Electronic Supporting Information to

# Synthesis and structural characterisation of solid titanium(IV) phosphate materials by means of X-ray absorption and NMR spectroscopy

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*CONTENT (Figures and Tables)*

***FIGURES***

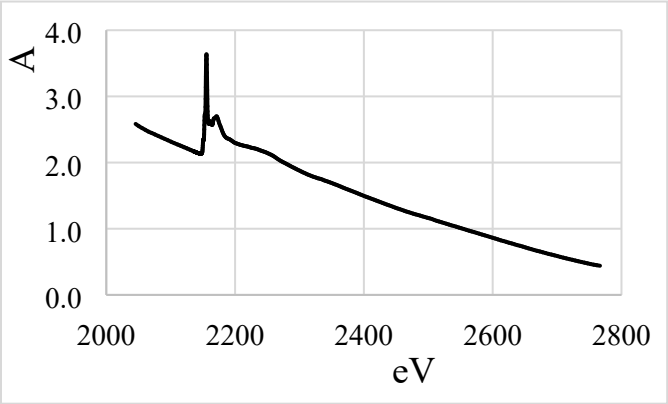


***Figure S1.*** X-ray transmission absorption spectrum of $\alpha$-TiP.

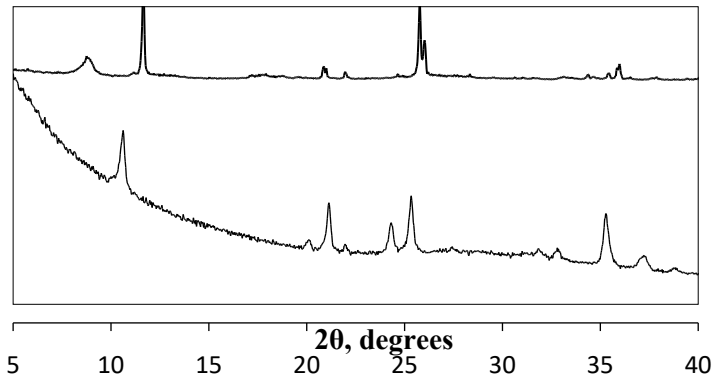


***Figure S2***. XRD diffractograms of LTP-H (sample 3, top), and LTP-Na (sample 5, lower).

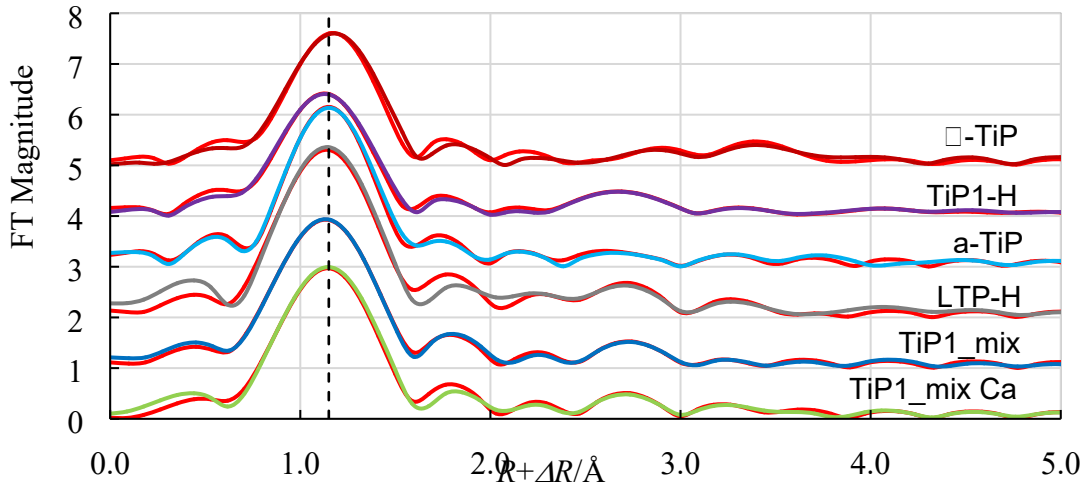


***Figure S3***. Fit of phosphorus K edge EXAFS data of titanium(IV) phosphates, experimental – coloured lines, models with structure parameters from Table 3, *main article* – red lines, sample 2-*α*–TiP (offset: 5), sample 1-TiP1-H (offset: 4), sample 4-a-TiP (offset: 3), sample 3-LTP-H (offset: 2), sample 9-TiP1-mix (offset: 1), and sample 10-TiP1-mix-Ca (no offset). Data for samples 5-8 are not of sufficient quality.

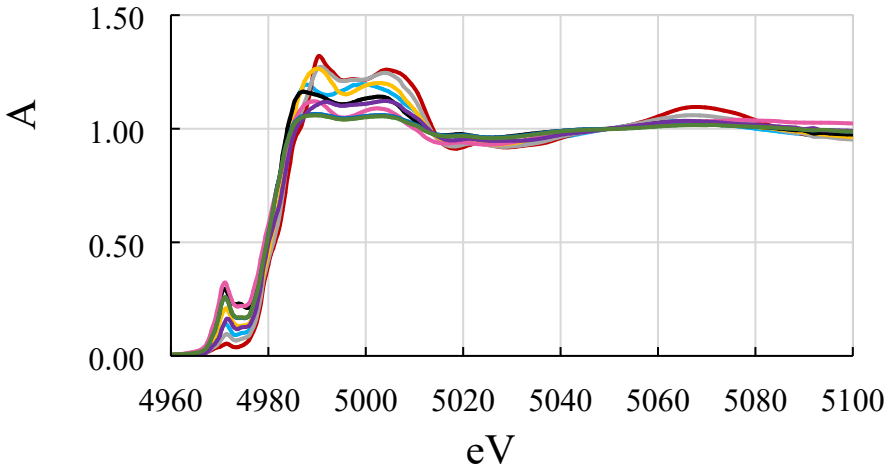


***Figure S4.*** Titanium K edge XANES spectra of titanium(IV) phosphates, sample 1-TiP1-H, sample 2-α-TiP, sample 3-LTP-H, sample 4-a-TiP, sample 5-LTP-Na, sample 6-**LTP-pro**, sample 7-TiP1-Na and sample 9-TiP1-mix and sample 10-TiP1-mixCa (overlapping spectra of samples 9 and 10). (samples 8 - no data available).

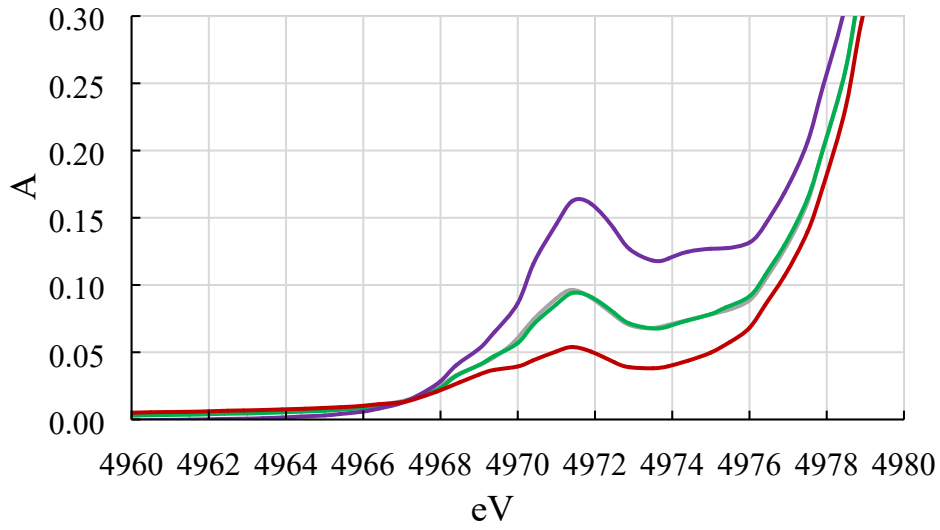


***Figure S5***. Fit of the Ti pre-edge of sample LTP-H using linear regression of the model compounds α-TiP and TiP1-H, the model consisting of 63% and 37% of the α-TiP and TiP1-H pre-edge spectra, respectively, is represented by the green line (nearly overlapped with the grey-line of LTP-H).

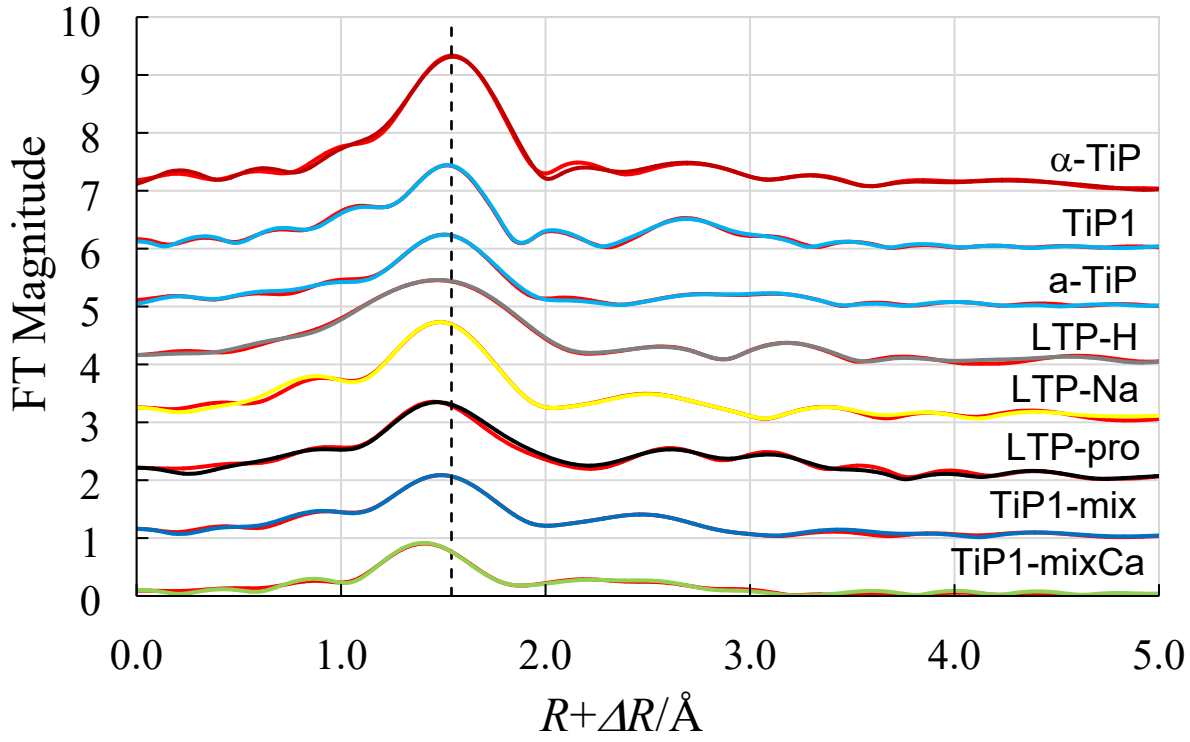


***Figure S6***. Fit of Fourier transforms of Ti *K* EXAFS data of titanium(IV) phosphates, experimental – coloured lines, models with structure parameters (in Table 3, *main article*) - red lines, s sample 2 - α–TiP, sample 1 – TiP1-H, sample 4 – aTiP, sample 3- LTP-H, sample 5 – LTP-Na, sample 6 – LTP_pro, sample 9 – TiP1-mix, and sample 10 – TiP1-mixCa, (sample 7 -data of insufficient quality, and no data for sample 8).

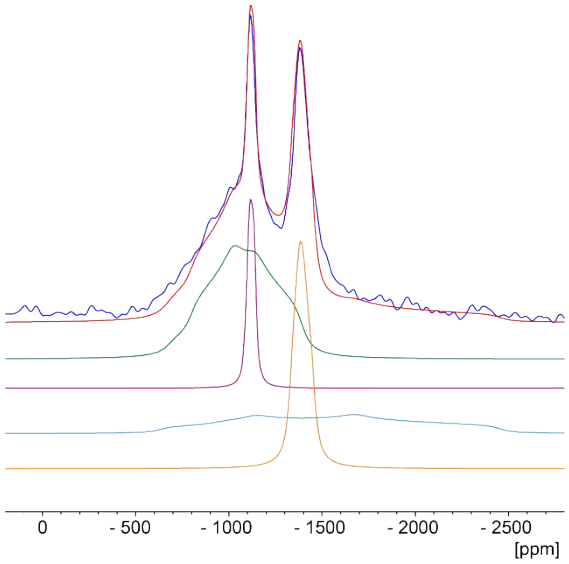


***Figure S7***. A simulation of the static spectrum of LTP-H. Experiment blue, simulation red. The $^{49}$Ti resonance of the large $C_Q$ site is shown in green, that of the small $C_Q$ site in mauve. The $^{47}$Ti resonance of the small $C_Q$ site is shown in orange and that of the large $C_Q$ site in light-blue. It was necessary to include the chemical shift anisotropy (CSA) in the simulation since using the shift and quadrupole parameters alone did not give a good fit to the spectrum for either of the contributions but because the lines are featureless there is considerable uncertainty in the precise CSA parameters and in the Euler angles. The parameters used in the simulation are given in Table S3.

***Table S1.*** Summary of crystalline titanium phosphate structures. The number before the chemical formula is the ICSD code in Inorganic Crystal Structure Database, *Inorganic Crystal Structure Database* 1.4.6, release 2021-2; FIZ Karlsruhe: Eggenstein-Leopoldshafen, Germany, 2021.

***68886 $Ti(HPO_4)_2{\cdot}H_2O$ ($\alpha$-TiP)***

A. N. Christensen, E. Krogh Andersen, I. G. Krogh Andersen, G. Alberti, M. Nielsen and M. S. Lehmann, X-ray powder diffraction study of layer compounds. The crystal structure of $\alpha$-$Ti(HPO_4)_2{\cdot}H_2O$ and a proposed structure for $\gamma$-$Ti(H_2PO_4)(PO_4){\cdot}2H_2O$. *Acta Chem. Scand.,* 1990, **44**, 865-872.
Unit cell: *P2₁/c*; *a*=8.630(2), *b*=5.006(1), *c*=16.189(3) Å, $\beta$=110.20(1) °.
O-Ti-O bond angles within $TiO_6$ unit: 84.576-94.808, 173.674-176.736 °.

Ti-O: 1.911, 1.944, 2.016, 2.032, 2.041, 2.062/**2.001 Å**
Ti···O: 3.527, 3.596, 3.661, 3.708, 3.846, 3.981, 4.017
Ti···P: 3.127, 3.191, 3.334, 3.420, 3.469/**3.308 Å**
Ti···Ti: 4.880, 4.961, 5.006, 5.006, 5.079, 5.157/

P-O: 1.384, 1.443, 1.444, 1.770/**1.510 Å**
P···O: 3.375, 3.398, 3.492, 3.654, 3.671, 3.695, 3.822, 3.837, 3.893, 3.922, 3.933, 3.983, 3.989
P···Ti: 3.334, 3.420/**3.377 Å**

***79193 $Ti(HPO_4)_2{\cdot}H_2O$ ($\alpha$-TiP)***

S. Bruque, M. A. G. Aranda, E. R. Losilla, P. Olivera-Pastor and P. Maireles-Torres, Synthesis optimization and crystal structures of layered metal(IV) hydrogen phosphates, $\alpha$-$M(HPO_4)_2{\cdot}(H_2O)$ (M=Ti,Sn,Pb). *Inorg. Chem.*, 1995, **34**, 893-899.
Unit cell: *P2₁/n*; *a*=8.6403(2), *b*=5.0093(1), *c*=15.5097(4) Å, $\beta$=101.324(2) °.
O-Ti-O bond angles within $TiO_6$ unit: 85.863-93.572, 173.938-178.352 °.

Ti-O: 1.844, 1.918, 1.927, 1.968, 1.991, 2.026/**1.952 Å**
Ti···O: 3.532, 3.605, 3.647, 3.663, 3.792, 3.844, 4.063
Ti···P: 3.251, 3.266, 3.290, 3.291, 3.325, 3.337**3.293 Å**
Ti···Ti: 4.995, 5.009, 5.009, 5.020, 5.039

P-O: 1.442, 1.471, 1.514, 1.530/1.505, 1.570, 1.572, 1.581/**1.523 Å**
P···O: 3.243, 3.358, 3.500, 3.516, 3.651, 3.709, 3.714, 3.751, 3.763, 3.906, 4.045
P···Ti: 3.251, 3.266, 3.290, 3.291, 3.325, 3.337

***82458 $Ti(HPO_4)_2{\cdot}H_2O$ ($\alpha$-TiP, neutron diffraction)***

M. A. Salvado, P. Pertierra, S. Garcia Granda, J. R. Garcia, J. Rodriguez and M. T. Fernandez Diaz, Neutron powder diffraction study of $\alpha$-$Ti(HPO_4)_2{\cdot}(H_2O)$ and $\alpha$-$Hf(HPO_4)_2{\cdot}(H_2O)$; H-atom positions. *Acta Crystallogr., Sect. B*, 1996, **52**, 896-898.
Unit cell: *P2₁/c*; *a*=8.6110(3), *b*=4.9933(2), *c*=16.1507(7) Å, $\beta$=110.206(3) °.
O-Ti-O bond angles within $TiO_6$ unit: 85.661-95.968, 171.380-177.311 °.

Ti-O: 1.835, 1.886, 1.911, 1.940, 1.960, 1.961/**1.916 Å**
Ti···O: 3.535, 3.546, 3.611, 3.754, 3.835, 3.841, 4.125
Ti···P: 3.218, 3.275, 3.286, 3.297, 3.314, 3.377/**3.295 Å**
Ti···Ti: 4.920, 4.984, 4.991, 4.993, 4.993, 5.054**/4.989 Å**

P-O: 1.501, 1.551, 1.560, 1.563/1.527, 1.559, 1.575, 1.586/**1.553 Å**
P···O: 3.221, 3.294, 3.517, 3.555, 3.587, 3.614, 3.634, 3.695, 3.737, 3.839, 4.035
P···Ti: 3.218, 3.275, 3.286, 3.297, 3.314, 3.377

***174475 $Ti(HPO_4)_2 \cdot H_2O$ ($\alpha$-TiP)***

V. A. Burnell, J. E. Readman, C. C. Tang, J. E. Parker, S. P. Thompson and J. A. Hriljac, Synthesis and structural characterisation using Rietveld and pair distribution function analysis of layered mixed titanium-zirconium phosphates. *J. Solid State Chem.*, 2010, **183**, 2196-2204.
Unit cell: $P2_1/c$; $a$=8.63267(6), $b$=5.00672(3), $c$=16.1902(2) Å, $\beta$=110.2065(6) °.
O-Ti-O bond angles within $TiO_6$ unit: 86.774-93.949, 175.171-178.966 °.

Ti-O: 1.907, 1.941, 1.941, 1.945, 1.962, 1.969/**1.944 Å**
Ti···O: 3.569, 3.586, 3.680, 3.739, 3.800, 3.825, 4.082
Ti···P: 3.233, 3.287, 3.290, 3.291, 3.312, 3.322/**3.289 Å**
Ti···Ti: 4.970, 4.988, 5.007, 5.007, 5.018, 5.036/

P-O: 1.470, 1.490, 1.569, 1.584/1.467, 1.512, 1.523, 1.582/**1.525 Å**
P···O: 3.240, 3.374, 3.501, 3.604, 3.610, 3.654, 3.663, 3.736, 3.759, 3.874, 3.990
P···Ti: 3.233, 3.287, 3.322/3.290, 3.291, 3.312

***51099 $Ti(PO_4)(H_2PO_4) \cdot H_2O$ ($\beta$-TiP)***

A. M. Krogh Andersen, P. Norby and T. Vogt, Determination of formation regions of titanium phosphates; determination of the crystal structure of beta-titanium phosphate, $Ti(PO_4)(H_2PO_4)$ from neutron powder data. *J. Solid State Chem.*, 1998, **140**, 266-271.
Unit cell: $P2_1/n$: $a$=18.9502(4), $b$=6.3126(1), $c$=5.1392(1) Å, $\beta$=105.366(2) °.
O-Ti-O bond angles within $TiO_6$ unit: 84.355-96.480, 170.399-177.839 °.

Ti-O: 1.910, 1.921, 1.927, 1.936, 1.942, 1.955/**1.932 Å**
Ti···O: 3.634, 3.701, 3.758, 3.763, 3.798, 3.826, 3.873, 3.973, 3.991, 4.104
Ti···P: 3.160, 3.270, 3.284, 3.340, 3.413, 3.420/**3.315 Å**
Ti···Ti: 5.030, 5.030, 5.139, 5.139, 5.151, 5.151

P-O: 1.485, 1.581, 1.602, 1.629/1.487, 1.507, 1.513, 1.582/**1.548 Å**
P···O: 3.312, 3.314, 3.430, 3.440, 3.526, 3.702, 3.792, 3.863, 3.903, 3.929, 3.996, 4.015
P···Ti: 3.160, 3.270, 3.284, 3.340, 3.413, 3.420

***174341 $Ti(PO_4)(H_2PO_4) \cdot H_2O$ ($\beta$-TiP)***

S. Garcia Granda, S. A. Khainakov, A. Espina, J. R. Garcia, G. R. Castro, J. Rocha and L. Mafra, Revisiting the thermal decomposition of layered $\gamma$-titanium phosphate and structural elucidaton of its intermediate phase. *Inorg. Chem.*, 2010, **49**, 2630-2638.
Unit cell: $P2_1$: $a$=5.036, $b$=6.264, $c$=23.67 Å, $\beta$=102.41 °.
O-Ti-O bond angles within $TiO_6$ unit: 80.143-106.546, 160.249-178.803 °.

Ti-O: 1.839, 1.899, 1.912, 1.962, 1.969, 2.059/1.755, 1.823, 1.968, 1.990, 1.993, 2.036/**1.938 Å**
Ti···O: 3.606, 3.618, 3.627, 3.809, 3.829, 3.882, 3.889, 3.900, 3.960, 3.989, 4.017
Ti···P: 3.236, 3.239, 3.260, 3.263, 3.310, 3.318, 3.409, 3.461/**3.312 Å**
Ti···Ti: 4.983, 4.983, 5.036, 5.036, 5.146, 5.146**/5.106 Å**

P-O: 1.492, 1.504, 1.510, 1.512/1.492, 1.504, 1.531, 1.546/1.494, 1.498, 1.499, 1.512/1.545, 1.553, 1.563, 1.581/**1.521 Å**
P···O: 3.315, 3.394, 3.439, 3.567, 3.599, 3.774, 3.851, 3.867, 3.878, 3.883, 3.889, 3.935, 3.995
P···Ti: 3.236, 3.239, 3.260, 3.263, 3.310, 3.318, 3.409, 3.461

***174340 $Ti(PO_4)(H_2PO_4)\cdot 2H_2O$ ($\gamma$-TiP)***

S. Garcia Granda, S. A. Khainakov, A. Espina, J. R. Garcia, G. R. Castro, J. Rocha and L. Mafra, Revisiting the thermal decomposition of layered $\gamma$-titanium phosphate and structural elucidaton of its intermediate phase. *Inorg. Chem.*, 2010, **49**, 2630-2638.
Unit cell: $P2_1$; $a$=5.1811(2), $b$=6.3479(2), $c$=23.725(2) Å, $\beta$=102.57(1) °.
O-Ti-O bond angles within $TiO_6$ unit: 76.072-102.325, 153.977-177.757 °.

Ti-O: 1.888, 1.922, 1.937, 1.966, 2.166, 2.284/1.832, 1.870, 1.902, 1.911, 1.946, 1.967/**1.966 Å**
Ti···O: 3.544, 3.617, 3.704, 3.710, 3.940, 3.960, 3.990, 3.994, 4.000
Ti···P: 3.224, 3.283, 3.327, 3.332, 3.380, 3.403, 3.413, 3.414, 3.443/**3.354 Å**
Ti···Ti: 5.040, 5.040, 5.146, 5.146, 5.181, 5.181**/5.122 Å**

P-O: 1.470, 1.523, 1.546, 1.554/1.527, 1.556, 1.623, 1.652/1.472, 1.493, 1.519, 1.574/1.544, 1.613, 1.622, 1.793/**1.568 Å**
P···O: 3.291, 3.343, 3.355, 3.621, 3.730, 3.730, 3.908, 3.919, 3.922, 3.940, 3.942, 3.969
P···Ti: 3.323, 3.224, 3.283, 3.327, 3.332, 3.380, 3.403, 3.413, 3.414, 3.443

***84307 $Ti_2O(PO_4)_2\cdot 2H_2O$***

M. A. Salvado, P. Pertierra, S. Garcia Granda, J. R. Garcia, M. T. Fernandez Diaz and E. Dooryhee, Crystal structure, including H-atom positions, of $Ti_2O(PO_4)_2(H_2O)_2$ determined from synchrotron X-ray and neutron powder data. *Eur. J. Solid State Inorg. Chem.,* 1997, **34**, 1237-1247.

Ti-O: 1.854, 1.910, 1.929, 1.957, 1.975, 2.019/1.764, 1.875, 1.875, 2.016, 2.136, 2.220/**1.961 Å**
Ti···O: 3.552, 3.670, 3.756, 3.800, 3.803, 3.855, 3.887, 3.972
Ti···P: 3.199, 3.288, 3.300, 3.301, 3.307, 3.319, 3.345, 3.389/**3.306 Å**
Ti···Ti: 3.484, 5.111, 5.113, 5.115, 5.115, 5.148, 5.180

P-O: 1.486, 1.510, 1.553, 1.577/1.490, 1.501, 1.528, 1.533/**1.522 Å**
P···O: 3.333, 3.423, 3.508, 3.645, 3.673, 3.744, 3.777, 3.840, 3.846, 3.915, 3.947, 3.952, 3.958
P···Ti: 3.199, 3.288, 3.300, 3.301, 3.307, 3.319, 3.345, 3.389

***84861 $Ti_2O(PO_4)_2\cdot 2H_2O$***

D. M. Poojary, A. I. Bortun, L. N. Bortun and A. Clearfield, Synthesis and X-ray powder structures of three novel titanium phosphate compounds. *J. Solid State Chem.*, 1997, **132**, 213-223.

Ti-O: 1.823, 1.928, 1.928, 1.962, 2.042, 2.138/1.942, 1.961, 1.961, 2.005, 2.030, 2.035/**1.980 Å**
Ti···O: 3.581, 3.584, 3.804, 3.895, 3.980
Ti···P: 3.218, 3.240, 3.255, 3.275, 3.284, 3.381, 3.383, 3.387/**3.303 Å**
Ti···Ti: 3.567, 5.063, 5.087, 5.089, 5.092, 5.109, 5.109

P-O: 1.497, 1.511, 1.521, 1.615/1.494, 1.532, 1.545, 1.579/**1.537 Å**
P···O: 3.253, 3.467, 3.598, 3.621, 3.745, 3.753, 3.762, 3.766, 3.779, 3.849, 3.967, 3.971, 3.983, 4.001
P···Ti: 3.218, 3.240, 3.255, 3.275, 3.284, 3.381, 3.383, 3.387

***160167 $Ti_2O(PO_4)_2 \cdot H_2O$***

S. Benmokhtar, A. El Jazouli, J. P. Chaminade, P. Gravereau, M. Menetrier and F. Bouree, New process of preparation, structure and physicochemical investigations of the new titanyl phosphate $Ti_2O(H_2O)(PO_4)_2$. *J. Solid State Chem.*, 2007, **180**, 2713-2722.

Ti-O: 1.840, 1.873, 1.886, 1.921, 1.957, 2.281/1.779, 1.848, 1.910, 1.959, 2.045, 2.264/**1.964 Å**
Ti···O: 3.533, 3.745, 3.822, 3.839, 3.906, 3.953, 3.972, 4.030
Ti···P: 3.232, 3.242, 3.302, 3.401/3.131, 3.183, 3.354, 3.393/**3.280 Å**
Ti···Ti: 3.473, 4.193, 4.981, 4.981, 4.990, 5.017, 5.181, 5.207, 5.217, 5.217

P-O: 1.452, 1.547, 1.580, 1.584/1.510, 1.519, 1.544, 1.589/**1.541 Å**
P···O: 3.291, 3.343, 3.355, 3.621, 3.730, 3.730, 3.908, 3.919, 3.922, 3.940, 3.942, 3.969
P···Ti: 3.232, 3.242, 3.302, 3.401/3.131, 3.183, 3.354, 3.393

***174339 $Ti_2(PO_4)_2(H_2P_2O_7)(H_2O)$***

S. Garcia Granda, S. A. Khainakov, A. Esina, J. R. Garcia, G. R. Castro, J. Rocha and L. Mafra, Revisiting the thermal decomposition of layered gamma-titanium phosphate and structural elucidation of its intermediate phase. *Inorg. Chem.*, 2010, **49**, 2630-2638.

Ti-O: 1.781, 1.912, 1.935, 1.956, 2.009, 2.201/**1.964 Å**
Ti···O: 3.438, 3.550, 3.582, 3.605, 3.621, 3.636, 3.639, 3.758, 3.824, 3.828, 3.995, 4.006**/3.707 Å**
Ti···P: 3.232, 3.242, 3.302, 3.401/3.131, 3.183, 3.354, 3.393/**3.343 Å**

***163900 $(Ti_{1.5}(H_2O)_2(PO_4)(HPO_4)(H_2PO_4)_{0.5}) \cdot H_2O$***

Y. Zhao, J. Yu, Y.-U. Kwon, Syntheses and structures of two reduced open-framework titanophosphates. *Bull. Korean Chem. Soc.*, 2008, **29**, 805-810.

Ti-O: (1.977, 1.978, 1.994, 1.994, 2.109, 2.110), (1.868, 1.914, 1.929, 1.944, 1.947, 1.961)/ (2.027 1.927/**1.977 Å**
Ti···P: 3.259, 3.284, 3.300, 3.305, 3.318, 3.362, 3.342, 3.414, 3.342, 3.355, 3.355/**3.331 Å**

***Table S2***. Summary of powder XRD data (the first reflection and the corresponding $d_{spacing}$) for different TiP sorbents (samples 1-5) along with the reported analogous data for $\alpha$-TiP and $TiO(OH)(H_2PO_4)\cdot\mathbf{2}H_2O$.

| *Sample No/colour code* | *Abbreviation* | *Chemical substance* | *pXRD 2 Θ, degree* | *pXRD d, Å* | *Ref* |
|---|---|---|---|---|---|
| Sample 1 / purple | **TiP1 / TiP-H** | $TiO(OH)(H_2PO_4)\cdot H_2O$ | 8.5 | 10.4 | 1, 2 |
| Sample 2 / red-brownish | **Alpha-TiP / αTiP** | $\alpha$-$Ti(HPO_4)_2\cdot H_2O$ | 11.6 | 7.6 | 1 |
| Sample 3 / grey | **LTP / LTP-H** | Linked units (TiP1 and $\alpha$-TiP) | 8.8<br>11.7 | 10.0<br>7.5 | 3 |
| Sample 4 / light-blue | **amorphous TiP / aTiP** | Different TiP units present | Featureless | - | 2 |
| Sample 5 / yellow | **LTP-Na** | Na-exchanged LTP-H | 10.5 | 8.4 | 3 (ESI- Fig. S1) |
| α- $Ti(HPO_4)_2\cdot H_2O$ | | | 11.6 | 7.6 | 4 |
| $TiO(OH)(H_2PO_4)\cdot 2H_2O$ | | | 8.8 | 10.0 | 5 |

## *References to Table S2*


1. M. Trublet, D. Rusanova and O. N. Antzutkin, Revisiting syntheses of Ti(IV)/$H_2PO_4$-$HPO_4$ functional ion-exchangers, properties and features. *New J. Chem.*, 2018, **42**, 838–845.
2. M. Trublet, M. V. Maslova, D. Rusanova and O. N. Antzutkin, Mild syntheses and surface characterization of amorphous $TiO(OH)(H_2PO_4)\cdot H_2O$ ion-exchanger. *Mater.Chem. Phys.*, 2016, **183**, 467-475.
3. M. Trublet and D. Rusanova, Complete Column Trials for Water Refinement Using Titanium(IV) Phosphate Sorbents. *ACS Sustain. Chem. Eng.*, 2018, **6**, 6157-6165.
4. A. N. Christensen, E. K. Andersen, I. G. G. Andersen, G. Alberti, M. Nielsen and M. S. Lehmann, X-Ray Powder Diffraction Study of Layer Compounds. The Crystal Structure of $\alpha$-$Ti(HPO_4)_2\cdot H_2O$ and a Proposed Structure for $\gamma$-$Ti(H_2PO_4)(PO_4))\cdot 2H_2O$. *Acta Chem. Scand.*, 1990, **44**, 865–872.
5. Y. J. Li, M. S. Whittingham, Hydrothermal synthesis of new metastable phases: preparation and intercalation of a new layered titanium phosphate, *Solid State Ionics*, 1993, **63-65**, 391-395.

***Table S3***. Simulation parameters used for the static $^{49}$Ti and $^{47}$Ti static NMR spectrum of LTP-H shown in Fig. S6.

| | $^{49}$Ti Site 1 | $^{49}$Ti Site 2 | $^{47}$Ti Site 1 | $^{47}$Ti Site 2 |
|---|---|---|---|---|
| $\delta_{iso}$ (ppm) | -1105 | -990 | -1372 | -1257 |
| $C_Q$ (MHz) | 2.4 | 8.8 | 2.9 | 10.8 |
| $\eta$ | 0.4 | 0.35 | 0.4 | 0.35 |
| $\Delta_{csa}$ (ppm) | 30 | 300 | 30 | 300 |
| $\eta_{csa}$ | 0.9 | 0.9 | 0.9 | 0.9 |
| $\alpha$ | 0 | 0 | 0 | 0 |
| $\beta$ | 0 | 0 | 0 | 0 |
| $\gamma$ | 0 | 0 | 0 | 0 |

$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Delta_{csa} = \delta_{33} - \delta_{iso}$, $\eta_{csa}=(\delta_{11}-\delta_{22})/(\delta_{33}-\delta_{iso})$
The Euler angles (α, β, γ) describe the relative orientation of the CS tensor with respect to the EFG system.

***Table S4.*** $^{49}$Ti NMR parameters for TiP1-H (sample 1, $TiO(OH)(H_2PO_4)\cdot H_2O$) and LTP-H (sample 3) combined with reported data.

| Sample | Nucleus | $\delta_{iso}$/ppm | $^{49}$Ti / $^{91}$Zr $C_Q$/MHz | $\eta_Q$ | Ref. |
|---|---|---|---|---|---|
| TiP1-H | $^{49}$Ti | −990 ± 10 | 8.4 ± 0.4 | 0.35 ± 0.1 | |
| LTP-H | $^{49}$Ti | −1105 ± 5 | 2.6 ± 0.2 | 0.4 ± 0.1 | this work |
| LTP-H | $^{49}$Ti | −990 ± 10 | 8.8 ± 0.4 | 0.35 ± 0.1 | |
| *alpha*-TiP | $^{49}$Ti | −820 ± 20 | 14.3 ± 0.5 | 0.05 ± 0.05 | |
| *beta*- TiP | $^{49}$Ti | −1130 ± 20 | 4.0 ± 0.2 | 0.8 ± 0.1 | |
| *gamma*-TiP | $^{49}$Ti | −1130 ± 20 | 4.9 ± 0.2 | 0.9 ± 0.1 | 1/2 |
| *alpha*-Na-TiP | $^{49}$Ti | −800 ± 20 | 13.5 ± 0.5 | 0.2 ± 0.05 | |
| *alpha*-ZrP | $^{91}$Zr | − 385 | 5.80 *(8.12)* | 0.27 | |
| *gamma*-ZrP | $^{91}$Zr | −390 | 9.20 *(12.88)* | 0.13 | 3 |
| Na-ZrP, site1 | $^{91}$Zr | −395 | 7.81 *(10.93)* | 0.97 | |
| Na-ZrP, site2 | $^{91}$Zr | −400 | 6.55 *(9.17)* | 0.99 | |

The values *in orange* correspond to the multiplied by 1.4 $C_Q$ parameters (*example*: 5.80 x 1.4 = 8.12) in order for the $C_Q$ parameters for TiP- materials to be compared to the analogous parameters for ZrP layered systems.

$$C_q = eq.eQ / h$$

$$eq = \partial^2 V / \partial z^2 = V_{zz}$$

$$V_{zz} = e\frac{3\cos^2\theta - 1}{r^6}$$

The $C_q$ depends on both the electric field gradient, written as *eq* (units V/m$^2$) and the quadrupole moment *eQ* and to compare $^{91}$Zr with $^{49}$Ti one needs to divide $C_q$ by the ratio of the quadrupole moments.

*eQ*($^{49}$Ti) = 24.7 x $10^{-30}$ m$^2$ and *eQ*($^{47}$Ti) = 30.2 x $10^{-30}$ m$^2$ and *eQ*($^{91}$Zr) = -17.6 x $10^{-30}$ m$^2$ (see doi: 10.1016/S0009-2614(00)00031-2)

Ratio *eQ*($^{91}$Zr)/*eQ*($^{49}$Ti) = 17.6/24.7 = 0.71, or multiple $C_q$($^{91}$Zr) by 1.4 to compare with $C_q$($^{49}$Ti).

***References to Table S4***


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