

Thermal Degradation of Polyoxotungstates—An Effective Method for the Preparation of Tungsten Bronzes

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The thermal degradation of ammonium salts of five polyoxotungstates, $[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ **I**, $[\text{As}_5^{\text{III}}\text{Ce}_4^{\text{III}}(\text{H}_2\text{O})_4\text{W}_{39}\text{O}_{143}]^{25-}$ **II**, $[\text{As}_3^{\text{III}}(\text{U}^{\text{VI}}\text{O}_2)_3(\text{H}_2\text{O})_6\text{W}_{30}\text{O}_{105}]^{15-}$ **III**, $[(\text{W}_5\text{O}_{18})_2\text{Ce}^{\text{III}}]^{9-}$ **IV**, and $[(\text{W}_5\text{O}_{18})_2\text{Th}^{\text{IV}}]^{8-}$ **V**, in hydrogen up to 500°C and in argon or nitrogen up to 950°C was studied by means of thermal analysis (TG, DSC), X-ray diffraction methods, chemical analysis, and susceptibility measurements. X-ray analyses of the resulting deeply colored, arsenic-free powders, revealed the formation of cubic tungsten bronzes of cerium(III) Ce_xWO_3 , $x = 0.066\text{--}0.162$ with lattice parameters ranging from $a = 3.820(3)$ to $3.836(3)$ Å, of thorium(IV) Th_xWO_3 , $x \sim 0.1$ with $a = 3.828(1)$ Å, and of uranium(IV) U_xWO_3 , $x \sim 0.1$ with $a = 3.797(1)$ Å as the main product in all experiments. These cubic bronzes were obtained in a one-step solid-state process at significantly lower temperatures than those reported previously by using classical methods of synthesis.

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INTRODUCTION

Tungsten bronzes are inert inorganic solids of general formula $M_x\text{WO}_3$, where M is an electropositive metal ion of appropriate size, and x has values between 0 and 1. Bronzes with alkali, alkaline earth, main group 3, NH_4^+ , or rare-earth ions have been well studied due to their electronic and magnetic properties (1–3). Cubic tungsten bronzes containing lanthanides or actinides have previously been synthesized by high-temperature ($T > 1000^\circ\text{C}$) solid-state processes that involve heating mixtures of powdered metal oxide $M_n\text{O}_m$ and WO_3 , with WO_2 or W , and by electrolytic reduction of a fused mixture of metal oxide or rare earth chloride and WO_3 (4–9).

The chemical resistance and thermal stability of tungsten bronzes suggests that they may be possible waste forms for

radioactive materials. As part of our investigation of polyoxotungstates for the separation and storage of radioactive waste storage the thermal degradation of ammonium salts of five polyoxoanions were studied, represented by four structural types, I, II, III, and IV or V, $[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ **I**, $[\text{As}_5^{\text{III}}\text{Ce}_4^{\text{III}}(\text{H}_2\text{O})_4\text{W}_{39}\text{O}_{143}]^{25-}$ **II**, $[\text{As}_3^{\text{III}}(\text{U}^{\text{VI}}\text{O}_2)_3(\text{H}_2\text{O})_6\text{W}_{30}\text{O}_{105}]^{15-}$ **III**, and $[(\text{W}_5\text{O}_{18})_2\text{Ce}^{\text{III}}]^{9-}$ **IV** or $[(\text{W}_5\text{O}_{18})_2\text{Th}^{\text{IV}}]^{8-}$ **V**; see Fig. 1. Thermal decomposition in Ar, N_2 , and H_2 was followed by means of thermal analyses, X-ray diffraction methods, and chemical analysis.

2. EXPERIMENTAL

Caution

Arsenic(III) compounds are toxic. Preparation should be carried out in a well-ventilated fume hood. Volatile arsenic compounds are generated during sample decomposition.

Synthesis and Sample Preparation

The compounds $(\text{NH}_4)_{70}\text{Na}_6[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}] \cdot 175\text{H}_2\text{O}$ (**Ia**), $(\text{NH}_4)_{25-x}\text{Na}_x[\text{As}_5^{\text{III}}\text{Ce}_4^{\text{III}}(\text{H}_2\text{O})_4\text{W}_{39}\text{O}_{143}] \cdot n\text{H}_2\text{O}$ (**Ia**), $(\text{NH}_4)_{15}[\text{As}_3^{\text{III}}(\text{U}^{\text{VI}}\text{O}_2)_3(\text{H}_2\text{O})_6\text{W}_{30}\text{O}_{105}] \cdot 25\text{H}_2\text{O}$ (**IIa**), $\text{Na}_9[(\text{W}_5\text{O}_{18})_2\text{Ce}^{\text{III}}] \cdot n\text{H}_2\text{O}$ (**IVa**) and $\text{Na}_8[(\text{W}_5\text{O}_{18})_2\text{Th}^{\text{IV}}] \cdot n\text{H}_2\text{O}$ (**Va**) were synthesized according to published methods (10–15). The sodium-free salts of **I**, **II**, **IV**, and **V** were obtained by means of the strong acid ion exchange resin DOWEX 50 in its NH_4^+ form. For this the crystalline salts **Ia**, **IIa**, **IVa**, and **Va** were dissolved in water (millipore) at room temperature before passing onto the resin: **Ia**, 4.4 g (0.1 mmol) in 50 mL H_2O , pH 6.7; **IIa**, 7.4 g (0.6 mmol) in 50 mL H_2O , pH 7.0; **IVa**, 14.6 g (4.5 mmol) in 50 mL H_2O , pH 7.7; **Va**, 3.5 g (1.0 mmol) in 10 mL H_2O , pH

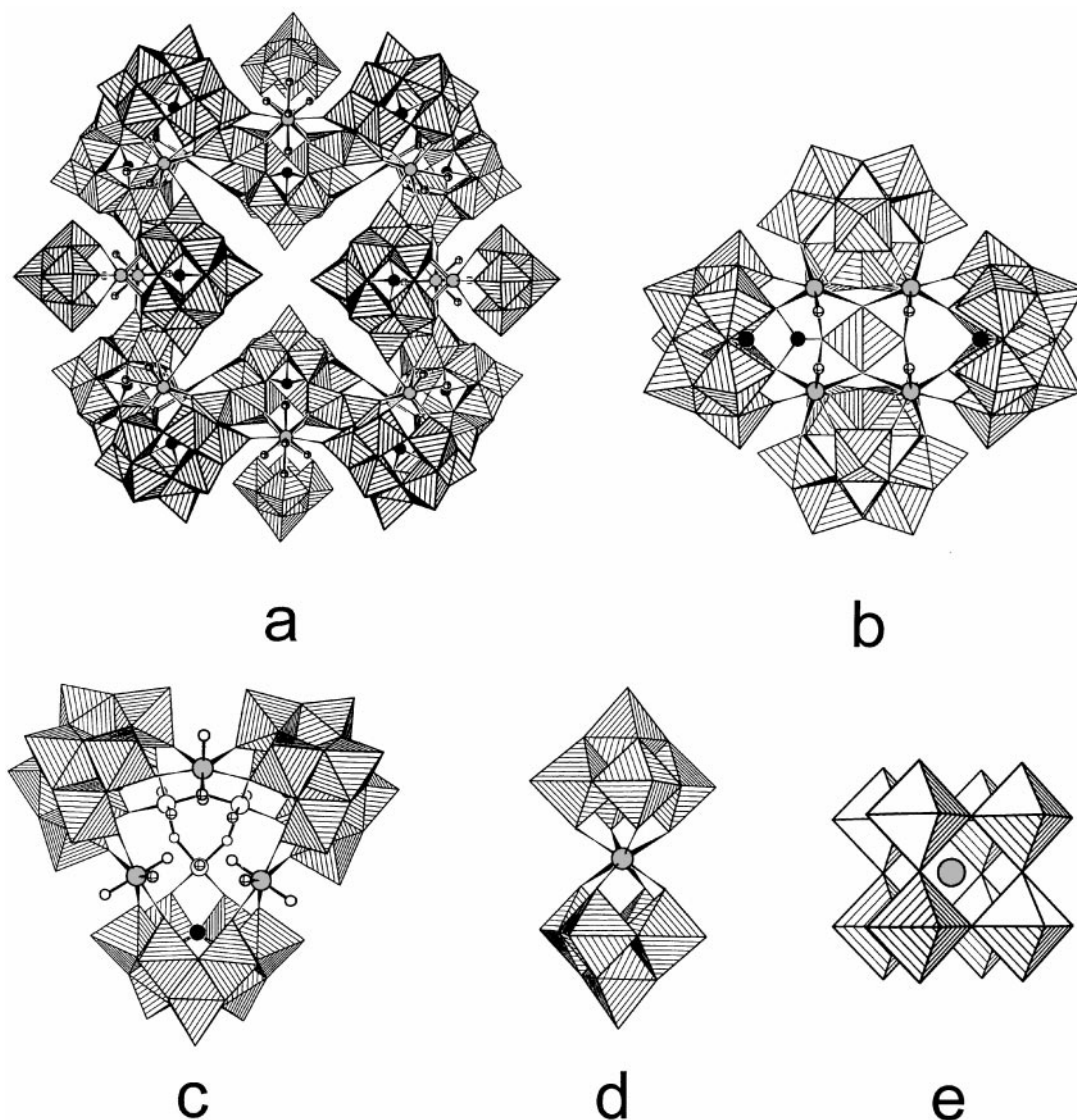


FIG. 1. Polyhedral views of (a) $[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ **I**, (b) $[\text{As}_5^{\text{III}}\text{Ce}_4^{\text{III}}(\text{H}_2\text{O})_4\text{W}_{39}\text{O}_{143}]^{25-}$ **II**, (c) $[\text{As}_3^{\text{III}}(\text{U}^{\text{VI}}\text{O}_2)_3(\text{H}_2\text{O})_6\text{W}_{30}\text{O}_{105}]^{15-}$ **III**, (d) $[(\text{W}_5\text{O}_{18})_2\text{M}]^{n-}$ $\text{M} = \text{Ce}^{\text{III}}$ **IV**, $\text{M} = \text{Th}^{\text{IV}}$ **V**, and (e) M_xWO_3 . Ln/An atoms are depicted as large gray circles; attached water ligands are drawn as small crossed circles.

7.4. The eluates were freeze-dried and the resulting yellow powders of $(\text{NH}_4)_{76}[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}] \cdot n\text{H}_2\text{O}$ (**Ib**), $(\text{NH}_4)_{25}[\text{As}_5^{\text{III}}\text{Ce}_4^{\text{III}}(\text{H}_2\text{O})_4\text{W}_{39}\text{O}_{143}] \cdot n\text{H}_2\text{O}$ (**IIb**), $(\text{NH}_4)_9[(\text{W}_5\text{O}_{18})_2\text{Ce}^{\text{III}}] \cdot n\text{H}_2\text{O}$ (**IVb**), and $(\text{NH}_4)_8[(\text{W}_5\text{O}_{18})_2\text{Th}^{\text{IV}}] \cdot n\text{H}_2\text{O}$ (**Vb**) were kept overnight in a desiccator filled with P_4O_{10} . Sodium analysis revealed the values **Ib** < 5 ppm, **IIb** 76 ppm and **IVb** 161 ppm.

Powdered samples (2–3 g) of **Ia**, **Ib**, **IIb**, and **IVb** were heated in a horizontal tube furnace in hydrogen (RT \rightarrow 500°C) and argon (RT \rightarrow 900°C) gas, with a flow rate of 80 L/h and a heating rate of 5 K/min. Once the final temperature of 900°C was reached, an isothermal treatment of 3–6 h was applied, and the samples were finally cooled down slowly overnight.

Thermal Analysis

The differential scanning calorimetric curves (DSC) were obtained in N_2 flow in the temperature range RT \rightarrow 725°C on a TA Instruments DSC 2910 analyzer, at a heating rate of 5 K/min and an initial sample weight of 15–20 mg using a platinum crucible. The thermogravimetric analyses (TGA) were performed under the same experimental conditions, RT \rightarrow 950°C on a TA Instruments TGA 2050 analyzer, using ceramic pans.

X-Ray Diffraction

Powder X-ray diffraction patterns were collected with a Rigaku D-Max Vertical Diffractometer using $\text{CuK}\alpha$

radiation with silicon as an internal standard for all thermally treated products (TG, DSC, and furnace).

Elemental Analysis

The elemental analyses for the starting materials and the thermally treated samples were carried out by E&R Micro-analytical Laboratory, NY, and Kanti Technologies Inc., NY. In order to determine the amount of reduced tungsten

present in the bronzes $M_x\text{WO}_3$ (and therefore x), samples ranging from 25–150 mg were oxidized in air and the increase in weight was determined, (TGA 2050, RT → 850°C, 5 K/min).

Magnetic Measurements

Magnetic susceptibilities were measured in the temperature range 4–300 K in an applied field of 1 T using a

TABLE 1
Experimental Conditions and Results for the Thermal Degradation of Compounds Ia–Vb

	Experimental conditions ^a	Products, color of powder	Yield (%)	Lattice parameter (Å)	Δm^b (%)
Ia^c	RT → 500°C H ₂ + 500°C → 900°C Ar + 6 h at 900°C Ar	Ce _x WO ₃ $x \sim 0.08$ NaCe(WO ₄) ₂ deep blue	~ 90 ~ 10	$a_0 = 3.821(3)$ cubic $a = 5.327(5)$, $c = 11.60(2)$ tetragonal	0.77
Ia^d	RT → 950°C Ar + 3 h at 950°C Ar	same as above			
Ib^e	RT → 50°C H ₂ + 500°C → 900°C Ar + 5 h at 900°C Ar	Ce _x WO ₃ $x \sim 0.162$ WO ₂ purple	~ 70 ~ 30	$a_0 = 3.836(3)$ $a = 5.532(21)$, $b = 4.898(18)$, $c = 5.590(34)$, $\beta = 118.8(2)^\circ$	3.28
Ib^f	RT → 900°C Ar + 5 h at 900°C Ar	Ce _x WO ₃ $x \sim 0.082$ blue	> 95	$a_0 = 3.824(1)$	0.80
IIb	RT → 900°C Ar + 6 h at 900°C Ar	Ce _x WO ₃ $x \sim 0.066$ Ce ₄ W ₉ O ₃₃ unknown blue-grayish	> 90 < 5 < 5	$a_0 = 3.820(2)$	0.58
IIIa	RT → 725°C N ₂ DSC	U _x WO ₃ $x \sim 0.1$ U ₅ W ₁₃ O ₅₀ black-grayish	> 95 < 5	$a_0 = 3.797(1)$	
IVb	RT → 725°C N ₂ DSC	Ce _x WO ₃ $x > 0.1$ (NH ₄) _{0.42} WO ₃ blue-grayish	~ 90 ~ 10	$a_0 = 3.822(1)$	
IVb	RT → 955°C N ₂ TGA	Ce _x WO ₃ $x \sim 0.1$ unknown blue-grayish	~ 90 ~ 10		
IVb	RT → 900°C Ar + 6 h at 900°C Ar	Ce _x WO ₃ $x \sim 0.118$ WO ₂ purple-brownish	~ 85 ~ 15	$a_0 = 3.830(1)$	2.00
Vb	RT → 725°C N ₂ DSC	Th _x WO ₃ $x > 0.1$ (NH ₄) _{0.42} WO ₃ black	~ 90 ~ 10	$a_0 = 3.837(1)$	
Vb	RT → 725°C N ₂ TGA	Th _x WO ₃ $x \sim 0.1$ WO ₂ black-purple	> 95 < 5	$a_0 = 3.828(1)$	1.40

Note. In footnotes c–f, the chemical analyses, exp. and (calc.), for the heated samples are given in percentages.

^a If not stated differently, thermal treatment was performed in a tube furnace.

^b Measured increase in weight through thermal treatment of the bronzes in air, RT → 850°C, 5 K/min, to determine the content of reduced tungsten.

^c W 73.67 (74.15), Ce 6.14 (6.11), Na 0.33 (0.37), As < 0.3 .

^d W 73.98 (74.15), Ce 6.57 (6.11), Na 0.44 (0.37), As 0.3.

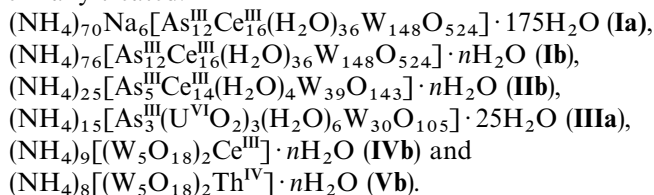
^e W 80.90 (81.16), Ce 6.74 (6.69), As < 3 ppm.

^f W 75.05 (74.25), Ce 5.74 (6.12), As < 3 ppm.

Metronique Ingegnerie MS03 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants (16).

RESULTS AND DISCUSSION

Six compounds, with sample amounts up to 3 g, were thermally treated:



This treatment led to intensely colored powders. X-ray analyses of these samples revealed the formation of a cubic tungsten bronze $M_x\text{WO}_3$, $x = 0.066\text{--}0.162$, as the main product for all experiments. Table 1 lists the experiments and summarizes the results.

As an example, the powder diffractograms of the degradation products of **Ia**, **Ib**, and **IIIa** are given in Figs. 2 and 3, revealing the characteristic reflection pattern of a cubic tungsten bronze (4, 17). Detailed high-temperature X-ray analysis of the degradation process of **Ia** and **Ib** in inert (Ar, N_2) as well as in reducing (H_2) atmospheres revealed the formation of the hexagonal tungsten bronze around 500°C . Further heating up to 900°C in argon led to the formation of the cubic cerium bronze $\text{Ce}_{0.087}\text{WO}_3$, starting at 600°C , and of the tetragonal phase $\text{NaCe}(\text{WO}_4)_2$ (18–20). The formation of this scheelite-like phase is due to the presence of sodium in the starting material **Ia**. Upon preparation of the

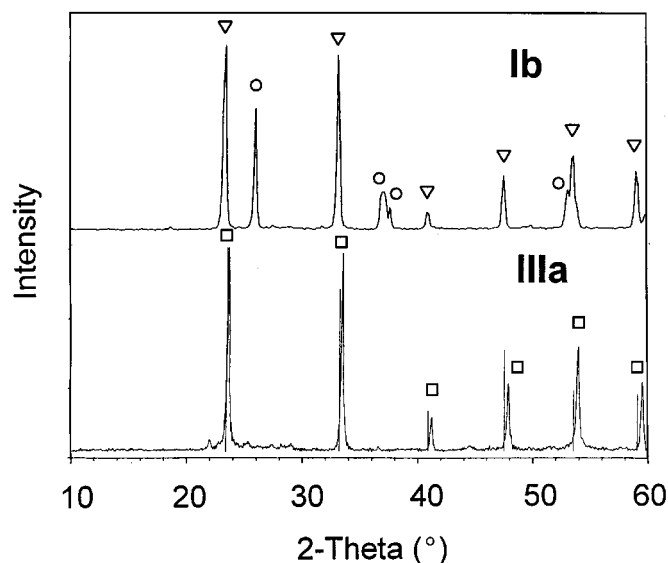


FIG. 3. Powder diffractograms of thermally treated samples of **Ib** RT \rightarrow 500°C in H_2 plus 500°C 6900°C in Ar and **IIIa** RT \rightarrow 725°C in N_2 , (∇) $\text{Ce}_{0.17}\text{WO}_3$, (\circ) WO_2 , (\square) $\text{U}_{0.1}\text{WO}_3$, with reference diffractogram of $\text{Na}_{0.39}\text{WO}_3$ $a = 3.816(1) \text{ \AA}$ (17).

sodium-free sample **Ib**, obtained from **Ia** via ion exchange and freeze drying, the thermal degradation led in H_2 (RT \rightarrow 500°C) and Ar ($500 \rightarrow 900^\circ\text{C}$) to the formation of $\text{Ce}_{0.162}\text{WO}_3$ and WO_2 (21). However, the decomposition of **Ib** carried out exclusively in argon (RT \rightarrow 900°C) quantitatively formed $\text{Ce}_{0.082}\text{WO}_3$. Reduction of **Ib** in H_2 up to 500°C increased the cerium content in Ce_xWO_3 , approaching the reported limit of $x = 0.186$ (22). The formation of WO_2 during the bronze preparation $M_x\text{WO}_3$ had been reported earlier and was observed for values of $x > 0.19$, $M = \text{La}$, and $x > 0.15$, $M = \text{Y}$ (23).

The degradation of **IIb** in Ar gave mainly the cubic bronze $\text{Ce}_{0.066}\text{WO}_3$. Two very minor phases were also observed, one of which was characterized as $\text{Ce}_4\text{W}_9\text{O}_{33}$ (24).

The study of the uranyl-containing sample **IIIa** in N_2 led to the formation of the cubic uranium(IV) bronze $\text{U}_{0.1}\text{WO}_3$, accompanied by a minor phase $< 5\%$ of $\text{U}_5\text{W}_{13}\text{O}_{50}$ at a remarkably low temperature of 725°C ; see Fig. 3 (5, 25, 26).

The degradation of the cerium-containing decatungstate **IVb** in Ar (RT \rightarrow 900°C) resulted in the formation of $\text{Ce}_{0.118}\text{WO}_3$ and WO_2 , similar to the decomposition of **Ib** in H_2 and Ar. The ratio between the phases was estimated as 85 to 15, based on comparative study of the intensities of the recorded diffractogram and the measured increase in weight upon oxidation of the powder in air. It might be speculated that this ratio is related to the structural arrangement in $[(\text{W}_5\text{O}_{18})_2\text{Ce}]^{9-}$, see Fig. 1. In this polyoxoanion, cerium obtains a nearest coordination to eight tungsten atoms, as

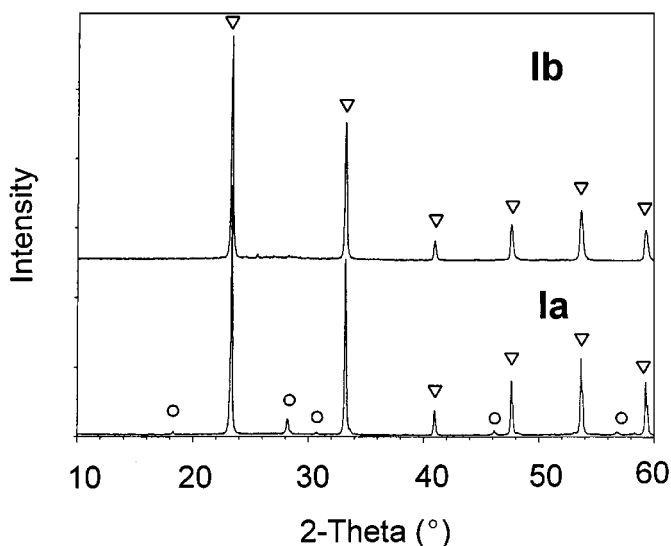


FIG. 2. Powder diffractograms of thermally treated samples of **Ia**, RT \rightarrow 500°C in H_2 and 500°C \rightarrow 900°C in Ar, and **Ib**, RT \rightarrow 900°C in Ar: (∇) Ce_xWO_3 ; (\circ) $\text{NaCe}(\text{WO}_4)_2$.

also occurs in the bronze; see Figs. 1d and 1e. However, it must be noted that the decomposition of **IVb** in the DSC and TG cell in N_2 did not show the formation of WO_2 . This effect might be the result of the smaller sample sizes (~ 20 mg versus ~ 2 g in the furnace experiments) resulting in a lower height of packing causing a shorter contact time of the reducing agent formed *in situ* in the powder. The bronze phase Ce_xWO_3 of ca. 90% and a second component of ca. 10%, described as a high-temperature phase $(NH_4)_{0.42}WO_3$, were found at $725^\circ C$ (DSC cell). Heating up to $950^\circ C$ formed the bronze $Ce_{0.1}WO_3$ of ca. 90% and an unidentified second phase of ca. 10% (TG cell) (27, 28). Similar results were obtained for the analogous thorium decatungstate **Vb**. The phases $Th_{0.1}WO_3$ and $(NH_4)_{0.42}WO_3$ were found to be present at $725^\circ C$. At $950^\circ C$ the bronze phase $Th_{0.1}WO_3$ and a very minor phase of WO_2 were detected. Figure 4 gives the plot for the determined values of x of the cubic bronzes Ce_xWO_3 versus the corresponding cubic cell parameter a_0 (\AA) and reveals a fairly good linear relation between these numbers ($r = 0.988$).

Formation of the cubic bronze phase under inert conditions, starting at a temperature as low as $600^\circ C$, is noteworthy. The decomposition of ammonium causes the reduction of tungsten and is presumably also responsible for the loss of arsenic, (most likely) in the form of AsH_3 . Thermal treatment in the temperature range up to $350^\circ C$ causes, as expected, the loss of H_2O and NH_3 . Characteristic weight losses of 2–4% at temperatures higher than $500^\circ C$ have been found for all studied compounds, see Fig. 5 for example.

Susceptibility measurements were performed for the bronzes M_xWO_3 with $M = Ce^{III}$, Th^{IV} , and U^{IV} for $x \sim 0.1$ in the temperature range 4–300 K. The Ce^{III} and U^{IV} samples had the magnetic moments expected for the isolated metal ions. The effective magnetic moment steadily decreased with decreasing temperature for both compounds,

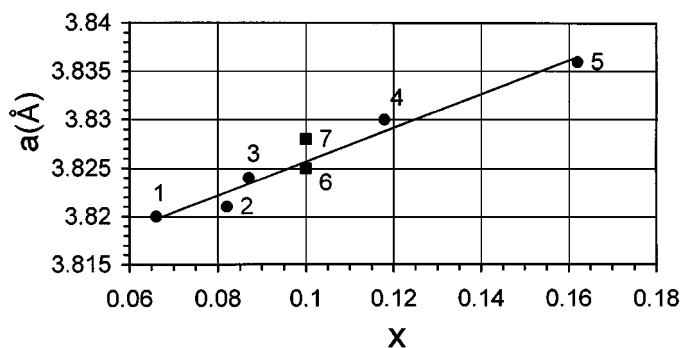


FIG. 4. Cell parameter a (\AA) for the cubic bronzes Ce_xWO_3 versus the value for x : (1) **IIb** RT \rightarrow $900^\circ C$, (2) **IIb** RT \rightarrow $950^\circ C$, (3) **Ia** RT \rightarrow $500^\circ C$ (H_2) \rightarrow $900^\circ C$ (Ar), (4) **IVb** RT \rightarrow $900^\circ C$, (5) **IIb** RT \rightarrow $500^\circ C$ (H_2) \rightarrow $900^\circ C$ (Ar), (6) Ref. (33); (7) Ref.(4).

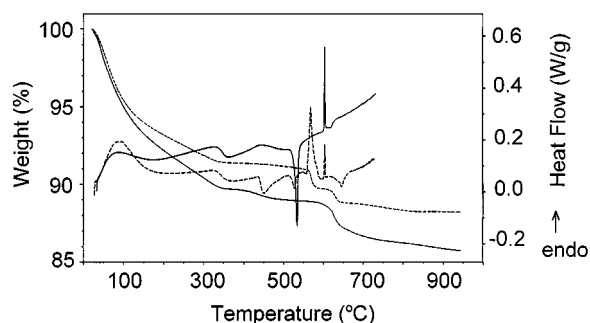


FIG. 5. TG-analyses and DSC experiments for **Ia** (dashed line) and **Ib** (solid line) in N_2 , 5 K/min.

confirming the results reported earlier (29). The value for the magnetic susceptibility of $Th_{0.1}WO_3$, on the other hand, remained essentially constant ($\chi = 125 \times 10^{-6}$ emu/mol) down to 30 K and then decreased rapidly, but no evidence of long-range magnetic order was observed.

There have been a only few previous reports on the formation of tungsten bronzes via the thermal degradation of polyoxometalates (30–32). The present work demonstrates that the lanthanide- and actinide-containing bronzes can be prepared by single-step solid-state processes in an inert atmosphere at temperatures significantly lower than those required in the “classical” literature syntheses. The use of pure precursor polyoxometalate salts, which contain the desired components of the bronzes dispersed at a molecular level and in the desired stoichiometry, can lead to materials of greater uniformity than is possible by heating of heterogeneous mixtures of components. The enormous variety of polyoxometalate compositions available offers the prospect of synthesizing new bronze-based materials, e.g., with mixtures of guest atoms, that exhibit different ranges of optical, magnetic, and electronic properties.

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