \gamma$ (deg) | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1364.4 | 678.7 | 583.5 | 575.3 |

**Table 6.** Indexed Powder Pattern of Intermediate I (Zr(HPO$_4$)$_2$)[a]

| $h$ | $k$ | $l$ | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ | $h$ | $k$ | $l$ | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 5.6007 | 5.5868 | 100 | 2 | 4 | 0 | 1.7398 | 1.7394 | 5 |
| 1 | 0 | 2 | 4.5036 | 4.4925 | 31 | 1 | 1 | 6 | 1.7129 | 1.7134 | 6 |
| 0 | 1 | 2 | 4.4179 | 4.4101 | 36 | 2 | 3 | 4 | 1.6919 | 1.6913 | 4 |
| 2 | 0 | 0 | 4.0859 | 4.0786 | 13 | 2 | 4 | 2 | 1.6559 | 1.6549 | 3 |
| 1 | 1 | 2 | 3.8863 | 3.8784 | 62 | 4 | 0 | 4 | 1.6288 | 1.6292 | 6 |
| 2 | 1 | 0 | 3.6083 | 3.6058 | 22 | 2 | 1 | 6 | 1.6100 | 1.6099 | 8 |
| 1 | 2 | 0 | 3.4796 | 3.4747 | 13 | 5 | 1 | 0 | 1.5987 | 1.5986 | 9 |
| 2 | 1 | 2 | 2.9997 | 2.9958 | 44 | 0 | 4 | 4 | 1.5659 | 1.5658 | 7 |
| 1 | 2 | 2 | 2.9245 | 2.9215 | 39 | 5 | 1 | 2 | 1.5328 | 1.5342 | 11 |
| 2 | 2 | 0 | 2.8004 | 2.7983 | 26 | 3 | 4 | 2 | 1.5083 | 1.5091 | 7 |
| 0 | 0 | 4 | 2.6986 | 2.6950 | 19 | 3 | 0 | 6 | 1.5012 | 1.5008 | 6 |
| 3 | 1 | 0 | 2.5677 | 2.5661 | 7 | 0 | 5 | 2 | 1.4793 | 1.4794 | 3 |
| 2 | 2 | 2 | 2.4857 | 2.4839 | 4 | 0 | 3 | 6 | 1.4726 | 1.4726 | 4 |
| 1 | 1 | 4 | 2.4311 | 2.4289 | 13 | 2 | 4 | 4 | 1.4622 | 1.4622 | 5 |
| 0 | 3 | 2 | 2.3157 | 2.3144 | 9 | 1 | 3 | 6 | 1.4493 | 1.4493 | 4 |
| 2 | 0 | 4 | 2.2518 | 2.2487 | 4 | 4 | 4 | 0 | 1.4002 | 1.3997 | 4 |
| 3 | 2 | 0 | 2.2228 | 2.2233 | 4 | 2 | 5 | 2 | 1.3910 | 1.3912 | 4 |
| 0 | 2 | 4 | 2.2090 | 2.2073 | 6 | 5 | 2 | 3 | 1.3878 | 1.3880 | 4 |
| 2 | 1 | 4 | 2.1611 | 2.1598 | 4 | 5 | 1 | 4 | 1.3754 | 1.3765 | 6 |
| 1 | 2 | 4 | 2.1324 | 2.1314 | 4 | 0 | 0 | 8 | 1.3493 | 1.3496 | 5 |
| 3 | 2 | 2 | 2.0553 | 2.0554 | 6 | 3 | 5 | 0 | 1.3394 | 1.3395 | 3 |
| 1 | 1 | 5 | 2.0144 | 2.0137 | 9 | 6 | 1 | 1 | 1.3309 | 1.3305 | 4 |
| 2 | 2 | 4 | 1.9432 | 1.9429 | 18 | 1 | 5 | 4 | 1.3189 | 1.3195 | 4 |
| 0 | 4 | 0 | 1.9228 | 1.9201 | 3 | 1 | 1 | 8 | 1.3118 | 1.3122 | 4 |
| 3 | 3 | 0 | 1.8669 | 1.8659 | 16 | 6 | 1 | 2 | 1.3015 | 1.3021 | 4 |
| 0 | 3 | 4 | 1.8587 | 1.8585 | 13 | 1 | 4 | 6 | 1.2970 | 1.2969 | 3 |
| 1 | 2 | 5 | 1.8345 | 1.8355 | 3 | 6 | 2 | 0 | 1.2838 | 1.2834 | 3 |
| 0 | 4 | 2 | 1.8113 | 1.8115 | 10 | 6 | 2 | 1 | 1.2749 | 1.2746 | 3 |
| 1 | 4 | 2 | 1.7684 | 1.7683 | 8 | 2 | 1 | 8 | 1.2638 | 1.2646 | 3 |

[a] Indexing is based on an orthorhombic unit cell: $a = 8.172(1)$, $b = 7.691(1)$, $c = 10.794(2)$ Å.

**Table 7.** Indexed Powder Pattern of Intermediate II (ZrP$_2$O$_7$)[a]

| $h$ | $k$ | $l$ | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ | $h$ | $k$ | $l$ | $d_{calc}$ (Å) | $d_{obs}$ (Å) | $I_{obs}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 5.1713 | 5.1647 | 35 | 4 | 2 | 0 | 1.7555 | 1.7559 | 5 |
| 1 | 0 | 2 | 4.4770 | 4.4783 | 10 | 1 | 0 | 6 | 1.7345 | 1.7355 | 3 |
| 2 | 0 | 0 | 4.1414 | 4.1433 | 100 | 0 | 1 | 6 | 1.7133 | 1.7143 | 6 |
| 1 | 1 | 2 | 3.7086 | 3.7070 | 23 | 1 | 3 | 4 | 1.6639 | 1.6638 | 8 |
| 2 | 1 | 0 | 3.5110 | 3.5099 | 21 | 3 | 3 | 2 | 1.6399 | 1.6384 | 3 |
| 1 | 2 | 0 | 3.0737 | 3.0700 | 7 | 5 | 1 | 0 | 1.6070 | 1.6086 | 4 |
| 2 | 1 | 2 | 2.9306 | 2.9290 | 18 | 2 | 1 | 6 | 1.5832 | 1.5838 | 6 |
| 0 | 0 | 4 | 2.6607 | 2.6601 | 28 | 3 | 3 | 3 | 1.5504 | 1.5502 | 3 |
| 2 | 2 | 0 | 2.5856 | 2.5848 | 6 | 2 | 4 | 0 | 1.5368 | 1.5372 | 5 |
| 3 | 1 | 0 | 2.5482 | 2.5476 | 7 | 3 | 0 | 6 | 1.4923 | 1.4911 | 3 |
| 3 | 0 | 2 | 2.4507 | 2.4512 | 7 | 4 | 2 | 4 | 1.4653 | 1.4650 | 5 |
| 1 | 1 | 4 | 2.3659 | 2.3656 | 6 | 4 | 3 | 2 | 1.4526 | 1.4538 | 4 |
| 1 | 2 | 3 | 2.3230 | 2.3234 | 4 | 3 | 3 | 4 | 1.4467 | 1.4457 | 4 |
| 3 | 1 | 2 | 2.2983 | 2.3002 | 4 | 3 | 4 | 1 | 1.4071 | 1.4072 | 3 |
| 2 | 0 | 4 | 2.2385 | 2.2363 | 4 | 5 | 1 | 4 | 1.3756 | 1.3753 | 4 |
| 1 | 3 | 0 | 2.1323 | 2.1327 | 5 | 1 | 2 | 7 | 1.3628 | 1.3626 | 3 |
| 0 | 2 | 4 | 2.0738 | 2.0744 | 7 | 3 | 0 | 7 | 1.3318 | 1.3316 | 4 |
| 1 | 2 | 4 | 2.0117 | 2.0123 | 5 | 2 | 3 | 6 | 1.3114 | 1.3115 | 3 |
| 4 | 1 | 0 | 1.9763 | 1.9743 | 5 | 1 | 4 | 5 | 1.2906 | 1.2908 | 3 |
| 2 | 2 | 4 | 1.8543 | 1.8552 | 11 | 5 | 3 | 6 | 1.0614 | 1.0615 | 2 |

[a] Indexing is based on an orthorhombic unit cell: $a = 8.283(2)$, $b = 6.620(2)$, $c = 10.643(2)$ Å.

that the composition of the material is unchanged. The unit cell volume is close to half of that of $\tau$-Zr(HPO$_4$)$_2$, which also indicates that no compositional change takes place in this transformation. At 315 °C a distinct change of the powder pattern is observed, and the second intermediate phase is formed. Indexing of a powder pattern of the pure phase shows that the phase is orthorhombic, with the unit cell parameters $a = 8.283(2)$, $b = 6.620(2)$, and $c = 10.643(2)$ Å. The indexed powder pattern is presented in Table 7. This temperature corresponds to the dehydroxylation temperature determined by TG. At 615 °C formation of zirconium pyrophosphate is observed. Some of the diffraction peaks from the intermediate phase coincide with those of the pyrophosphate, indicating a structural relationship between these phases. Structural investigations of these intermediate phases are in progress.

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**Supporting Information Available:** A listing of anisotropic thermal parameters (1 page). One X-ray crystallographic file, in CIF format, is available. Ordering and access information is given on any current masthead page.

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