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Synthesis of the Hexagonal Form of Tungsten Trioxide from Peroxopolytungstate via Ammonium Paratungstate Decahydrate

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Two types of crystalline $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$ were precipitated in sequence when an ammonia solution of peroxopolytungstate was neutralized with hydrochloric acid. It was found by X-ray diffraction that one of them is an unknown phase of ammonium paratungstate, and the other is the reported one. Heating the former, it turned directly to common triclinic WO_3. On the other hand, the latter yielded the hexagonal form of WO_3 (h-WO_3) in the temperature range 350—370 °C. This is a new synthetic method of h-WO_3, though the final precursor is a known compound. The color of h-WO_3 thus formed was pale yellow and contained a small amount of residual ammonia ($N/W = 0.017$ in molar ratio). Its crystallographic c-axis (7.689 Å) was shorter than than the reported value (7.798 Å) for the same WO_3 phase synthesized from $3WO_3\cdot H_2O$.

Although hexagonal tungsten bronzes M_xWO_3 have long been known, their empty framework itself (the hexagonal form of tungsten trioxide, h-WO_3, see Fig. 1) has been synthesized only comparatively recently from a $3WO_3\cdot H_2O$ precursor by Gerand et al.[1] Since then, h-WO_3 has been extensively investigated, especially as an intercalation host. As a result, it has been revealed that the compound is promising as a negative-electrode material for rechargeable lithium batteries.[2,3] Because of such practical usefulness, a variety of alternative synthetic routes of this compound have been developed, as tabulated in Table 1. A typical one is via ammonium tungsten bronzes formed by reducing $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ in a hydrogen atmosphere at relatively low temperature. Whittigham et al.[4] obtained h-WO_3 by the thermal decomposition of $(NH_4OH)_xWO_3$. This final intermediate was prepared by the liquid-phase oxidation of an ammonium bronze with hydrogen peroxide. Schollhorn et al.[5] synthesized the same tungsten oxide phase through a simpler path where a bronze precursor was directly oxidized using gaseous Cl_2. Recently, Kumagai et al.[3] reported that h-WO_3 was formed from lithium tungstate under a strong acidic hydrothermal condition at 100 °C.

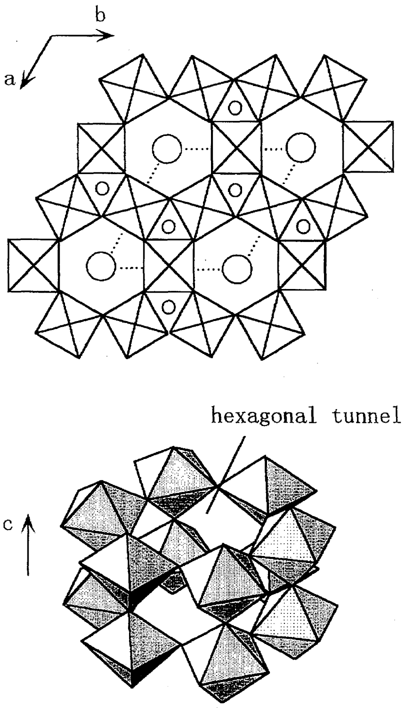

Fig. 1. Arrangement of $[W\text{-}O_6]$ octahedra in the structure of hexagonal WO_3. Cross-section in the ab-plane perpendicular to the c-axis. Large and small open circles refer to positions in hexagonal and triangular tunnels, respectively.

Previously, one of the present authors and others[6] reported that a compound in the h-WO_3 phase with a small quantity of NH_4^+ ($N/W = 0.017$) was obtained by the thermal decomposition of a crystalline product precipitated when an ammonia solution of peroxopolytungstic acid was neutralized with hydrochloric acid. (Peroxopolytungstic acid is an amorphous substance formed by the reaction of metallic tungsten with hydrogen peroxide.[7]) This synthetic procedure is much simpler and easier than those mentioned above. However, the product h-WO_3 was often contaminated with other phase, mainly triclinic WO_3, depending on the runs of the synthesis. Moreover, it contained a small, but not negligible, amount of ammonium ions in its structure. Thus, further studies are needed to establish this synthesis.

The purpose of the present study was to reexamine the synthetic route to obtain pure and single-phase h-WO_3. We report here on the results, while particularly focusing on the relationship between the products and intermediate precursor compounds. We also discuss the effect of the ammonium content on the structure of the product h-WO_3 phase, since

Table 1. Starting Materials, Colors and Lattice Parameters of Reported h-WO_3s

Starting Material	Precursor	h-WO_3			Ref.
		Color	a (Å)	c (Å)	
Na_2WO_4	$3WO_3 \cdot H_2O$	White	7.298(2)	7.798(3)	(1)
Li_2WO_4	$WO_3 \cdot yH_2O$ ($y = 0.8$—1.1)	No reported	7.293	7.750	(3)
$(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$	$(NH_4OH)_xWO_3$	Pale blue green	7.323(6)	7.810(3)	(4)
$(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$	$(NH_4OH)_xWO_3$	Yellow	7.326(6)	7.722(5)	(13)
$(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$	$(NH_4)_{0.30}WO_3$	Pale yellow	7.328	7.623	(5)
W-IPA, aq soln NH_3	$(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 10H_2O$	Pale yellow	7.313(3)	7.689(0)	(6)

we have not succeeded to synthesize a compound completely free of ammonium ion.

Experimental

The starting material, peroxopolytungstic acid (W-IPA), was prepared according to a previously reported method.[7] In short, metallic tungsten powder was dissolved in a 15% aqueous solution of hydrogen peroxide. A thus-obtained clear solution was almost colorless and strongly acidic ($pH \approx 1$). After decomposing excessive hydrogen peroxide catalytically with a platinated platinum net, the solution was dried using a rotary evaporator at room temperature, to yield a pale-yellow amorphous glassy substance (W-IPA), the empirical formula of which was approximately $WO_3 \cdot 0.5H_2O_2 \cdot 2H_2O$. The structure of W-IPA polyanion has been estimated from the X-ray RDF by Nanba et al.[8]

The procedure to obtain the intermediate precursors was similar, but not identical, to our previous method[6] in some operations, as pointed out later. 8.0 ml of ammonia water (28%) was added to a stirred solution of W-IPA (8.01 g/80 ml of water). The solution was very slightly clouded. White suspended matter, probably $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$, was filtered and the supernatant was heated to 80 °C. After cooling to room temperature, it showed a pH of about 9.9. Then, hydrochloric acid was added until its pH fell to 7.3. Colorless crystals (denoted as Precursor-I) were readily generated in the solution. After Precursor-I was separated by filtration, the supernatant was left at room temperature. Then, other colorless needle-like crystals (Precursor-II) began to appear within 30—60 min. Precipitation lasted for more than 40 h. In previous work, we did not perform this separation operation, because we had not found that two different crystals were yielded from the same solution. Both crystal samples were rinsed with water and dried at 70 °C for 1 d. The tungsten-based yield of Precursor-I and -II were roughly 30 and 60%. To obtain h-WO_3, those precursors were heated in air at the desired temperature, typically, 300—400 °C.

Elemental analysis (for N and H) was performed using a Fisons EA 1108 gas-chromatographic CHN analyzer. The tungsten contents were determined by thermo-gravimetry with a MAC science 2000s TG/DTA system. The infrared spectra were recorded as KBr pellets on a Shimadzu 8100 FT-IR spectrometer. The data collection and calculation for the single-crystal X-ray diffraction of precursor compounds were carried out on a MAC science MXC 18K diffractometer using Mo $K\alpha$ radiation and the CRYSTAN program, respectively. Powder X-ray patterns were recorded by a Rigaku RINT system using monochromatized Cu $K\alpha$ radiation.

Results and Discussion

1. Characterization of Precursor Compounds: Elemental analyses of Precursor-I and -II:

Found: N, 4.52; H, 2.01; W, 68.7%. Found: N, 4.36; H, 1.92; W, 68.2% (in wt%). Respectively, indicating that both compounds take the same composition. We found that this composition agrees very well with that of $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 10H_2O$, Calcd for $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 10H_2O$: N, 4.32; H, 1.99; W, 68.1 wt%. Although no powder X-ray data of ammonium tungstates (except "tetrahydrate", #24-45) are filed in JCPDS, Allmann[9] reported single-crystal data of a paratungstate with the same composition, synthesized by an old reported method[10] different from the present one. According to his calculation, the compound is orthorhombic: $Pbca$, $a = 19.07$, $b = 24.42$, $c = 10.915$ Å, $V = 5083$ Å^3, $Z = 4$, and $R = 8.5\%$, which are in almost complete agreement with our X-ray data taken with a single crystal of Precursor II: $Pbca$, $a = 18.958(2)$, $b = 24.390(3)$, $c = 10.934(2)$ Å, $V = 5055.82(1)$ Å^3, $Z = 4$, and $R = 4.9\%$. The observed powder-diffraction profile of Precursor-II agrees with that calculated from the single-crystal data, as shown in Fig. 2(a). These facts confirm that Precursor-II is the same ammonium paratungstate investigated by Allmann. We also

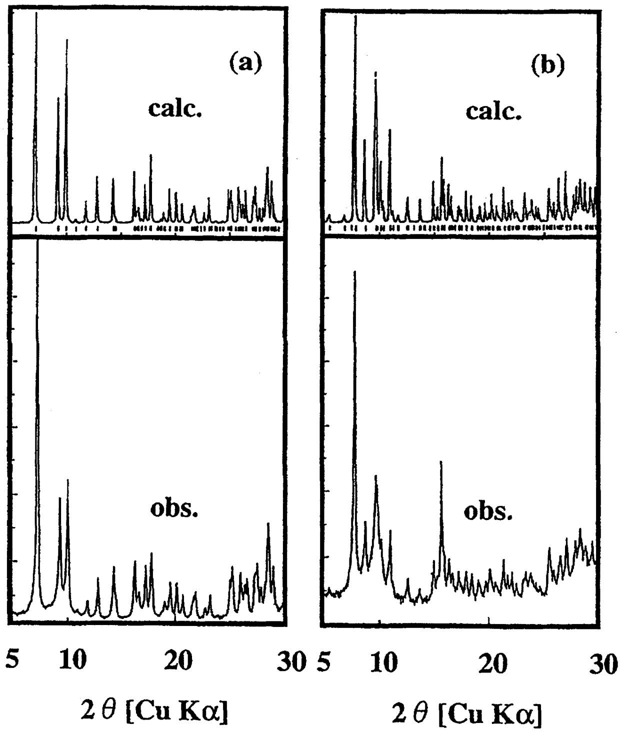

Fig. 2. Comparison of calculated and observed powder X-ray profile: (a) Precursor-II and (b) Precursor-I.

confirmed that the same compound was synthesized by a reported method[10] using H_2WO_4 as the starting material.

The powder pattern of Precursor-I (Fig. 2(b)) does not agree with any reported data for ammonium tungsten oxides to our knowledge, suggesting that this compound is a new type of ammonium paratungstate. Its single-crystal X-ray data are as follows: Trinclinic, $P\bar{1}$, $a = 11.9361(25)$, $b = 13.1686(28)$, $c = 16.5617(44)$ Å, $\alpha = 77.768(19)$, $\beta = 82.889(18)$, $\gamma = 88.745(18)$°, $V = 2524.50(99)$ Å^3, $Z = 2$, and $R = 5.1\%$. It is reasonable for both compounds (Precursor-I and -II) to have the same composition, because the doubled volume of the former ($Z = 2$) is almost the same as that of the latter ($Z = 4$). Further details of this new compound and its structural relationship with known ammonium paratungstates will be discussed elsewhere.

2. Thermal Decomposition Products from the Precursors: Both Precursor-I and -II were decomposed into the usual triclinic WO_3 at high temperature (> 400 °C). However, they show quite different decomposition behaviors at lower temperature, though there is no conspicuous difference, except for the polyanion's arrangement in their crystal structures. As show in Fig. 3, Precursor-II turns to a hexagonal phase at a temperature near 320 °C after passing an amorphous state at 200—300 °C. The formation range of this hexagonal compound in a pure phase is relatively narrow, i.e., 330—380 °C. It is noted that the Precursor-II synthesized by the method using H_2WO_4 also gave h-WO_3 in the same temperature range.

The powder profile of a sample formed at 370 °C is indexed on a hexagonal unit cell with $a = 7.313(3)$ and $c = 7.689(0)$ Å, as shown in Table 2 and Fig. 4, where weak peaks (marked with ⋆), not obeying this rule, suggest the existence of a superstructure with $a' = 2a$, which is often observed for tungsten bronzes based on the h-WO_3 framework.[11,12] Elemental analysis and infrared spectrometry showed that the compound contained almost no water, but had nitrogen as NH_4^+ ($N/W = 0.017$ in mole ratio). Thus, the hexagonal pale-yellow substance formed in this temperature region from Precursor-II was h-WO_3 containing a small amount of NH_4^+.

Precursor-I was also turned into amorphous matter in the range 200—300 °C. However, heating it at higher temperature, around 320 °C, started to yield the triclinic form of WO_3 without passing the h-WO_3 state. No h-WO_3 phase was obtained under any synthetic condition we selected for the temperature, reaction time and atmosphere.

For a comparison, we also investigated the thermal-decomposition process of commercially available tetrahydrate, $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$. It was found that this compound gave only triclinic WO_3. By heating it at 350 °C in air, for example, triclinic WO_3 was produced from an amorphous intermediate after prolonged heating (2—3 h). The facts including this suggest that not only the polyanion, but also the secondary or whole crystal structure of Precursor-II, are essential for the formation of a special metastable product, h-WO_3 in the present case. It is interesting that only Pre-

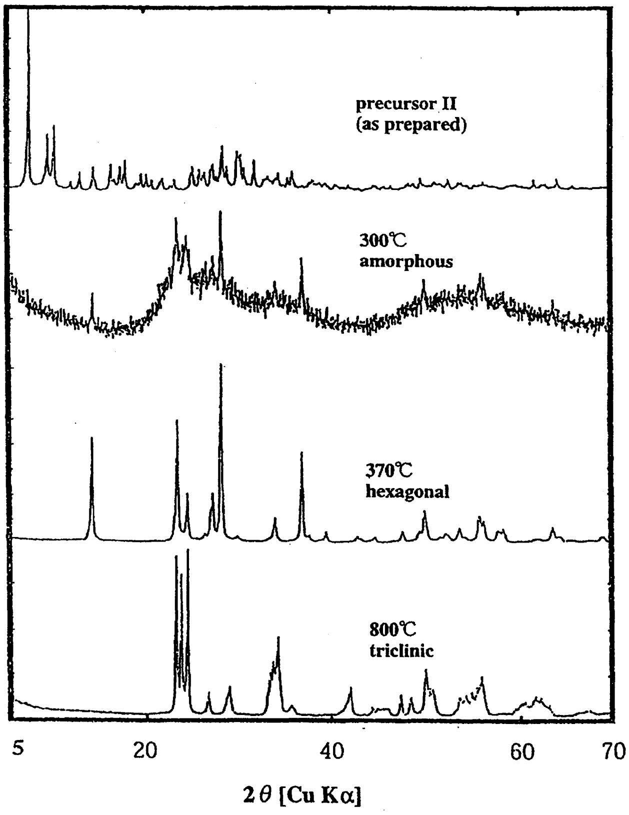

Fig. 3. Powder X-ray profiles recorded with Precursor-II treated at various temperatures (heating rate 10 °C min^{-1}).

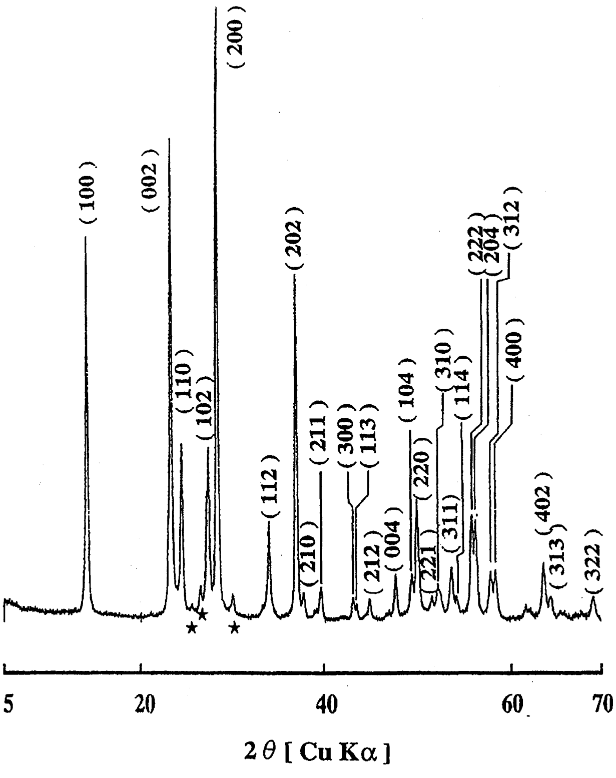

Fig. 4. Powder X-ray pattern of h-WO_3 phase obtained by heating Precursor-II at 370 °C for 1 h in air ($a = 7.313(3)$ and $c = 7.689(0)$ Å. Weak peaks marked by ⋆ can be indexed with $a' = 2a$).

Table 2. Powder X-Ray Diffraction Data Observed and Calculated

$a=7.313(3)$ $c=7.689(0)$			$a=14.62(7)$ $c=7.689(0)$		
hkl	*d* (obsd)	*d* (calcd)	*hkl*	*d* (obsd)	*d* (calcd)
100	6.3372	6.3335	310	3.5231	3.5133
002	3.8275	3.8445	112	3.3985	3.4030
110	3.6628	3.6567	212	3.0194	2.9977
102	3.2782	3.2867			
200	3.1707	3.1668			
112	2.6467	2.6496			
202	2.4416	2.4443			
210	2.3976	2.3938			
211	2.2925	2.2856			
300	2.1120	2.1112			
113	2.0961	2.0988			
212	2.0300	2.0321			
004	1.9141	1.9223			
104	1.8511	1.8394			
220	1.8316	1.8283			
221	1.7771	1.7787			
310	1.7571	1.7566			
311	1.7137	1.7125			
114	1.6977	1.7015			
222	1.6516	1.6511			
204	1.6414	1.6432			
312	1.5984	1.5977			
400	1.5843	1.5834			
402	1.4642	1.4641			
313	1.4495	1.4490			
322	1.3599	1.3592			

cursor-II leads to the h-WO_3 phase, though Precursor-I, II and this tetrahydrate are composed of the same paratungstate anions. This fact suggests that not only the primary structure of polyanion, itself, but also the secondary or whole crystal structure of precursor materials, are related to the product structure. In this connection, further structural studies are needed in relation to the amorphous intermediate phases, through which triclinic or hexagonal WO_3 compounds are generated.

3. Residual Ammonium Ion and Its Effect on the Structure: As the formation temperature of the h-WO_3 phase is raised, an infrared band at 1400 cm^{-1} due to residual ammonium vibration ($\nu_4(NH_4^+)$) is decreased, as shown in Fig. 5. These spectra were recorded at room temperature with samples prepared by heating Precursor-II at indicated temperatures for 1 h. The residual ammonium content also depended on the time of heating. The analytical N contents (in terms of N/W molar ratio) for several h-WO_3 samples, prepared under various conditions and confirmed to be pure or almost pure by X-ray, are tabulated in Table 3. We have not succeeded in obtaining the compound with a NH_4/W ratio less than 0.003.

The hexagonal lattice parameters of those h-WO_3 samples are plotted against their ammonium content in Fig. 6(a) and (b). The *a*-axis does not so much depend on the ammonium content and lies in the range 7.31—7.32 Å, which is comparable with that of the same hexagonal phase synthesized through ammonium tungsten bronze by Schollhorn et al.[5] or Whittigham et al.,[4] but is considerably longer than the 7.298 Å reported for h-WO_3 from $3WO_3 \cdot H_2O$ by Gerand et al.[1] On the other hand, the *c*-axis depends much more strongly on the ammonium content. Short values of this parameter (i.e., 7.68—7.70 Å) observed in the $N/W=0.017$—0.029 range are again close to the *c*-axis value of Schollhorn's h-WO_3 (7.623 Å). It would, therefore, seem that his h-WO_3 contains ammonium ions to such an extent as mentioned above. As the ammonium content is lowered, the *c*-axis is elongated sharply, as shown in Fig. 6(b). However, even a sample with such a small N/W value as 0.003 still shows a much shorter *c*-axis length than Gerand's h-WO_3, which is free from NH_4^+, because its precursor contains no nitrogen species.

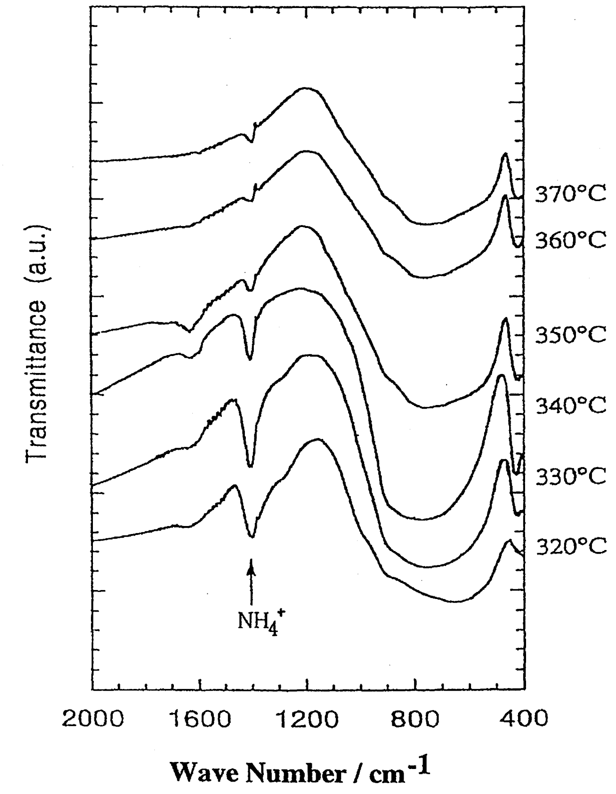

Fig. 5. Infrared spectra of h-WO_3 samples obtained at various temperatures. (A band around 1400 cm^{-1} is due to NH_4^+).

Table 3. Analytical N Contents and Lattice Parameters for h-WO_3s Prepared under Various Conditions

The molar ratios of residual ammonium (N/W)	*a* axis (Å)	*c* axis (Å)	Remarks
0.003	7.325(5)	7.751(6)	Hexagonal[a)]
0.011	7.319(7)	7.704(0)	Hexagonal[a)]
0.017	7.313(3)	7.689(0)	Hexagonal
0.019	7.312(4)	7.683(0)	Hexagonal
0.029	7.317(5)	7.692(0)	Hexagonal

a) New peaks appear as shoulders of (002), (102) peaks and in front of (004) peak.

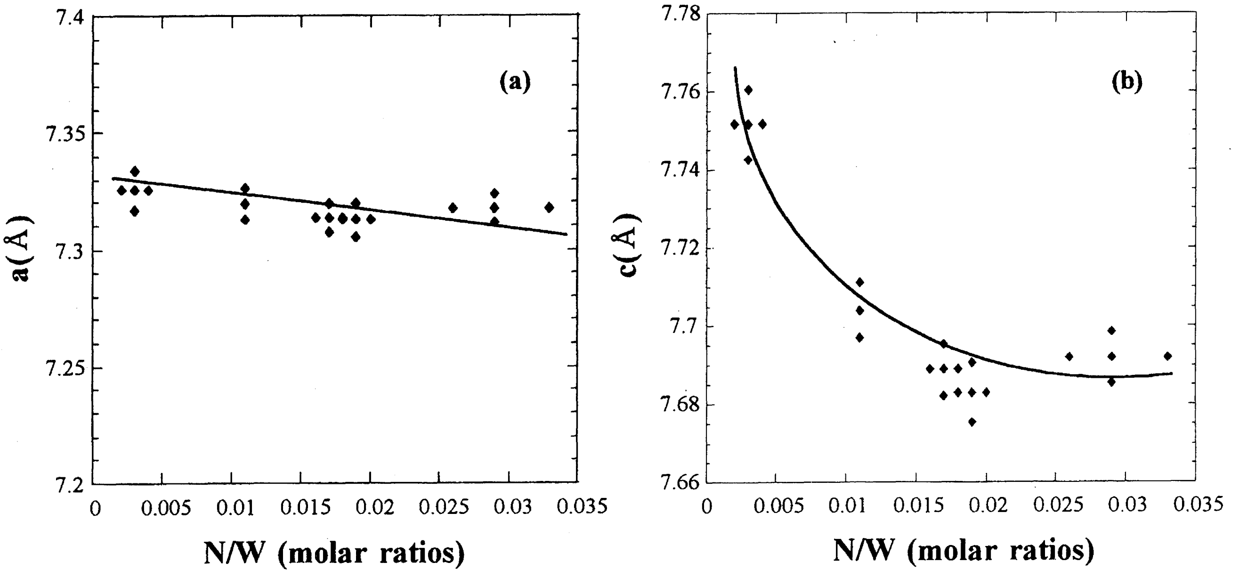

Fig. 6. Plots of lattice parameters against ammonium content (N/W in molar ratios) in h-WO_3 prepared under various conditions ((a) *a*-axis vs. N/W and (b) *c*-axis vs. N/W).

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