6804 *Inorg. Chem.* **2009**, *48*, 6804–6811
DOI: 10.1021/ic900738m

Inorganic Chemistry
Article

Revisiting Tungsten Trioxide Hydrates (TTHs) Synthesis - Is There Anything New?

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Received April 15, 2009

We report a very simple precipitation route to prepare a layered perovskite-type structure, tungsten trioxide hydrate (TTH), with the nominal chemical formula of $WO_3\cdot1.3H_2O$ ($\equiv$ $1/2H_2W_2O_7\cdot1.6H_2O$), using aqueous Na_2WO_4 and $SrCl_2$. Our investigation shows that the concentration of HCl used to dissolve the $SrCl_2$ plays a crucial role in the stabilization of different structure types of layered TTHs. Highly acidic $SrCl_2$ (dissolved in 9 M HCl) solution yields an orthorhombic layered TTH of $WO_3\cdot2H_2O$, while $SrCl_2$ dissolved in 3 M HCl appears to give an A-site-deficient Ruddlesdon–Popper (RP) related double-perovskite-type layered structure (DOLS-TTH). A well-known scheelite-type structure is obtained under weakly basic conditions (pH = 10.3 for $Na_2WO_{4(aq)}$, 7.0 for $SrCl_{2(aq)}$). Previously, RP-type a DOLS of $H_2W_2O_7\cdot0.58H_2O$ was prepared, using an acid-leaching method, from the corresponding $n = 2$ member of the layered Aurivillius phase (AP) $Bi_2W_2O_9$. Powder X-ray diffraction showed the formation of layered RP DOLS with a large d spacing $\sim$12.5 Å, which is consistent with acid-leaching (Kuto et al. *Inorg. Chem.* **2003**, *42*, 4479–4484; Wang et al. *J. Solid State Chem.* **2007**, *180*, 1125–1129) and exfoliation (Schaak et al. *Chem. Commun.* **2002**, 706–707) methods for synthesized TTHs. The proposed DOLS-TTH structure of newly prepared TTHs was further confirmed by an intercalation reaction using *n*-octylamine (C8A). A transmission electron microscopy study showed the formation of nanosized particles, and scanning electron microscopy coupled with energy dispersive X-ray analysis showed the absence of Na and Sr in the air-dried, as-precipitated products under acidic conditions. The bulk electrical (proton) conductivity of presently prepared TTHs was found to be on the order of 10^{-4}–10^{-3} S/cm at room temperature in wet N_2.

Introduction

The chemistry of tungsten trioxide hydrates (TTHs), also well-known as tungstic acids, has been studied since the early 1900s.[1−3] Several different chemical compositions, crystal structures, and microstructures were identified for $WO_3\cdot nH_2O$ (n = 0, 0.33, 0.5, 1, and 2).[1,3,4] The water content in the TTHs appears to be very crucial in the stabilization of different types of crystal structures. For example, $WO_3\cdot2H_2O$ exhibits a layered structure (space group $P2_1/n$; a = 10.4840(43) Å; b = 13.8041(56) Å; c = 10.5733(43) Å; β = 91.0418(2)°),[5] which consists of a corner-sharing single-sheet of $WO_5(OH_2)$, and the second water molecule is occupied between the interlayers (Figure 1a). A similar structure was reported for the corresponding Mo analogue.[6] The monohydrate WO_3H_2O has been prepared using many different chemical synthesis methods, including a gentle dehydration of the $WO_3\cdot2H_2O$, precipitation from sodium tungstate using dilute mineral acids, and acid-leaching of $LiMW_2O_8$ (M = Al, Fe).[7−10] A single-crystal X-ray diffraction study showed that the WO_3H_2O crystallizes in an orthorhombic space group, *Pmnb*, with a = 5.249 Å, b = 10.711 Å, and c = 5.133 Å (Figure 1b).[4] The structure is characterized by highly distorted corner-sharing $WO_5(OH_2)$ octahedral units coordinated with five oxygen atoms and a water molecule. The sheets of $WO_5(OH_2)$ polyhedra are held together by hydrogen bonding and possess a layered structure.

Among the other TTHs, the existence of hemihydrate $WO_3\cdot0.5H_2O$ has been claimed by a few authors,[11−13] while $WO_3\cdot0.33H_2O$ has been investigated by large numbers of research groups around the world.[10,11,14,15] Hemihydrate

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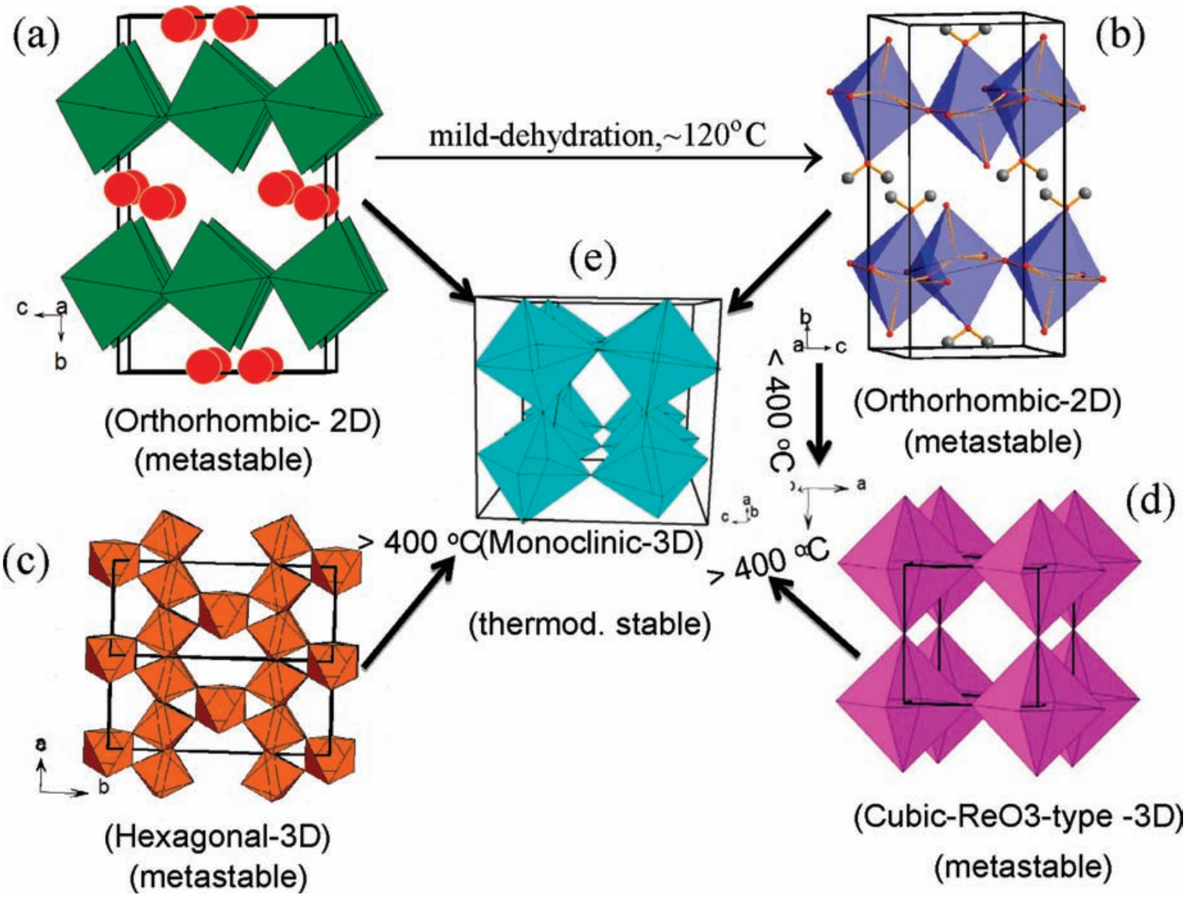

Figure 1. Idealized crystal structure of (a) $WO_3 \cdot 2H_2O$ prepared by precipitation of Na_2WO_4 at highly acidic pH, (b) $WO_3 \cdot H_2O$ prepared from sample "a" by mild dehydration reaction, (c) hexagonal WO_3 prepared by heating $WO_3 \cdot 0.33H_2O$ at 270−350 °C, (d) ReO_3-type perovskite structure prepared by heating sample "a" or "b" at about 350 °C, and (e) thermodynamically stable monoclinic WO_3 prepared by heating samples "a"−"d" above 400 °C.

was found to be crystallized in cubic pyrochlore ($Fd\bar{3}m$; a = 10.270 (3) Å) structures and consists of six-member WO_6 corner-sharing octahedra and water molecules that are present in the tunnel of six-corner-sharing WO_3. A powder X-ray diffraction (PXRD) study showed that $WO_3 \cdot 0.33H_2O$ crystallizes in orthorhombic space group *Fmm*2 with a = 7.359(3) Å, b = 12.513(6) Å, and c = 7.704(5) Å.[11] Interestingly, anhydrous WO_3 crystallizes as a metastable (thermodynamically unstable) phase in a variety of inorganic crystal structures, including hexagonal[16] (a = 7.323(6) Å, c = 3.905(3) Å; Figure 1c), A-site-deficient ReO_3-type perovskite (a = 3.812(7) Å;[9] Figure 1d), and thermodynamically stable monoclinic (a = 7.306(1) Å, b = 7.540(1) Å, c = 7.692(1) Å, β = 90.881(5)°;[9] Figures 1e). These metastable WO_3 structures are commonly prepared by utilizing soft-chemical (*chimie douce*) methods (e.g., dehydration) and are impossible to synthesize using the conventional solid-state method.[17,18] A similar topotactic dehydration reaction has been reported for molybdenum trioxide dihydrate.[19]

It is interesting to mention that very recently Schaak and Mallouk[20] and Kudo et al.[21] prepared independently a novel A-site-deficient double-perovskite-type layered structure (double-octahedral layered structure, DOLS) with chemical formulas of $H_2W_2O_7$[20] and $H_2W_2O_7 \cdot 0.58H_2O$[21] from the layered double-perovskite-sheet Aurivillius phase (AP) $Bi_2W_2O_9$ employing acid leaching at ambient temperature for 3 days. This can be expressed by the chemical reaction[20]

$$Bi_2W_2O_9 \xrightarrow[-2BiOCl]{6M\ HCl_{excess}} H_2W_2O_7$$

It has been suggested that, during the transformation reaction, the double-perovskite blocks remain intact; hence, the reaction appears to be a topochemical conversion.[20,21] The new metastable layered $H_2W_2O_7$ phase may be described as an n = 2 member of an A-site-deficient layered Ruddelsdon−Popper (RP)[22] or AP-related[23] structure, since both of these phases have a comparable lattice constants. For example, the c axis of $H_2W_2O_7 \cdot 0.58H_2O$[21] was found to be 22.1(1) Å, which is comparable to that of the n = 2 (where n = 2 represents the number of corner-sharing perovskite slabs) member of the RP phase, $Sr_3Ti_2O_7$ (c = 20.38 Å),[21] and the

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$n = 2$ member of the AP phase, $Bi_2W_2O_9$ ($c = 23.7063(5)$ Å).[21] The fundamental difference between the RP $Sr_3Ti_2O_7$ and AP structure $Bi_2W_2O_9$ is that the Sr occupies the A-site cuboctahedra site[22] and falls between the perovskite-like layers in the RP phase, while in the AP phase, the $\{Bi_2O_2\}^{2-}$ separates the A-site-deficient perovskite-like layer.[23]

In our continuing pursuit[24-27] of the development of solid oxide ion electrolytes for intermediate-temperature solid oxide fuel cells, we intended to prepare oxide ion-conducting doped $SrWO_4$ by using a precipitation reaction. In our first experiment, we dissolved $SrCO_3$ in dilute HCl instead of aqueous $SrCl_2$. Astonishingly, we observed a greenish yellow precipitate instead of the expected white-color $SrWO_4$. A PXRD study showed the formation of a layered structure, rather than the regular tetragonal scheelite-type structure.[28] Hitherto, A-site-deficient DOLS tungsten trioxide hydrates (TTHs) were prepared generally by acid leaching;[20,21] here, we report a simple precipitation reaction method to synthesize RP-related structure DOLS-TTH involving Na_2WO_4 and $SrCl_2$ + 3 M HCl. This paper describes the preparation, dehydration properties, intercalation reaction, microstructure, and particle size characterizations as well as the electrical (proton) conductivity of the new metastable TTHs.

Experimental Section

Preparation of A-Site-Deficient Layered Perovskite-Type $WO_3\cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7\cdot 1.6H_2O$). The desired amount of high-purity $SrCl_2$ (99.7%, Fisher Scientific) was dissolved in a minimum quantity of 3 M HCl (Hydrochloric acid GR, ACS; EMD Chemical Inc.) and the result called solution A. In another beaker, appropriate amounts of high-purity $Na_2WO_4\cdot 2H_2O$ (99%, Alfa Aesar) were dissolved in a minimum amount of deionized water, until a colorless solution was formed (solution B; pH = 10.3). The pH of the solutions was determined using a pH meter (Accument pH Meter 910; Fisher Scientific). Upon complete dissolution, the two solutions were poured together into a third, clean, large glass beaker, and a light green precipitate was formed instantly. The resultant solution had a pH close to 1. The precipitate was washed thoroughly with deionized water multiple times using a decanting method, after which the precipitate was vacuum-filtered and dried at ambient room temperature on a watch glass overnight. The precipitate was then scraped off the watch glass and placed in a ball mill (Pulverisette, Fritsch, Germany) for about 15 min at 200 rpm using zirconia balls to ensure efficient grinding of the solid precipitate into a powderlike form.

Preparation of Layered Structure $WO_3\cdot 2H_2O$. In beaker A, appropriate amounts of high-purity $SrCl_2$ (99.7%, Fisher Scientific) were dissolved using 9 M HCl (hydrochloric acid GR, ACS; EMD Chemical Inc.) in a clean beaker (A). In a second beaker B, appropriate amounts of high-purity $Na_2WO_4\cdot 2H_2O$ (99%, Alfa Aesar) were dissolved in deionized water, until forming a colorless solution with a pH of 10.3. Upon complete dissolution of both compounds in beakers A and B, the two solutions were poured together into a large glass beaker, upon which a bright yellow precipitate was formed. The precipitate was washed thoroughly with water using a decanting method multiple times, after which the precipitate was vacuum-filtered and was left to fully dry at ambient room temperature on a watch glass overnight.

Phase, Microstructure, Thermal, and Electrical Characterization. The powder sample was characterized by PXRD using a Bruker D8 powder X-ray diffractometer (Cu Kα, 40 kV, 40 mA) at room temperature with a 2θ step scan width of 0.02°. The lattice constant was determined from the PXRD data by least-squares refinements. Scanning electron microscopy (SEM; Philips XL30 SEM) coupled with an energy-dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM; Hitachi H700, TEM, Japan) were used for chemical composition and microstructure characterization.

Thermogravimetric analysis (TGA) was performed for as-precipitated materials in the temperature range 25−800 °C using a Netzsch 449C Simultaneous Thermal Analyzer in the air (5 °C/min). Further characterization involves Fourier transform infrared spectroscopy (FTIR) using a NEXUS 470 FT-IR spectrometer. The powder sample was dispersed in KBr pellets for measurements. Before FTIR measurements, the KBr powder was dried continuously at about 100 °C in a vacuum oven. The alternating current (AC) electrical conductivity (Solartron SI 1260; 100 mV; 0.01 Hz to 7 MHz) was measured using Pt−C electrodes in wet N_2 (water kept at room temperature) for five days. A two-probe electrochemical cell was employed for electrical characterization.

Results and Discussion

Synthesis and PXRD Characterization. Figure 2 shows the PXRD patterns of three different crystal structure products obtained by precipitation from aqueous Na_2WO_4 and $SrCl_2$ (dissolved in 3 M HCl, 9 M HCl, and water). Using 3 M HCl, we clearly see the formation of a new layered structure (Figure 2a) that is similar to that of $H_2W_2O_7\cdot 0.58H_2O$.[20,21] The first peak with d spacing of about 12.5 Å is consistent with a double-perovskite slab containing layered structure compounds, including $Bi_2W_2O_9$,[21] $CaEu_2Ti_2O_8$ (13.56 Å),[29] and $Sr_3Ti_2O_7$,[22] which corroborates with the layered DOLS TTHs. However, the present synthesis showed a very broad peak, suggesting a poor crystallinity. This unexpected result was repeated several times, and our results continually showed a similar XRD pattern. Also, it is very important to mention that the $n = 1$ member of the RP phase $ALnTiO_4$ (A = Na, K; Ln = La or rare earth) shows a very similar interlayer spacing.[30] The large unit cell in the $ALnTiO_4$ structure is due to alternative ordering of alkali and rare earth ions around the corner-sharing single sheet of TiO_6 octahedra. The $n = 2$ members of the Dion−Jacobson phases $A'[A_{n-1}B_nO_{3n+1}]$[31] (A′ = alkali metal; A = alkaline earth, rare earth; B = Nb, Ta, Ti) exhibit, generally, slightly lower layer spacing compared to those of the corresponding ($n = 2$ member) RP phase.[32]

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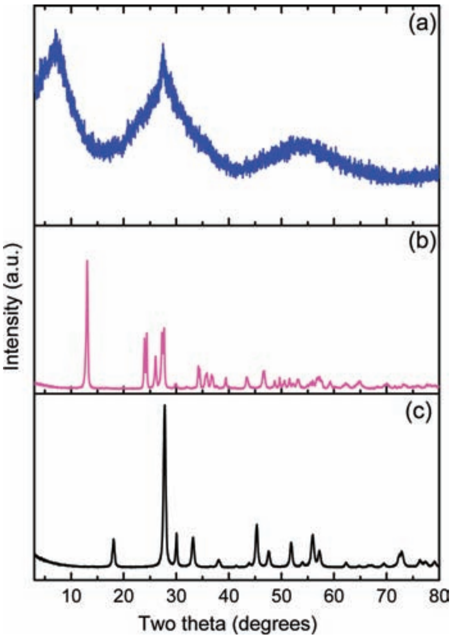

Figure 2. Powder XRD patterns of precipitate obtained from aqueous Na_2WO_4 and $SrCl_2$ + HCl, (a) 3 M HCl and (b) 9 M HCl. For comparison, in part c, we show the formation of a tetragonal scheelite structure using aqueous Na_2WO_4 and $SrCl_2$ + H_2O. Sample "a" shows first peak at a d spacing of about 12.5 Å, which may be corresponding to the 0 0 L peak of the $n = 2$ member of the Ruddlesden−Popper (RP) type phase.[22,36] Kudo et al.[21] and Wang et al.[36] reported similar PXRD spectra to that of sample "a" for A-site-deficient RP double octahdera − slab-layered tungsten trioxide hydrate (TTH).

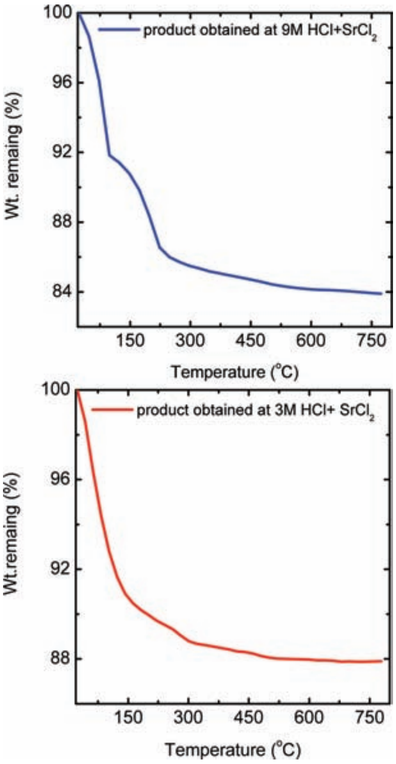

Figure 3. TGA curves of as-precipitated products obtained at 9 M (top) and 3 M HCl (bottom). The total weight loss corresponds to the nominal chemical formula of $WO_3 \cdot 2H_2O$ (top) and $WO_3 \cdot .3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$) (bottom).

Potential Mechanism of Layered TTHs Formation and Role of pH. Pecquenard et al.[33] confirmed an octahedral coordinated dimeric peroxo anion $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ in the peroxotungustic acid using ^{183}W NMR. Several authors reported different types of tungstate single anions and polyanions, including $[WO_3(O_2)]^{2-}$ and $[W_2O_5(O_2)_2(H_2O)_2]^{2-}$.[33] Therefore, it was suggested that it is very difficult to predict the exact nature of tungstate anions in the solution during the precipitation reaction.[33] Using $SrCl_2$ dissolved in 9 M HCl, we observed a crystalline orthorhombic-layered structure (Figure 2b), and it was found to be consistent with literature.[9] We could index all of the peaks of this well-known tungsten dihydrate on an orthorhombic cell (see Supporting Information Table S1). By changing the HCl concentration used for $SrCl_2$ solution, we were able to prepare new DOLS layered structure TTH products.

In order to understand the crystal structure and role of acidic $SrCl_2$ in the precipitation reaction, we have performed precipitation reactions using weakly basic (pH = 10.3) Na_2WO_4 and neutral $SrCl_2$ (pH = 7) solutions. As reported in the literature,[28] our results showed the formation of a scheelite structure in which the W atom is in the four-fold oxygen coordination site.[28b] It is also believed that a similar W coordination is present in Na_2WO_4 (both in solid and aqueous forms),[28] and hence the "metathesis" reaction, that is, $SrCl_{2(aq)} + Na_2WO_{4(aq)} \rightarrow SrWO_{4(aq)} + 2NaCl_{(aq)}$, was proposed.[28a] On the basis of the PXRD investigation (Figure 2c) under weakly basic conditions, we would anticipate a tetrahedral tungstate anion $[WO_4]^{2-}$ might exist which helps to form the scheelite structure.[28,33] Dimeric anions, with a coordination sphere of W^{VI}, might be formed in the less acidic solution, which helps to form a layered perovskite-related RP or Aurivillius-type structure.[22,23] For comparison, we performed the precipitation reaction using 3 and 9 M HCl without $SrCl_2$, and the products were found to be similar to that of an orthorhombic-layered structure (Figure 2b) TTH. Accordingly, further spectroscopy experiments may be required to deeply understand the various chemical species present in solution to elucidate the actual mechanism for the formation of different layered TTHs.

Bhuvanesh et al.[10] prepared two different types of TTHs with nominal chemical formulas of $WO_3 \cdot 0.33H_2O$ and $WO_3 \cdot H_2O$ by acid-leaching a three-dimensional structure $LiMW_2O_8$ (M = Al, Fe) using different concentrations of HNO_3. The monohydrate was prepared by using 6 M HNO_3 and one-third of a hydrate in concentrated HNO_3. A similar result was reported employing acid-leaching of brannerite structure $LiVWO_6$.[30] In the present work, a dihydrate is obtained using 9 M HCl + $SrCl_2$, and 1.3 hydrates are obtained with 3 M HCl + $SrCl_2$. The conversion of $LiMW_2O_8$ into TTHs appears not be a topochemical reaction,[10] unlike from the Aurivilius phase to layered TTHs.[20,21] Since the present work involves direct precipitation from the aqueous solution, it also seems to be a nontopochemical synthesis route to layered TTHs, and the crystal structure of the precipitate is controlled by the intrinsic acidity of solutions.[10,34]

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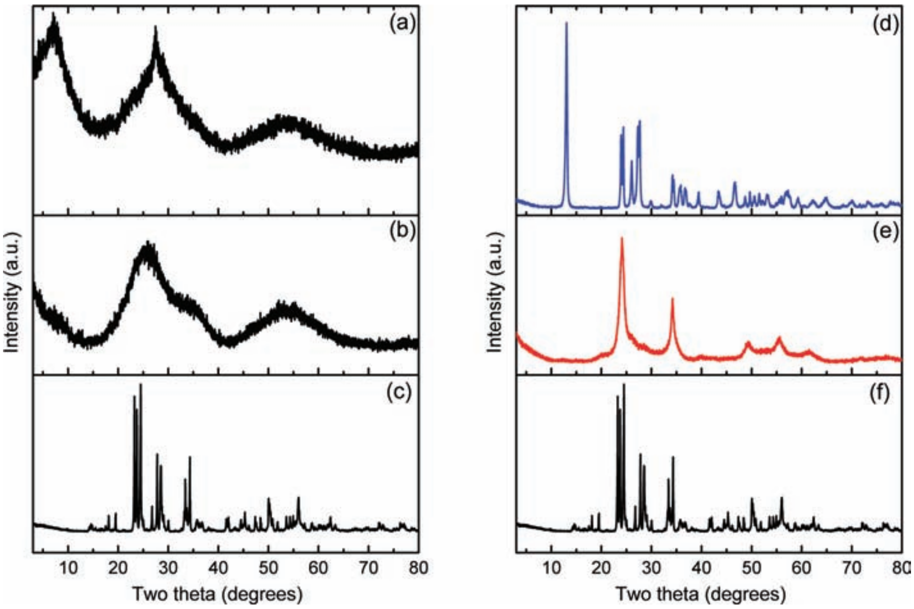

Figure 4. Left-hand side: (a) as-precipitated double perovskite slab layered $WO_3 \cdot 1.3H_2O$ ($\equiv$ $1/2H_2W_2O_7 \cdot 1.6H_2O$), (b) ReO_3 three-dimensional perovskite-related sample prepared at 375 °C from sample "a", and (c) monoclinic WO_3 obtained at 800 °C from sample "a". Right-hand side: (d) as-prepared orthorhombic layered structure $WO_3 \cdot 2H_2O$ (a = 10.463(5); b = 8.605(3); c = 9.030(2) Å), (e) ReO_3 three-dimensional perovskite-related sample prepared at 375 °C from sample "d", and (f) monoclinic WO_3 obtained at 800 °C from sample "d".

Thermogravimetric and Infrared Spectroscopy Characterization. The chemical composition of as-precipitated and air-dried products was stabilized using TGA and IR studies. The TGA of the highly acidic (9 M HCl) product showed a total weight loss attributed to $2H_2O$, while the 3 M HCl sample showed a $1.3H_2O$ per formula unit of WO_3 (Figure 3). However, the hydration depends on the washing and drying conditions. Several authors employed a similar precipitation reaction to prepare $WO_3 \cdot 2H_2O$.[1−3] So far, to the best of our knowledge, the layered $WO_3 \cdot 1.3H_2O$ ($\equiv$ $1/2H_2W_2O_7 \cdot 1.6H_2O$) was not prepared by a simple precipitation reaction using Na_2WO_4, $SrCl_2$, and HCl. The EDX analysis shows peaks due to W in the as-prepared $WO_3 \cdot 2H_2O$ and $WO_3 \cdot 1.3H_2O$, and no peaks due to Na, Sr, and Cl atoms were observed (see Supporting Information Figures S1 and S2). This shows that we have very thoroughly washed the precipitate and is consistent with TGA data.

As anticipated, the mild dehydration of both precipitates at 300−375 °C gives an A-site-deficient ReO_3 perovskite (Figure 4, and see Supporting Information Figure S3).[9] We see the main diffraction peaks corresponding to a three-dimensional ABO_3 perovskite-like structure from both products (Figure 4b,e). However, the highly acidic (9 M HCl) product gives a better crystalline product (Figure 4b), and the less acidic (3 M HCl) product yields a highly disordered structure pattern (Figure 4e). Such amorphous-like patterns for solution-based solid-state synthesis are quite commonly observed. Table S2 (Supporting Information) shows the indexed PXRD data of the ReO_3 product obtained from $WO_3 \cdot 2H_2O$ (Figure 4e). At high temperatures, thermodynamically stable monoclinic WO_3 was observed.[9] In Figures 5 and S4 (see Supporting Information), we show the IR spectra of the air-dried, as-precipitated products using 3 M HCl + $SrCl_2$ and 9 M HCl + $SrCl_2$, respectively. On mild dehydration and at high temperatures, the peaks due to OH groups were absent. The high-temperature IR spectra (Figures 5c and S4c, see Supporting Information) are found to be consistent with commercially available monoclinic WO_3 (99.8%, Alfa Aesar).

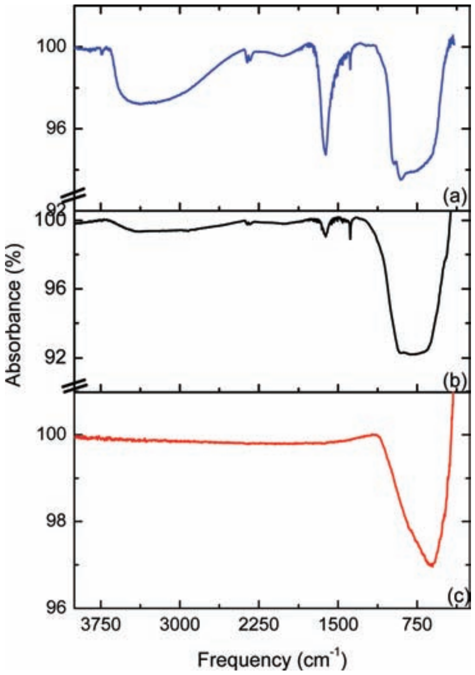

Figure 5. FTIR curves of (a) as-precipitated layered perovskite $WO_3 \cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$) obtained using 3 M HCl + $SrCl_2$, (b) ReO_3 three-dimensional perovskite-related sample prepared at 375 °C from sample "a", and (c) monoclinic WO_3 obtained at 800 °C from sample "a".

Proposed Structure for $WO_3 \cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$). In Figure 6, we show the idealized crystal structure of A-site-deficient DOLS TTH prepared using Na_2WO_4 and $SrCl_2$. The proposed DOLS TTH was further confirmed by

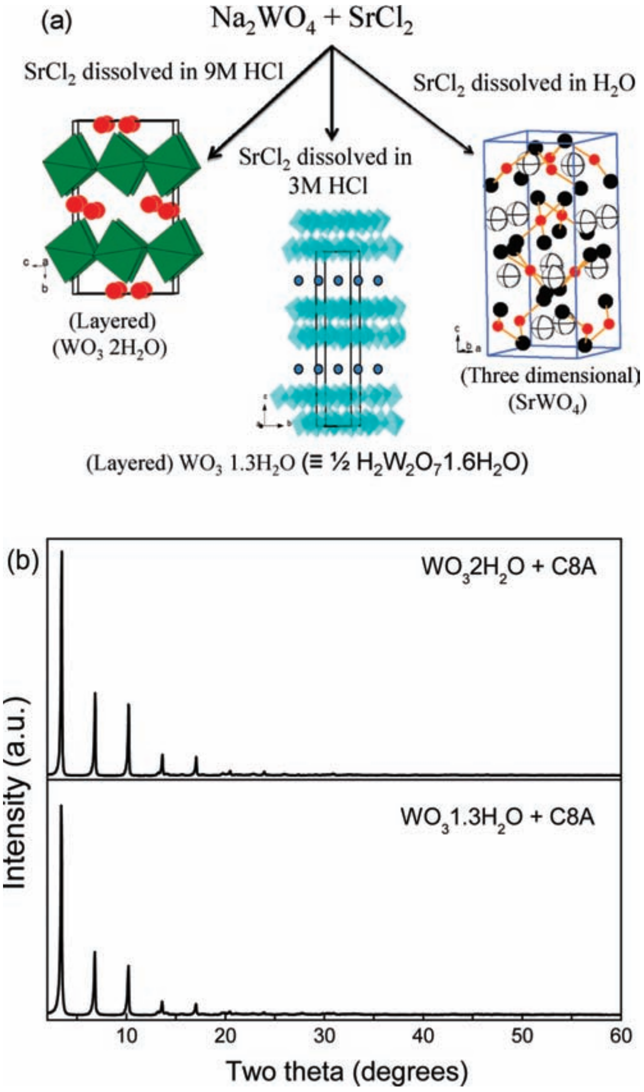

Figure 6. (a) Idealized schematic structure showing the formation of A-site-deficient double-perovskite-sheet layered RP-type structure at 3 M HCl, layered $WO_2 \cdot 2H_2O$ using 9 M HCl, and scheelite under weak basic conditions. (b) PXRD pattern of *n*-octylamine (C8A) intercalated and layered $WO_3 \cdot 1.3H_2O$ (≡ $1/2H_2W_2O_7 \cdot 1.6H_2O$) and $WO_3 \cdot 2H_2O$. A comparable XRD has been reported recently by Shimizu et al. for the C8A intercalated $n = 2$ member of the RP phase $H_2ATa_2O_7$ (A = Sr, or $La_{2/3}$)[35] and Kudo et al.[21] and Wang et al.[36] for the C8A intercalated A-site cation-deficient double perovskite-sheet layered RP-type $H_2W_2O_7$.

its intercalation property. We have examined the intercalation behavior of newly prepared $WO_3 \cdot 1.3H_2O$ with *n*-octylamine (C8A) at room temperature for about 12 h. For comparison, we also performed identical intercalation for $WO_3 \cdot 2H_2O$. About 2 g of the TTH product was treated with 40 mL of an *n*-octylamine (C8A) and hexane mixture. Very interestingly, we see both layered TTHs changed to a white color within a few minutes, and PXRD shows the evidence of an intercalation reaction, which is found to be consistent with the intercalation chemistry of TTHs and layered perovskite-related structures.[9,21,31,35−37]

Figure 6b shows the PXRD pattern of C8A-intercalated $WO_3 \cdot 1.3H_2O$ (≡ $1/2H_2W_2O_7 \cdot 1.6H_2O$) and $WO_3 \cdot 2H_2O$ with a huge interlayer space of 25.8 Å and 25.5 Å, respectively, which is found to be similar to that of Kudo et al.'s work on DOL $H_2W_2O_7$.[21] It is also important to note that the interlayer distance, d_{00L}, of the C8A-intercalated TTH falls within the range of Shimizu et al.'s report on the C8A intercalation in the $n = 2$ member of the DOLS RP phase $H_2ATa_2O_7$ (A = Sr, or $La_{2/3}$),[35] Gopalakrishnan et al.'s report on the C8A-treated $n = 2$ member of Dion−Jacobson-type double-perovskite-slab $HLaNb_2O_7$,[31c] and Wang et al.'s work on layered anhydrous A-site-deficient DOLS $H_2W_2O_7$[36] and is comparable to that of Jacobson et al.'s predicted interlayer space for amine intercalation in multiple octahedral-containing layered perovskites[31a,31d] and also layered structure $HNbMoO_6$.[31e,31f] Thus, the amine intercalation properties strongly support the TGA and PXRD results and confirm the anticipated DOLS for $WO_3 \cdot 1.3H_2O$ (≡ $1/2H_2W_2O_7 \cdot 1.6H_2O$). The TGA and XRD measurements show that the high-temperature product is stable WO_3, and no other potential phases are present in the air-dried precipitated product. The present work shows a very simple precipitation reaction using Na_2WO_4 and 3 M HCl + $SrCl_2$, which are very convenient, compared to earlier methods reported in the literature.[20,21] However, further experimental methods, including electron diffraction and high-resolution electron microscopy are invoked to identify the actual member of the layered perovskite family.

Microstructure and Particle Size of TTHs. The SEM (Figures S1 and S2, Supporting Information) and TEM (Figure 7) were employed to characterize the microstructure of the as-prepared $WO_3 \cdot 1.3H_2O$ and $WO_3 \cdot 2H_2O$. Interestingly, we see a large particle in the SEM, while nanosized particles were found in the TEM. The large particle in the SEM might be due to the accumulation of small-sized crystallites. It is anticipated that the low-temperature chemical synthesis can produce the nanosized particles. In the present work, we see that the pH has a significant effect on the size of the particle distribution of the products. In Figure 8, we also show the TEM images of C8A-treated $WO_3 \cdot 1.3 H_2O$ and $WO_3 \cdot 2H_2O$ and show the expected nanosized particles.

Electrical Conductivity of THHs. Figure 9 shows the AC resistivity plots of $WO_3 \cdot 1.3H_2O$ and $WO_3 \cdot 2H_2O$ in N_2 and 3% H_2O at 23 °C for five days. A straight line and a depressed semicircle were observed in the low- and high-frequency regions, respectively. Similar impedance plots were reported for other low-temperature proton conductors, including $WO_3 \cdot 2H_2O$,[5] Nafion,[38,39] and the NH_4PO_3/MO_2 composite.[40] The impedance also decreases with increasing time in a wet atmosphere, indicating that the electrical conductivity depends on humidity. A similar behavior was recently observed for the Ta-substituted double-perovskite-type $Ba_2Ca_{2/3}Nb_{4/3}O_6$.[41]

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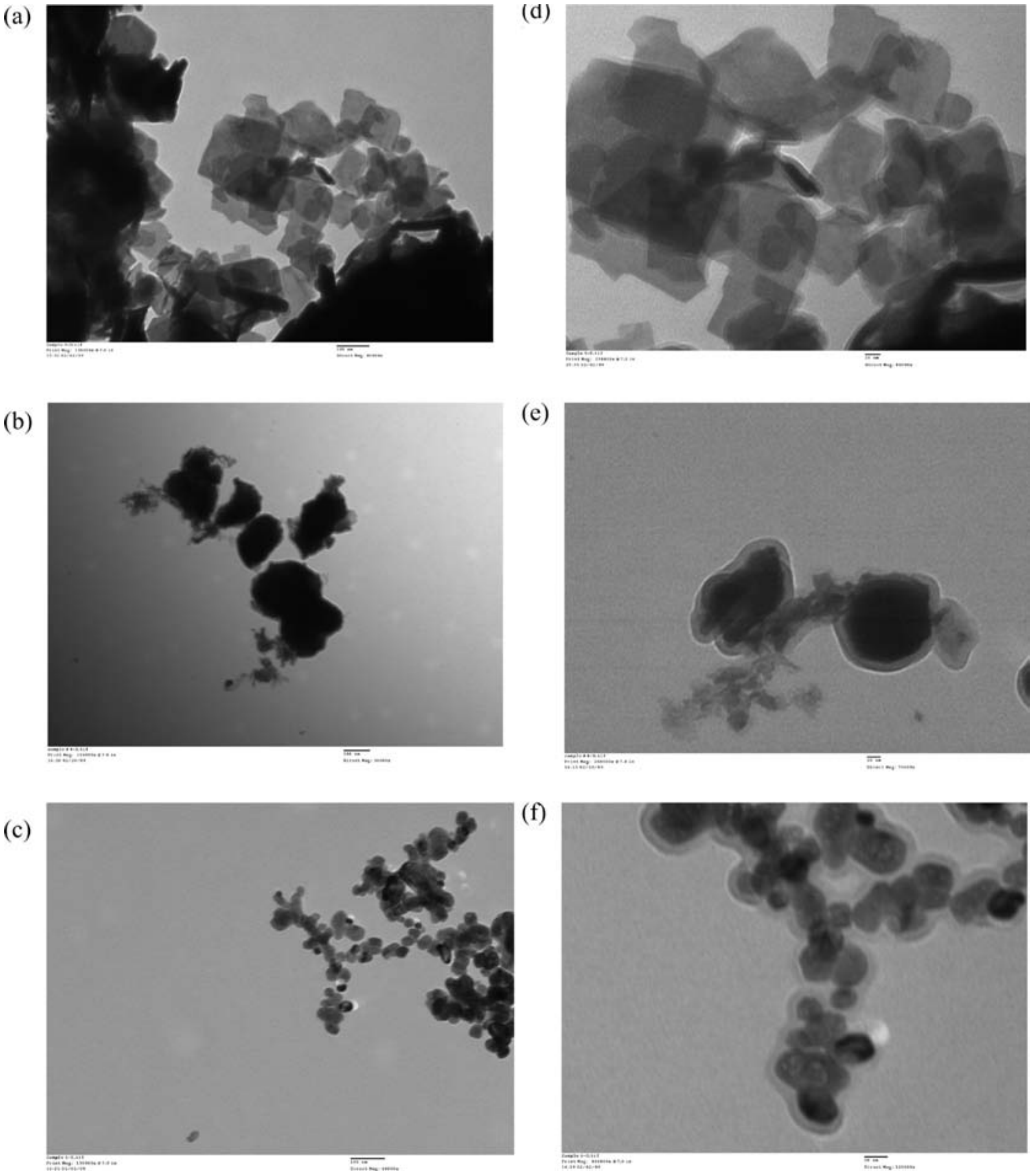

Figure 7. TEM images of (a) the air-dried, as-precipitated, layered $WO_3 \cdot 2H_2O$ prepared using 9 M HCl + $SrCl_2$, (b) the A-site cation-deficient, layered perovskite-type $WO_3 \cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$) obtained using 3 M HCl + $SrCl_2$, and (c) air-dried, as-precipitated scheelite-type $SrWO_4$ product obtained under weak basic conditions. The left side images (a−c) are taken on the 100 nm scale, and the right-side images (d−f) are obtained at 20 nm.

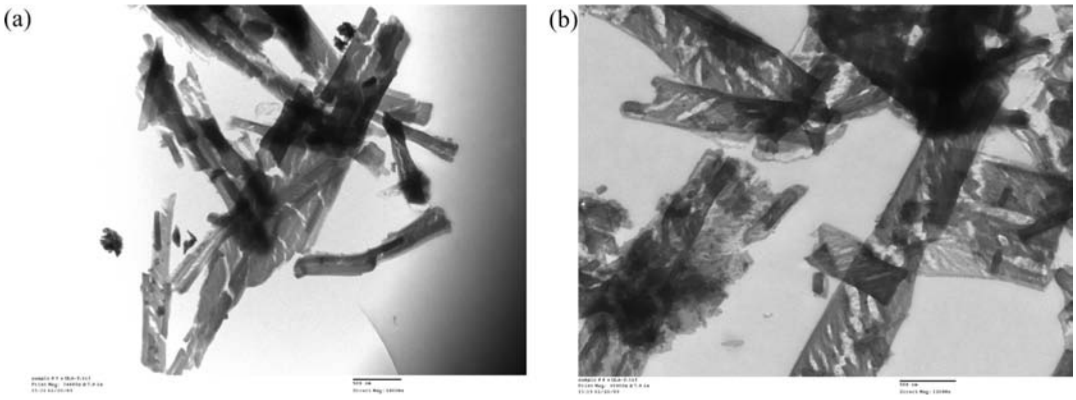

Figure 8. TEM images (500 nm scale) of *n*-octylamine (C8A) intercalated (a) $WO_3 \cdot 2H_2O$ and (b) $WO_3 \cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$).

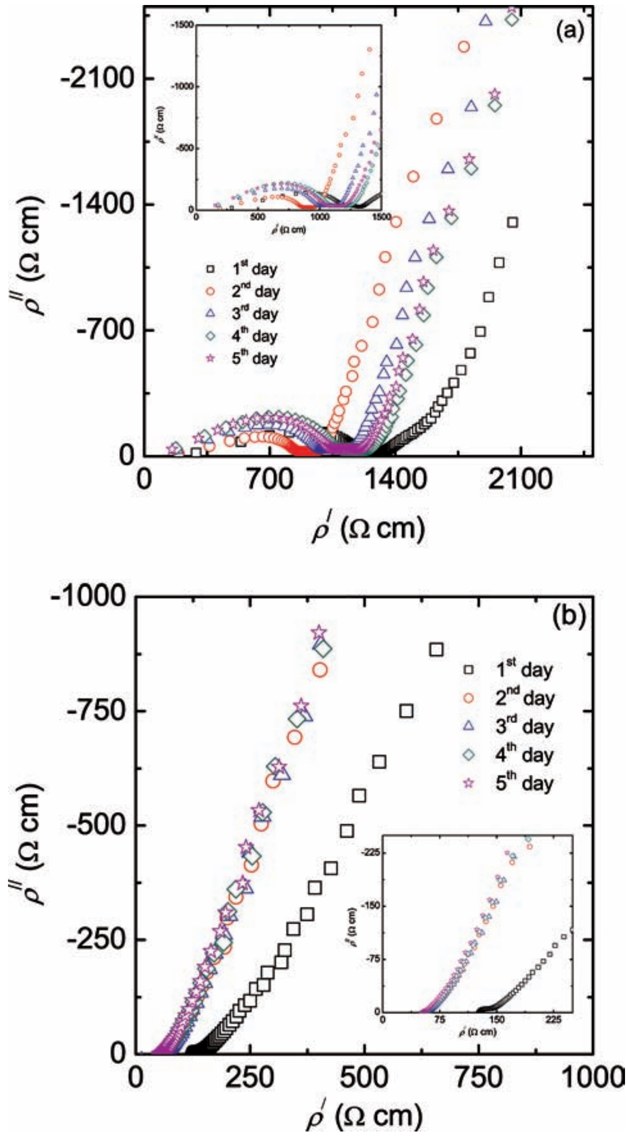

Figure 9. AC resistivity plots in N_2 + 3% H_2O at 23 °C of (a) $WO_3 \cdot 1.3H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$) and (b) $WO_3 \cdot 2H_2O$. Inset shows the expanded view.

The proton conductivity was calculated using the high-frequency intercept to the real axis and was found to be in the range of 10^{-4} to 10^{-2} S/cm at room temperature.

Conclusions

In summary, we demonstrated a convenient precipitation method to synthesize metastable double-perovskite-sheet layered TTH structures, with a chemical formula of $WO_3 \cdot 1.3\ H_2O$ ($\equiv 1/2H_2W_2O_7 \cdot 1.6H_2O$), using aqueous Na_2WO_4 and $SrCl_2$ dissolved in 3 M HCl. Highly acidic $SrCl_2$ (9 M HCl) yields a regular orthorhombic-layered TTH of $WO_3 \cdot 2H_2O$ and scheelite-type structure $SrWO_4$ under neutral conditions. The first diffraction peak of the presently synthesized DOL is found to be comparable to that of the corresponding $n = 2$ member of the layered perovskite-type structure. Proposed layered structures were further confirmed by a C8 amine intercalation reaction. The TEM study shows the formation of nanosized particles, and SEM coupled with EDX showed the absence of Na and Sr atoms in the air-dried, as-precipitated products under acidic conditions. Between the two samples investigated, $WO_3 \cdot 2H_2O$ showed the highest proton conductivity of ~10^{-2} S/cm at room temperature in N_2 and 3% H_2O.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Canada Foundation for Innovation (CFI) for financial support. We also thank Dr. George K. H. Shimizu at the Department of Chemistry, University of Calgary, for providing the TGA facility. We thank Dr. Todd Sutherland for providing C8 amine for the intercalation reaction. We also wish to acknowledge the Microscopy and Imaging Facility (MIF) of the University of Calgary for supporting SEM and TEM studies.

Supporting Information Available: Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.