Crystal Structures of Two Titanium Phosphate-Based Proton Conductors: Ab Initio Structure Solution and Materials Properties

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ABSTRACT: Transition-metal phosphates show a wide range of chemical compositions, variations of the valence states, and crystal structures. They are commercially used as solid-state catalysts, cathode materials in rechargeable batteries, or potential candidates for proton-exchange membranes in fuel cells. Here, we report on the successful ab initio structure determination of two novel titanium pyrophosphates, Ti(III)p and Ti(IV)p, from powder X-ray diffraction (PXRD) data. The low-symmetry space groups P21/c for Ti(III)p and P1 for Ti(IV)p required the combination of spectroscopic and diffraction techniques for structure determination. In Ti(III)p, trivalent titanium ions occupy the center of TiO6 octahedra, coordinated by five pyrophosphate groups, one of them as a bidentate ligand. This secondary coordination causes the formation of one-dimensional six-membered ring channels with a diameter d_{max} of 3.93(2) Å, which is stabilized by NH$_4^+$ ions. Annealing Ti(III)p in inert atmospheres results in the formation of a new compound, denoted as Ti(IV)p. The structure of this compound shows a similar three-dimensional framework consisting of [PO$_4$]$^{3-}$ tetrahedra and Ti$^{IV+}$O$_6$ octahedra and an empty one-dimensional channel with a diameter d_{max} of 5.07(1) Å. The in situ PXRD of the transformation of Ti(III)p to Ti(IV)p reveals a two-step mechanism, i.e., the decomposition of NH$_4^+$ ions in a first step and subsequent structure relaxation. The specific proton conductivity and activation energy of the proton migration of Ti(III)p, governed by the Grotthus mechanism, belong to the highest and lowest, respectively, ever reported for this class of materials, which reveals its potential application in electrochemical devices like fuel cells and water electrolyzers in the intermediate temperature range.

INTRODUCTION

Transition-metal phosphates (TMPs) are a class of functional materials that are not only studied for fundamental understanding but also applied in industrial applications. The members of the TMP family show a wide range of chemical compositions and a wide variety of crystal structures with variable metal coordination and different phosphate structure units. The phosphate units are differentiated in orthophosphates ([PO$_4$]$^{3-}$) and different condensed phosphates, pyrophosphates ([P$_2$O$_7$]$^{4-}$) and metaphosphates, consisting either of [PO$_4$]$^-$ chains or [P$_n$O$_{3n+1}$]$^{n-}$ rings (Figure 1). The structural properties of TMPs determine their potential as efficient and environmentally sustainable cathode materials in rechargeable batteries. The orthophosphate LiFePO$_4$ is a well-known example for a successful energy storage material showing high capacity and charge–discharge reversibility, together with the economic requirements of low cost and environmental friendliness. Among TMPs, vanadyl pyrophosphate [VO(P$_2$O$_7$)] is especially interesting because it is the only commercially used solid-state catalyst for the selective oxidation of butane to maleic anhydride. Operando and in situ Raman studies of the activation of the hemihydrate VOHPO$_4$·0.5H$_2$O to the active VO(P$_2$O$_7$) revealed a complex activation process including different reorganization processes on the crystallite surface and in the crystalline bulk material. Titanium phosphates belong to the intensively studied TMP compounds. They show promising behavior as photocatalysts, solid acids, N$_2$ absorbents in the Haber–Bosh process, and proton conductors, in particular in the intermediate temperature range. The wide application range of titanium phosphates is caused by their structural variety. The structure of monoclinic metaphosphate Ti(PO$_4$)$_2$ is formed by isolated [TiO$_6$]$^{12-}$ octahedra connected with [PO$_4$]$^{3-}$ tetrahedral (n = 3, 6) zigzag chains propagating along the crystallographic a
The orthorhombic titanium phosphate TiPO₄ crystallizes in the space group Cmcm and is formed by chains of edge-sharing TiO₆ octahedra connected via corner-sharing [PO₄]³⁻ groups propagating along the crystallographic c axis. The orthophosphate TiPO₄ shows an interesting structural behavior if pressurized in a diamond anvil cell. Above 46 GPa, the phosphorus atom is coordinated by five oxygen atoms, forming a chain of trigonal bipyramids [PO₄]³⁻ along the [101] direction. Two open-framework structures, Ti₃−(PO₄)₃·2H₂O and its dehydrated form, Ti₃O(PO₄)₂, are also formed by [PO₄]³⁻ and TiO₆ polyhedra. Both structures contain two one-dimensional chains, [P₂O₉]₄⁻, along the crystallographic a axis with n = 6 and 8. In Ti₃O(PO₄)₂·2H₂O, one of the two independent titanium sites is coordinated by two water molecules, forming a highly distorted TiO₆ octahedron. In the dehydration process, the titanium coordination changes to a TiO₆ tetrahedron, creating new acidic sites on the surface of the particle.

Titanium pyrophosphate along with other metal pyrophosphates, MP₂O₇ (M = Sn, Ti, Si, Ge, Zr, Ce), is a potential candidate for proton-exchange membranes in next-generation fuel cells, working in the intermediate temperature range. Their proton conductivity at temperatures between 273 and 673 K under water-free conditions makes these compounds particularly suitable for this application. Most MP₂O₇ compounds (M = Sn, Pb, Ti, Zr, Hf, U, Ce) can be described via a cubic parent structure with the formula unit Z = 4 and lattice parameter a ≈ 8 Å but show a superstructure similar to that of a cubic 3 × 3 × 3 supercell with Z = 108. The first description of the TiP₂O₇ structure by Levi and Peyronel obtained in a powder X-ray diffractometry (PXRD) study resulted also in a small cubic unit cell in Pa₃ with a = 7.80(1) Å. Recent PXRD and single-crystal structure analyses showed that TiP₂O₇ consists of a cubic superstructure in Pa₃ with lattice parameter a = 23.6383(2) Å. In both proposed structure models, titanium is coordinated in a quite regular TiO₆ octahedron with typical Ti−O bond lengths [r(Ti−O) = 1.88(2)−1.98(2) Å] and O−Ti−O angles close to 90°. In the structure model reported by Levi and Peyronel, all pyrophosphate groups occupy positions on the 3-fold rotation axis. In the superstructure, four of the six independent pyrophosphate groups show P−O−P angles between 139(1) and 145(1)° and between 141.5(1) and 144.5(1)°. The P−O₈ (with O₈ as the bridging oxygen atom in the pyrophosphate group) bond distances of the bent pyrophosphates show a variety of possible bond lengths [r(P−O₈) = 1.57(1)−1.60(1) Å].

In a recent publication, we introduced a novel synthesis route for TMPs using metal oxides and NH₄(H₂PO₄) as a phosphorus source instead of phosphate-based precursors. The specific feature of this synthesis route is the reducing property of NH₄(H₂PO₄), which stabilizes low-valent transition-metal compounds. With this synthesis route, two novel titanium phosphates with unknown structures could be obtained, hereafter referred to as Ti(III)p and Ti(IV)p. Ti(III)p is formed by annealing the reaction mixture to 573 K. Interestingly, this new phase contains trivalent titanium cations. The combination of the analytical results obtained by energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS) and analysis of the gaseous decomposition products via thermogravimetric analysis/differential scanning calorimetry coupled with mass spectroscopy (TGA/DSC–MS) resulted in the chemical composition NH₄Ti(III)pP₂O₇. A preliminary discussion of the Raman spectra indicates that Ti(III)p and Ti(IV)p are not of the same structure. At elevated temperatures, Ti(III)p reacts to the well-known cubic TiP₂O₇ structure in air. On the contrary, annealing Ti(III)p in inert atmospheres causes the formation of another yet unknown titanium phosphate structure (Ti(IV)p). In the TGA/DSC–MS experiment, two endothermic signals at ~723 and ~762 K are observed during this reaction. Both signals correlate with the decomposition of NH₄⁺ and the release of hydrogen (H₂) and ammonia (NH₃), as evidenced by the MS data. The XPS data of Ti(IV)p show, as contrasted to Ti(III)p, solely Ti in the oxidation state IV+. The H₂ release and the oxidation of Ti(III) to Ti(IV) imply the redox reaction 2Ti(III) + 2H₂O → 2Ti(IV) + H₂ upon heating in inert atmospheres, resulting in the chemical composition TiIV₃P₂O₇ for Ti(IV)p.

Here, we now report on the ab initio structure determination of the two new pyrophosphate phases (Ti(III)p and Ti(IV)p) from the PXRD data. Especially, the structure of Ti(III)p as the only pyrophosphate phase with solely trivalent titanium ions in the bulk material is of special interest and, to the best of our knowledge, unique. Even though Ti(IV)p contains tetravalent titanium ions and pyrophosphate groups similar to the well-known cubic TiP₂O₇, the PXRD data indicate significant structural differences. To solve the structures of both phases, first, the local structure/coordination of both compounds was analyzed via spectroscopic and total scattering methods. With the knowledge of the average local structure, the average bulk crystal structure was derived. In addition, the reaction from Ti(III)p to Ti(IV)p via two endothermic processes was studied with in situ temperature-dependent (TD) PXRD and Raman spectroscopy.

**Experimental Section**

**Material Synthesis.** The Ti(III)p sample was prepared via the molten salt synthesis from a dried mixture of TiO₂ (P25, Degussa, phase mixture of anatase and rutile, ≥99.5%) and NH₄(H₂PO₄) (Fluka, ≥97.0%). The reaction mixture was heated to 573 K for 2 h in a protective N₂ atmosphere. Ti(IV)p was obtained by annealing Ti(III)p under a protective atmosphere at 773 K for 4 h. The well-known cubic TiP₂O₇ was crystallized by heating Ti(III)p to 523 K in air. A detailed description of the synthesis approaches can be found in work by Stegmann et al.
PXRD. The PXRD experiments were performed on a STADI P diffractometer (STOE and Cie GmbH, Darmstadt, Germany) in transmission mode (θ/2θ = 0.5 mm) using Cu Kα radiation. The instrument was equipped with a primary Ge(111) monochromator and a position-sensitive detector system. The diffraction patterns of Ti(III)p and Ti(IV)p were recorded with a step size of 0.01° 2θ and a measuring time of 30 and 60 s step−1, respectively. From Ti(III)p, the TD data (303–823 K) were collected on an X'Pert Pro diffractometer (Panalytical BV, Amelo, The Netherlands) equipped with a divergence slit (0.25°), an antiscatter slit (0.5°), a Soller slit (0.04 rad), and a mask (5 mm). The data were recorded with an X'Celerator Scientific detector system. Additionally, an XRR-900 reflection beamline (Anton Paar GmbH, Graz, Austria) was installed. The PXRD data were collected in a diffraction range of 10−36° 2θ with a step width of 0.0167 step°. The sample was heated with 10 K min−1 to 823 K in an N2 atmosphere. The PXRD data were collected in 100 K steps in the temperature range from 100 to 300 K, in 5 K steps from 350 to 440 K, and in 50 K steps from 450 to 550 K. Hereafter, the sample was kept in synthetic air for 3 h. All PXRD patterns were analyzed with the DiffractionPlus Topas 6 software (Bruker AXS GmbH, Karlsruhe, Germany).27

Total Scattering Experiments and Subsequent Pair Distribution Function (PDF) Analysis. The data for the total scattering experiment and subsequent PDF analysis were collected at Petra III (Beamline P02.1, DESY, Hamburg, Germany) using a wavelength of 0.20709 Å. For data collection, a Varex XRD 4343DT instrument was equipped with a primary Ge(111) monochromator (AXS GmbH, Karlsruhe, Germany).27 The sample was heated to 923 K at 10 K min−1 steps from 350 to 440 K, and in 50 K steps from 450 to 550 K. An excitation wavelength of 785 nm; the laser power was tuned to 30 mW. An InVia spectrometer (Renishaw Ltd., Wotton-under-Edge, U.K.) was used. An increase in the laser power was used. Additionally, a TD measurement of Ti(III)p was performed in a CCR reaction cell (Linkam scientific instruments, Epsom, U.K.). The sample was heated to 923 K at 10 K min−1 in a N2 atmosphere.

Density Functional Theory (DFT) Calculation. DFT calculations for Ti(III)p and Ti(IV)p were carried out with the CASTEP code, version 17.32 All calculations used the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with the pair-wise dispersion correction devised by Tkatchenko and Scheﬄer.33,34 In each case, the coordinates of all atoms were optimized, fixing the unit cell parameters to experimental values. Spin-polarized calculations were performed for Ti(III)p. These calculations used on-the-fly-generated (OTFG) ultrasoft pseudopotentials and a cutoff energy of 750 eV for the plane-wave basis set. The first Brillouin zone was sampled using a 3 × 2 × 3 k mesh, corresponding to five irreducible k points. Because CASTEP does not support linear response calculations for systems with unpaired electrons, vibrational frequencies were calculated using the finite displacement method. Because of this methodological limitation, no Raman intensities could be predicted for Ti(III)p. DFT calculations for Ti(IV)p used OTFG norm-conserving pseudopotentials and a cutoff energy of 1200 eV. The first Brillouin zone was sampled using a 3 × 2 × 3 k mesh (nine irreducible k points). For this system, the vibrational calculation made use of the linear response method, enabling the prediction of Raman intensities.34,35 The calculation of 31P NMR shifts for Ti(IV)p employed the gauge-including projector-augmented-wave method implemented in CASTEP, using OTFG ultrasoft pseudopotentials with a cutoff energy of 871 eV.36,37 The reference calculation for NH4H2PO4 was carried out based on a fully ordered structure model of this compound proposed by Baur (space group P212121), again optimizing all atomic coordinates.40

Electrochemical Impedance Spectroscopy (EIS). The EIS measurements of Ti(III)p and Ti(IV)p were performed with an IM6 Zahner (Messeysyteme) impedance spectrum analyzer under hydrated [samples under deionized (DI) water] and anhydrous conditions (N2 atmosphere). For this purpose, powders of Ti(III)p and Ti(IV)p were pelletized although a compressive force of 14 ton cm−2 and clamped between golden stainless steel electrodes in a two-electrode cell. The EIS spectra were recorded at a direct-current voltage of 0 mV and a sinusoidal voltage perturbation of 100 mV in the frequency range of 4 MHz to 10 Hz. The proton conductivities were detected by fitting the half-circles in the Nyquist spectra.

RESULTS

Average Local Structure Analysis. The investigation of the chemical compositions of Ti(III)p and Ti(IV)p results in the stoichiometric formulas NH4[TiP2O7] and TiP2O7.26 The XPS spectra of Ti(III)p indicate tri- and tetravalent titanium species, while for Ti(IV)p, only tetravalent titanium species were found. For the structure determination, the average local structure was determined via Raman spectroscopy as well as complementary PDF data analysis. The obtained information about the polyhedral coordination was used for the ab initio crystal structure solution of both structures from PXRD. Spectroscopic methods like Raman spectroscopy enable analysis of the coordination polyhedra. The Raman spectrum of Ti(III)p shows the P symmetric stretching vibration of PO4 polyhedra [ν(P−O)] in the range from ~900 to 1200 cm−1 and the PO−P deformation vibration at 920 cm−1.25,41,42 In particular, stretching modes show a high correlation of the Raman shift with the bond length, which itself depends heavily on the second coordination sphere of PO4 polyhedra.25 This allows orthophosphates [Tes(P−O) = 150−185 pm; υ(P−O) = 900−1100 cm−1], pyrophosphates [Tes(P−O) = 145−156 Å; υ(P−O) = 975−1250 cm−1], or metaphosphates [Tes(P−O) = 145−154 Å; υ(P−O) = 1050−1150 cm−1] to be assigned.35,36 The symmetrical stretching vibration υ(P−O) of Ti(III)p [1035(1)−1135(1) cm−1] fits well to both pyro- and metaphosphates. The spectrum of Ti(III)p shows also the P−O−P symmetric stretching vibration [υs(P−O−P)] at 765(1) cm−1, together with the P−O−P deformation vibration [ω(P−O−P) = 920(1) cm−1], which are both characteristic for bent pyro- and metaphosphates.25,40 Also, tetrahedrally coordinated TiO4 polyhedra and Ti−O−Ti chains show a stretching mode at ~750 cm−1, but because of the appearance of characteristic TiO6 octahedral modes at 399, 519, and 639 cm−1, TiO4 and Ti−O−Ti chains are regarded as unlikely.24,41−43 The broadness of the TiO6 modes implies highly distorted octahedra. In the spectral range

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The experimental PDF of Ti(III)p (Figure 3a,b) shows atom pair correlations at 1.544(1) Å and 2.372(2) pm fitting well to the known P−O [r(P−O) = 1.845−1.858 Å] and O−O [r(O−O) = 2.48(2) Å] distances in the [P2O7]4− group. The Ti−O pair correlation at 2.026(1) Å is remarkable, which is significantly elongated in comparison to the typical bond distances of TiIV−O in titanium phosphates, which vary between 1.885(1) and 1.945(1) Å.26,27 The observed Ti−O pair correlation of Ti(III)p [r(Ti−O) = 2.026(1) Å] is in good agreement with the TiIII−O distances [r(TiIII−O) = 2.033(2)−2.029(2) Å] in Ti(PO3)3.23,24 Thus, the PDF data are clear proof for the incorporation of TiIII in the crystal structure of Ti(III)p. The TiIII species observed by surface-sensitive XPS is solely located on the crystal surfaces, while the bulk structure contains TiIV.26 The P−P distances at 2.881(2) Å correlate well to pyrophosphates [TiP2O7]: r(P−P) = 2.99 Å, which is also in agreement with the Raman results (Figure 2a).24 Additional pair correlations from the secondary coordination sphere in the range from 3.92 to 4.46 Å can be correlated to the P−O (3.501−4.776 Å) and P−P (4.103−4.786 Å) distances.25 The PDF analysis implies that the Ti(III)p structure consists of pyrophosphates connected by TiIII−O6 polyhedra.

The comparison of the PDFs of Ti(III)p (Figure 3a,b) and Ti(IV)p (Figure 3c,d) shows the presence of similar coordination polyhedra. After the reaction of Ti(III)p to Ti(IV)p, the P−O and P−P pair correlations remain almost unchanged at 1.549(4) and 2.880(4) Å (Figure 3c,d). In addition, the O−O distances remain quite similar [Ti(IV)p, 2.557(3) Å; Ti(III)p, 2.522(2) Å]. This indicates that the pyrophosphate unit remains stable during the reaction. The major differences are observed for the Ti−O pair correlation, which shortens significantly to 1.933(1) Å. Also, the Ti−P pair correlation shifts to smaller distances [3.2756(9) Å] mirroring the oxidation of TiIII to TiIV during the reaction of Ti(III)p to Ti(IV)p.24

The experimental PDFs of Ti(III)p (Figure 3a,b) and Ti(IV)p (Figure 3c,d) show both similarities to the PDF of TiP2O7 (Figure 3e,f) for short pair correlations. The pair correlations belonging to the first and second coordination spheres around the metal atoms up to ∼4.50 Å illustrate the structural relationship of the three compounds. However, the differences appearing at longer distances indicate major differences in the long-range order.

Analysis of the experimental PDF data reveals the incorporation of trivalent titanium species in the bulk structure of Ti(III)p. Further, the average local structure consists of TiO6 octahedra and pyrophosphates [P2O7]4−. Ti(IV)p, on the other hand, consists of tetravalent titanium ions. Analysis of the spectroscopic and scattering data reveals intact TiO6 octahedra and pyrophosphate [P2O7]4− units. The Raman spectra indicate a more regular coordination polyhedron.

**Average Bulk Structure Determination of the Ti(III)p Structure.** Indexing of the PXRD data of Ti(III)p results in a monoclinic unit cell with the metric parameters a = 7.5339 Å, b = 10.2642 Å, c = 8.2657 Å, and β = 105.86° (goodness of fit = 616.46). A Pawley fit of the measured data in space group P21/c, with the refined metric parameters summarized in Table 1, shows the best agreement.

The structure of Ti(III)p was determined via *simulated annealing* (ab initio structure solution). For the input file, the information about the unit cell metric and the obtained chemical composition (NH4+, P2O7, and TiIII) was
combined. For the pyrophosphate and ammonium groups, rigid bodies (Figure S1) were constructed. In the case of pyrophosphates, the rotational degree of freedom of the $P\cdash O\cdash P$ bonds was taken into account. The resulting structure models obtained by the simulated annealing approach were subsequently refined with the Rietveld method (Figure 4a). The refinement shows a good agreement between the model and the measured data with a residual value $R_{wp}$ of 7.94%. The crystal structure of Ti(III)p (Figure 5a,b) consists of TiO$_6$ octahedra connected via corner-sharing [P$_2$O$_7$]$^4^-$ polyhedra. Each TiO$_6$ octahedron is coordinated by five [P$_2$O$_7$]$^4^-$ groups: four as single-side ligands and one as a bidentate ligand. This is different from that in the well-known cubic TiP$_2$O$_7$ structure, where every [P$_2$O$_7$]$^4^-$ group is connected to the tetravalent titanium via an individually coordinating bond, resulting in an arrangement of [P$_2$O$_7$]$^4^-$ and TiO$_6$, which can be related to the NaCl-type structure. Ti(III)p consists of two [TiP$_4$O$_{12}$] layers (Figure 5c), translated relative to each other. The three-dimensional arrangement of these layers results in one-dimensional channels $[d_{\text{min}} = 2.46(1)$ Å; $d_{\text{max}} = 3.93(1)$ Å] running along the crystallographic $c$ axis (Figure 5a). The channels are stabilized by NH$_4^+$ ions coordinating the negatively charged [TiP$_2$O$_7$]$^-$ framework (Figure 5a). The calculation of the Fourier difference map (Figure S2) shows a residual electron density surrounding the incorporated NH$_4^+$ ions. This can be explained by the dynamical disorder of NH$_4^+$ and/or stacking faults in the structure resulting in partial blocking of the channels. The Ti(III)p structure can be related to the high-voltage pyrophosphate cathode material Li$_2$FeP$_2$O$_7$ also crystallizing in $P\overline{2}_1/c$ [$a = 11.01589(7)$ Å, $b = 9.75416(6)$ Å, $c = 9.80462(6)$ Å, and $\beta = 101.5444(6)^\circ$]$_{9,45,46}$. Li$_2$FeP$_2$O$_7$ consists of a three-dimensional arrangement of undulating [Fe$_4$P$_8$O$_{32}$]$^\infty$ layers building a channel system that is occupied by Li$^+$ ions. As such, the channel structure of Ti(III)p may prove appropriate for ion conductivity, provided the framework structure is stable when NH$_4^+$ is exchanged with other cations.

A more detailed discussion of the structural parameters of the two materials is provided in the Supporting Information.

To validate the structure model determined by simulated annealing and subsequent Rietveld refinement, a refinement of the PDF data based on the determined structure model from simulated annealing and subsequent Rietveld refinement was performed. For the fitting procedure, the scaling factor, spherical shape correction factor, Debye–Waller factors for each atomic species, lattice parameters, and $\delta_1$ values were combined. For the pyrophosphate and ammonium groups, rigid bodies (Figure S1) were constructed. In the case of pyrophosphates, the rotational degree of freedom of the P–O–P bonds was taken into account.

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**Table 1. Metric Parameters Obtained from Pawley Fitting**

| Structure Model | Symmetry | $R_{wp}$ (%) |
|-----------------|----------|--------------|
| Ti(III)p $P\overline{2}_1/c$ | $R_{wp} = 6.35\%$* | |
| Ti(IV)p $P\bar{1}$ | $R_{wp} = 5.91\%$* | |

$*R_{wp}$: weighted-profile $R$ factor.

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Figure 3. Experimental and fitted PDF data of (a and b) Ti(III)p, (c and d) Ti(IV)p, and (e and f) TiP$_2$O$_7$ and the respective difference curves (gray). In parts b, d, and f, the corresponding atom pairs are marked with lines.
because of low intensities. Thus, the fitting of the total scattering experiments as well as the high comparability of the measured and theoretical spectra derived from DFT calculations corroborate the successful structure solution of the Ti(III)p phase.

**Average Bulk Structure Determination of the Ti(IV)p Structure.** The indexing of the PXRD data of the Ti(IV)p phase resulted in a triclinic unit cell in space group P1 (goodness of fit = 46.05). The lattice parameters derived by subsequent Pawley fitting are listed in Table 1. For structure determination of Ti(IV)p via a *simulated annealing* technique, the unit cell information and a rigid body of the [P2O7]6− group (*Figure S1*) were combined. The subsequent Rietveld refinement shows good agreement of the calculated and measured data with an Rwp value of 5.64% (*Figure 4b*). The resulting structure model (*Figure Sb,d*) reveals that the [TiP2O7] layers (*Figure 5d*) and the channel system [dmin = 2.01(1) Å; dmax = 5.07(1) Å; *Figure 5b*) are maintained during the release of NH3 and H2, which go along with the oxidation of TiIII to TiIV. Calculation of the Fourier difference map (*Figure S2*) shows a residual electron density in the channel system, which might result from water adsorbed from ambient air.

The geometric structure parameters of Ti(IV)p are summarized and discussed in detail in Tables S2 and S4.

To also validate the determined structure of Ti(IV)p, the structure model was refined against the respective PDF data (*Figure 3c,d*). The refinement shows a good match at large distances (Rw = 28.4246). The PDF calculated from the refined structure model with elongated bridging P−O distances [r(P−O1) = 1.60(1) Å] and somewhat shorter terminal P−O distances [r(P−O2−O7) = 1.54(4) Å] shows good agreement with the PDF of the measured data. Besides, the intramolecular P−P [2.83(1) Å] and O−O (between ~2.40 and 2.50 Å) distances fit well to the described model. Moreover, also the Ti−O distances in the TiO6 octahedra fit well with the model. The improved fit in the higher r range indicates a higher long-range order displaying structural relaxation during the release of NH3 and H2 and oxidation of the titanium, resulting in a more regular channel structure (*Figure 5*).

Further, the structural model was validated by spectroscopy. *Figure 2b* displays the calculated Raman spectrum including theoretical intensities. Both the calculated intensities and the positions fit well to the experimental spectrum (*Figure 2b*). The biggest deviation between the calculated and measured data is the shift of the deformation mode of the pyrophosphate ν2[P−O−P] = 920(1) cm−1. This mode highly depends on the P−O−P angle. Determination of the latter via PXRD underlies systematic errors. A noteworthy similarity is the comparable intensity of the observed and calculated symmetrical stretching vibrations υs(P−O[P] 765(1) cm−1), indicating the change in the P−O−P angle as described earlier. Similar to the Ti(III)p model, a shift of the calculated Raman modes of Ti(IV)p to lower wavenumbers is observed, a phenomenon that is commonly observed for DFT calculation using the PBE functional.

Finally, support for the validity of the structural solution found for Ti(IV)p comes from 31P NMR. NMR spectroscopy is very sensitive to the local geometry around the nucleus studied. *Figure 6* shows that the two inequivalent phosphorus sites in the pyrophosphate units give rise to well-resolved resonance lines at ~28.7 and ~32.1 ppm. The line widths (full width at half-height, fwhh) for both resonance lines measured
varied between 120 and 150 Hz. The additional shoulder at about −26 ppm and the other broad lines at the low-field side are assigned to crystal defects and amorphous byproducts. The relative intensities of these additional contributions varied from sample to sample, with a total intensity in the range of 5−12% of the phosphorus detected. Not only the isotropic chemical shifts but also its anisotropy contain information about the local geometry around the nucleus. The two parameters describing the chemical shift anisotropy, the span $\Omega$ and skew $\kappa$, can be extracted from the MAS NMR spectra by a well-established procedure.$^{31,46}$ To determine these parameters for the two phosphorus atoms in Ti(IV)p, we used spectra taken at three different spinning speeds (Figure 7). The thus-obtained data are reported in Table 2 together with the results of DFT calculations (CASTEP).

We regard the data derived from the spectra measured at 3 and 5 kHz as the most reliable ones. In general, the highest reliability for the determination of shift tensor components from MAS NMR spectra is achieved when the central band is surrounded by five to seven spinning sidebands of significant intensities.$^{49}$ Furthermore, at low spinning speeds, any thermal effects caused by frictional heating can be neglected.$^{50}$ From the data given in Table 2, the assignment of the two resonance lines in Figure 6 is obvious. The differences between the calculated and experimental isotropic chemical shifts fall into the range obtained for other phosphates.$^{51}$ Not only the isotropic chemical shifts but also the spans $\Omega$ are nicely reproduced by the DFT calculations. The low-field line has a considerably smaller span than the high-field one, in both theory and experiment. The only significant differences occur for the values of the skew $\kappa$, i.e., of the parameter that describes the position of $\delta_{22}$ ($\sigma_{22}$) with respect to $\delta_{11}$ ($\sigma_{11}$) and $\delta_{33}$ ($\sigma_{33}$). Similarly good agreement with the experiment in the span values and comparably large deviations in the skew values have been observed in previous DFT investigations on inorganic phosphates, which used an analogous computational approach.$^{52,53}$

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**Figure 5.** (a) Crystal structure of Ti(III)p viewed along the one-dimensional channel with incorporated NH$_4^+$ ions. (b) Crystal structure of Ti(IV)p displaying the empty one-dimensional channels. (c) [TiP$_4$O$_{12}$] layers of the Ti(III)p structure in the $ab$ plane. For the sake of clarity, the NH$_4^+$ ions are not included. (d) [TiP$_4$O$_{12}$] layers in the Ti(IV)p structure displayed in the $ab$ plane.

**Figure 6.** $^{31}$P MAS NMR spectrum of the same Ti(IV)p sample that was used for the PXRD measurement ($\nu_{\text{MAS}} = 10$ kHz). The dashed blue line depicts the same spectrum magnified by a factor of 8. The width of both resonance lines (fwhh) is about 140 Hz. The assignment is based on the results of DFT calculations.
Because the DFT calculations are based on the structural data, the rather good agreement between the experimental and calculated chemical shift data delivers sound evidence for the validity of the structure solution.

Both novel titanium phosphate structures belong to the class of transition-metal pyrophosphates, MP$_2$O$_7$. Most MP$_2$O$_7$ compounds (M = Si, Sn, Pb, Ti, Zr, Hf, U, Ce) crystallize in a $3 \times 3 \times 3$ superstructure in the space group $P$6$_3$. In MP$_2$O$_7$ structures, all TiO$_6$ octahedra are connected via corner-sharing oxygen atoms to six [P$_2$O$_7$]$^-$ groups. Hereby, the pyrophosphates and TiO$_6$ octahedra are arranged in a loosely NaCl-type structure. The usage of NH$_4$(H$_2$PO$_2$) in the synthesis causes not only the stabilization of titanium in the oxidation state III$^+$ but also the incorporation of NH$_4^+$ ions in the channels of the structure. Both the change in the oxidation state and the incorporation of NH$_4^+$ ions in Ti(III)p cause a change in the arrangement of the TiO$_6$ octahedra and [P$_2$O$_7$]$^-$ groups. Unlike in the cubic TiP$_2$O$_7$ structure, five [P$_2$O$_7$]$^-$ groups are connected via corner-sharing oxygen atoms and one [P$_2$O$_7$]$^-$ group is connected via two oxygen atoms. This arrangement causes the formation of big one-dimensional channels stabilized by the NH$_4^+$ ions.

Heating Ti(III)p causes the thermal decomposition of NH$_4^+$ and the oxidation of Ti$^{III}$ to Ti$^{IV}$. In air, Ti(III)p reacts to the well-known TiP$_2$O$_7$. As described above, the reaction includes major changes in the Ti−P network. Heating of Ti(III)p in inert atmospheres, on the other hand, results in the formation of Ti(IV)p. Despite the fact that this reaction is also driven by the decomposition of NH$_4^+$ and the oxidation of titanium, the Ti−P network of Ti(III)p remains stable.

### Proton Conductivities of Ti(III)p and Ti(IV)p

As mentioned above, Ti(III)p shows a structure related to the known cathode material Li$_2$FeP$_2$O$_7$. Both consist of a channel system stabilized by incorporated ions. Consequently, we studied the proton conductivities of Ti(III)p and Ti(IV)p. Impedance spectroscopy on Ti(III)p and Ti(IV)p was performed under hydrated and anhydrous conditions. While the anhydrous samples do not allow an efficient proton migration, showing conductivities in the range of $10^{-6}$ S cm$^{-1}$, the presence of liquid water increases the conductivities by 3 orders of magnitude (Figure S5) to the range of $10^{-3}$ S cm$^{-1}$. The high proton conductivities under fully hydrated conditions (samples immersed in DI water) were accompanied by low activation energies for the proton transport of 0.17 and 0.4 eV for Ti(III)p and Ti(IV)p, respectively, as shown by the Arrhenius plots in Figure 8.

### Table 2. Chemical Shift Data for Ti(IV)p as Obtained by $^{31}$P MAS NMR and DFT Calculations

| $\nu_{\text{MAS}}$ (kHz) | $\delta_{\text{iso}}$ (ppm) | $\Omega$ (ppm) | $\kappa$ |
|------------------------|-----------------|----------------|----------------|
|                         | P1              | P2            | P1              | P2            | P1 | P2       |
| MAS NMR                |                 |               |                 |               |     |
| 3                      | −28.7           | −32.1         | 101.4           | 110.0         | −0.45 | −0.63 |
| 5                      | −28.7           | −32.1         | 101.3           | 110.3         | −0.45 | −0.63 |
| 8                      | −28.7           | −32.1         | 104.4           | 111.1         | −0.39 | −0.62 |
| CASTEP                 | −27.1           | −31.3         | 100.7           | 110.3         | −0.54 | −0.89 |

\[31P\] MAS NMR spectra of Ti(IV)p measured at different spinning speeds. The data were shifted for the sake of clarity. The experimental spectra (black curves) are shown in comparison with those calculated using the parameters given in Table 2 for $\nu_{\text{MAS}} = 5$ kHz (red curves).

![Figure 7. 31P MAS NMR spectra of Ti(IV)p measured at different spinning speeds. The data were shifted for the sake of clarity. The experimental spectra (black curves) are shown in comparison with those calculated using the parameters given in Table 2 for $\nu_{\text{MAS}} = 5$ kHz (red curves).](https://doi.org/10.1021/acs.inorgchem.1c02613)

![Figure 8. Arrhenius plots of the conductivities of Ti(III)p (blue) and Ti(IV)p (red) as a function of the temperature under fully hydrated (under DI water) conditions.](https://doi.org/10.1021/acs.inorgchem.1c02613)
triclinic Ti(IV)p to the cubic TiP₂O₇ structure with both titanium ions in the oxidation state IV⁺. To investigate the structural relationship of Ti(III)p, Ti(IV)p, and cubic TiP₂O₇, in situ TD PXRD experiments were performed.

Ti(III)p was heated first to 823 K under an inert atmosphere to study the phase transition Ti(III)p → Ti(IV)p. In a second step, the atmosphere was switched to synthetic air and the sample was kept at 823 K for 180 min. The reflections of monoclinic Ti(III)p remain unchanged up to 633 K (Figure 9). In the temperature range from 638 to 658 K, the reflections shift to higher diffraction angles, indicating a negative thermal expansion. This contraction of the unit cell correlates with thermal decomposition of the incorporated NH₄⁺ ions to NH₃ and H⁺. The TGA–MS results imply a successive reduction of the formed H⁺ ions to H₂. These signals can be correlated to two events visible in the in situ PXRD data: first, thermal decomposition of NH₄⁺ to NH₃ and H₂ and, second, subsequent relaxation of the Ti(IV)p structure. Stegmann et al. observed in the DSC data two exothermic signals (T = 723 and 763 K) that can be correlated to the two-step reaction. The differences in temperatures between the X-ray diffraction and DSC experiments are caused by different instrumental setups.

Also in situ Raman spectra were recorded upon heating Ti(III)p to 823 K in an inert atmosphere (Figure S3). From ambient temperature to 628 K, the characteristic Raman modes of Ti(III)p are observed. In the temperature range from 633 to 643 K, the intensities of all modes decrease. The in situ PXRD data reveal that in this temperature window thermal decomposition of NH₄⁺ together with the formation to Ti(IV)p proceeds. At higher temperatures (T > 643 K), the characteristic modes of Ti(IV)p are observed.

In a subsequent in situ PXRD experiment performed at 823 K in synthetic dried air (Figure S4), Ti(IV)p was retained for 3 h. Under these conditions, no reaction of Ti(IV)p to cubic TiP₂O₇ could be detected. However, during the synthesis in air, a phase transformation from Ti(IV)p to TiP₂O₇ was observed. The major structural difference of Ti(III)p and Ti(IV)p compared to TiP₂O₇ is in the connection of the gaseous species, the appearance of reflections belonging to triclinic Ti(IV)p is detected. Above 658 K, only the Ti(IV)p phase is observed.

The evolution of the lattice parameters of Ti(III)p with temperature reveals the formation of the high-temperature phase Ti(IV)p (Figure 10a,b). In particular, the lattice parameter b and the angle β are sensitive indicators for the phase transformation. The lattice parameters of Ti(IV)p scatter up to 633 K (Figure 10b). Above this temperature, all metric parameters show a sudden increase to a more or less stable value. The sole exception is the angle γ, which decreases after remaining at a small plateau (698 < T < 723 K). The TiD evolution of the metric parameters of Ti(IV)p implies a subsequent relaxation and order of the newly formed phase. As mentioned above, the TGA–MS data of the reaction of Ti(III)p to Ti(IV)p exhibit two distinct endothermic signals. These signals can be correlated to two events visible in the in situ PXRD data: first, thermal decomposition of NH₄⁺ to NH₃ and H₂ and, second, subsequent relaxation of the Ti(IV)p structure. Stegmann et al. observed in the DSC data two exothermic signals (T = 723 and 763 K) that can be correlated to the two-step reaction. The differences in temperatures between the X-ray diffraction and DSC experiments are caused by different instrumental setups.

Figure 9. PXRD data obtained during heating of Ti(III)p in an inert atmosphere.

Figure 10. (a) Evolution of the unit cell parameters of Ti(III)p with temperature: the lattice parameters a, b, and c and the angle β. (b) Plus the unit cell parameters of Ti(IV)p: the lattice parameters a, b, and c and the angles α, β, and γ.
transformation to Ti(IV)p upon annealing in inert atmospheres. The phase transformation of either Ti(III)p or Ti(IV)p to TiP₂O₇ would necessarily cause a change in the connectivity because, in the latter structure, the titanium(IV) cation is surrounded by six monodentate [P₂O₇]⁴⁻ groups. Because the phase transformation to TiP₂O₇ proceeds in an ambient atmosphere, Ti(III)p reacts to Ti(IV)p at 633 K. Above 633 K, a contraction of the structure correlated with the decomposition of NH₄⁺ to NH₃ and the simultaneous redox reaction 2H⁺ + 2Ti³⁺ → H₂ + 2Ti⁴⁺ is observed. Besides, the formation of Ti(IV)p is detected at 633 K. The evolution of the metric parameters of Ti(IV)p with temperature implies relaxation and ordering of the newly formed phase at 723 K. The reaction of Ti(IV)p to cubic TiP₂O₇ at 823 K, which readily proceeds in ambient air, could not be detected in dried synthetic air, showing the temperature stability of the local configuration in the absence of water.

The proton conductivity of the newly synthesized phosphates Ti(III)p and Ti(IV)p seems to be based on the Grotthuss mechanism. The specific proton conductivity and the activation energy of the proton migration of Ti(III)p belong to the highest and lowest, respectively, ever reported for this class of materials and indicate its potential application as a proton-conducting electrolyte for electrochemical devices like fuel cells and water electrolyzers, working in the intermediate temperature range.

## CONCLUSION

The structure determination of two novel titanium pyrophosphate structures, Ti(III)p and Ti(IV)p, has been successfully carried out by combining complementary diffraction and spectroscopic techniques. By this stepwise approach, first, the average local atomic structure and then the bulk crystal structure were determined. Previous studies of Ti(III)p discussed the chemical composition NH₄TiP₂O₇. The XPS data indicated tri- and tetravalent titanium cations on the surface of the compound, while for Ti(IV)p, only tetravalent titanium was observed. By total scattering experiments with subsequent PDF analysis, the presence of only trivalent titanium species was confirmed in the bulk structure of Ti(III)p. The tetravalent species observed by XPS originate from surface oxidation of the Ti(III)p sample. The PDF data of Ti(IV)p show tetravalent species in accordance with the XPS data. The coordination polyhedra were studied via Raman spectroscopy and total scattering experiments, resulting in primary building units similar to those known for cubic TiP₂O₇. All structures consist of pyrophosphate units and TiO₆ octahedra. In the case of Ti(III)p, additional NH₄⁺ cations and highly distorted TiO₆ octahedra are observed.

The proton conductivity of the newly synthesized phosphates Ti(III)p and Ti(IV)p seems to be based on the Grotthuss mechanism. The specific proton conductivity and the activation energy of the proton migration of Ti(III)p belong to the highest and lowest, respectively, ever reported for this class of materials and indicate its potential application as a proton-conducting electrolyte for electrochemical devices like fuel cells and water electrolyzers, working in the intermediate temperature range.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02613.

Geometrical information on the rigid bodies used for refinement, fractional coordinates of the solved structure models, a detailed discussion of the resulting geometrical parameters (bond angles and bond distances), residual electron densities, detailed discussion of the modeling of the PDF data, additional TD Raman data of Ti(III)p under an inert atmosphere, and the TD PXRD data of Ti(IV)p collected at 823 K in synthetic air plus the TD proton conductivities of Ti(III)p and Ti(IV)p (PDF)

### Accession Codes

CCDC 2105122 and 2105123 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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