A New Open-structured Titanophosphate with Intersecting 12-Ring Channels

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A novel mixed valent titanophosphate open-structure was hydrothermally synthesized; the connections of TiO_6 and PO_4 groups generate a porous architecture with two types of 12-MR channels.

Microporous metal phosphates have been substantially pursued for their properties of redox catalysis, photochemistry, and magnetism.[1] Titanium has been of particular interest as a framework component. Titanium-substituted zeolites and microporous titanosilicates, such as ETS-4 and ETS-10, have shown enhanced catalytic performances.[2] Also, titanium phosphates have shown their importance in materials science, such as the SHG crystal $KTiOPO_4$, the ion-exchange and adsorptive properties of α-$Ti(HPO_4)_2$, γ-$Ti(H_2PO_4)(PO_4)\cdot H_2O$, the NASICON-type $MTi_2(PO_4)_3$ as fast ionic conductors or low thermal expansion ceramics.[3] However, open-structured titanophosphates are still limited in the literature. The first synthetic example was reported for the pursuit of new KTP-related SHG materials in 1994.[4] Two layered structures were then reported.[5] Followed were three porous structures.[6] Several new compounds were isolated by Ferey's and Pang's groups in the past few years.[7] The first microporous reduced titanophosphate was reported by Sevov and Ekambaram,[8] which is rare and interesting for catalytic and magnetic properties. More recently, two reduced titanium gallophosphates were isolated, including a zeolitic phase having 10-MR channels and reversible oxidation state of Ti^{III} and Ti^{IV}.[9] Herein, the synthesis and structure of a new titanophosphate, $[NH_4][Ti^{IV}Ti^{III}(H_2O)_2(PO_4)_2(HPO_4)]$ (denoted as TJPU-2, TJPU = Tianjin Polytechnic University), was reported.

TJPU-2 was hydrothermally synthesized from a mixture of 0.2 g of metallic Ti powder, 0.2 g of $ZnCl_2$, 1.5 mL of H_3PO_4, 0.2 g of diethylenetriamine (DETA), and deionized water at 170 °C for 5 days. The reaction produced blue rectangular crystals. The blue color of the product indicated the existence of Ti^{III} species in the obtained compound. The presence of Zn cation affected the product greatly. The EDAX measurements on three different crystals gave an average P:Ti ratio of 1.5. Only a trace amount of zinc was detected, which could be neglected. High quality crystals only formed in the presence of 0.15–0.2 g of $ZnCl_2$. Attempts to isolating TJPU-2 in the absence of $ZnCl_2$ produced blue powders with the same structure of TJPU-2 indicated by powder X-ray diffraction. Zinc was suggested to serve as a mineralizer. The well-matched experimental and simulated powder XRD patterns (Supporting Information (SI) Figure 1)[14] of TJPU-2 demonstrated the phase purity. Thermogravimetric analysis (SI Figure 2)[14] shows a three-step mass loss between room temperature to 1000 °C. The total 18.8 wt % mass losses are attributed to the liberation of water and NH_3 and the loss of hydroxy groups.

Structure refinement reveals that TJPU-2 crystallizes in orthorhombic space group *Pnna*.[10] The asymmetric unit (SI Figure 3)[14] contains twelve non-hydrogen atoms (two Ti, two P, seven O, and one N). Both of the two unique P atoms were in monophosphate configurations with the bond lengths of 1.504(5)–1.541(5) Å and bond angles of 107.9(3)–112.2(3)°. The terminal O(6) atom attached to P(2) atom was assigned to hydroxy group with elongated P–O distance [P(2)–O(6), 1.538(5) Å]. The titanium atoms were all octahedrally coordinated by six O atoms with the bond lengths ranging from 1.897(5)–2.051(5) Å and bond angles in the range of 85.5(3)–180°. In the case of Ti(1), all six oxygen atoms were jointed to the adjacent P atoms. Ti(2) located at an inversion center. While O(1) and O(5) of $Ti(2)O_6$ octahedron were linked to P atoms, O(7) belonged to terminal coordinated water molecules in a trans configuration, forming a $Ti(2)O_4(H_2O)_2$ octahedron. The hydrogen atoms of water molecules and hydroxy groups were found in difference Fourier maps in the single-crystal X-ray diffraction analysis. The highly disordered nitrogen atoms vibrate between four site with each in 0.125 occupation. No attempt was made to ride the hydrogen atoms to N atom. Bond valence sum calculations[11] give the oxidation states of Ti are 4.38 for Ti(1) and 3.17 for Ti(2), indicating the mixed valence feature of TJPU-2 (SI Figure 4).[14] The magnetic susceptibility of TJPU-2 was measured to determine the presence of Ti^{III} (SI Figure 5).[14] The paramagnetic behavior over $2 \leq T \leq 300$ K gives experimental support for the presence of Ti^{III}. The curve is fitted with $\chi_m = C_m/(T - \theta) + \mathrm{TIP}$, where C_m and θ are the Curie and Weiss constants respectively. The curie constant indicates the magnetic moments of 1.734 μ_B that is consistent with a single unpaired electron per formula unit. Hence, TJPU-2 was formulated as $[NH_4][Ti^{IV}Ti^{III}(H_2O)_2(PO_4)_2(HPO_4)]$.

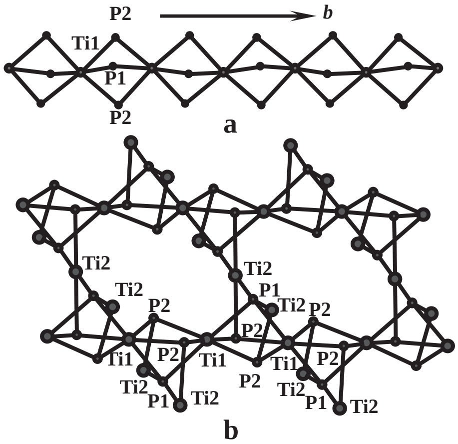

Figure 1. The trible connected chain running along *b* axis (a) bridged by $Ti(2)O_6$ to form 3-D structure (b). Oxygen atoms are omitted for clarity.

The extended structure of TJPU-2 is a macroanionic

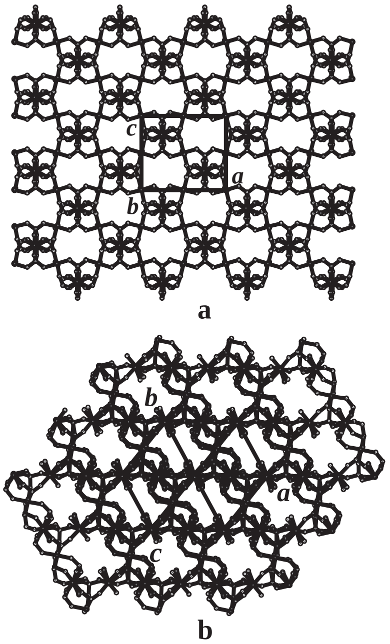

Figure 2. The structures of the two types of 12-ring channels in TJPU-2: (a) viewed along *b* direction; (b) viewed along [111] direction. Water molecules and ammonium cations are omitted for clarity.

$[Ti^{IV}Ti^{III}(H_2O)_2(PO_4)_2(HPO_4)_{0.5}]^{-1}$. The structure could be elucidated as the following steps. Ti(1) is linked to P(1) and P(2) atoms through O(2), O(3), and O(4) atoms, forming an infinite triple-bridged chain running along *b* axis (Figure 1a). Thus each $Ti(1)O_6$ octahedron shares three phosphates with each of its neighbors on either side. In someways, it can be compared to 1-D polymers for aluminophosphates $[AlP_2O_8H_x]^{-(3-x)}$,[12] which have tetrahedral Al centers spanned by two phosphates to each neighbor in a similar manner. This chain structure has been observed in $[enH_2][Zr(HPO_4)_3]$.[13] In compound $[enH_2][Zr(HPO_4)_3]$, the chain structures are separated by organoamines and stabilized by complex H bonds. In TJPU-2, however, the chains were bridged by $Ti(2)O_6$ octahedron, generating a three-dimensional architecture (Figure 2b). The connection of $Ti(2)O_6$ and the chains generates two types of intersecting 12-ring apertures (Figure 2). One set of distorted 12-ring opening runs along *b* axis with the elongated hexagonol shape and with its window in chair configuration. The dimensions of this channel are 5.2 × 8.5 Å (SI Figure 6).[14] Another type of tunnels runs along [111] direction with the dumbbell shape. The channels are blocked by the coordinated water and hydroxy groups with O(7)–O(7) distance of 5.33 Å and O(6)–O(6) distance of 2.67 Å. The ammonium cations are also located in the channel spaces with H bond to the framework. No attempts are performed to elucidate possible H-bond configurations because of the high degree of disorder of ammonium cation.

In summary, a novel titanophosphate was hydrothermally synthesized. The two unique Ti atoms in TJPU-2 are in Ti^{III} and Ti^{IV} oxidation state, respectively. The linkages of $Ti^{IV}O_6$ and PO_4 groups generate the motif of infinite chain running along the *b* direction. Bridging these chains by $Ti^{III}O_6$ groups produces a three-dimensional framework with two types of 12-MR channels.

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10 Crystal data of TJPU-2: $[NH_4][Ti^{IV}Ti^{III}(H_2O)_2(PO_4)_2(HPO_4)]$, $M_r = 436.80$, orthorhombic space group *Pnna*, $a = 12.809(3)$, $b = 9.3747(19)$, $c = 11.205(2)$, $V = 1345.5(5)\,Å^3$, $Z = 4$, $D_{calcd} = 2.156\,g\,cm^{-3}$, μ (Mo Kα) $= 1.614\,cm^{-1}$. A crystal with dimensions of $0.2 \times 0.12 \times 0.06\,mm^3$ was selected and mounted on a Siemens SMART CCD diffractometer. Reflections were recorded at $273 \pm 2\,K$. 10458 reflections were collected with 1523 unique and 1247 observed ($R_{int} = 0.0753$). Data processing was accomplished with SAINT program. The structure was solved by direct methods. Refinements on F^2 by full-matrix least-squares were performed by using the SHELXTL97 crystallographic software package. Direct phase determination yielded the positions of Ti, P, and a part of oxygen atoms, and the rest oxygen atoms and nitrogen atom were located in successive difference Fourier syntheses. The hydrogen atoms of HPO_4 and water molecule were found in the final difference Fourier map. All non-hydrogen atoms were refined anisotropically. The final residuals wR_2 (for all data) was 0.1368 and R_1 was 0.0646 with $S = 1.099$.

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14 Supporting Information is available electronically on the CJS-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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