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Synthesis and Characterization of Reduced Molybdenum Oxides with Hydroxylamine Hydrochloride in Aqueous Solutions

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Reduction of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, with hydroxylamine hydrochloride. $NH_2OH\cdot HCl$, at ambient temperature in aqueous solutions results in amorphous $MoO_3\cdot nH_2O$ oxide. Subsequent heat treatment of this oxide yields $Mo_{1-\delta}O_2$ or a hydrogen molybdenum bronze, H_xMoO_3 ($x \cong 1$), both crystalline in nature. The samples have been characterized by X-ray diffraction, differential scanning calorimetry, scanning and transmission electron microscopies, thermogravimetric analysis, infrared spectroscopy, and galvanostatic electrochemical characterization. © 1999 Academic Press

INTRODUCTION

MoO_3 has an unusual layered structure (Fig. 1) in which infinite chains of vertex-sharing MoO_6 octahedra are fused together by edge-sharing to form corrugated layers; the layers are stacked parallel to one another and are separated by a van der Waals gap of ≈ 7 Å. At ambient temperature, chemical (1) or electrochemical reduction (2, 3) in aqueous acidic media leads to the formation of hydrogen molybdenum bronzes H_xMoO_3 ($0 < x < 2$). In these compounds, hydrogen is inserted reversibly into the MoO_3. The close resemblance of the powder X-ray patterns of reduced phases to MoO_3 itself and their ability to participate in the topotactic reaction mechanism has led Glemser and coworkers (4, 5) to call these a *genotypic* series. Four distinct phases have been identified: blue, orthorhombic for $0.23 < x < 0.4$; blue, monoclinic for $0.85 < x < 1.04$; red, monoclinic for $1.55 < x < 1.72$; and green, monoclinic for $x \approx 2.0$. Such phases have been prepared (6) by reduction of crystallined MoO_3 with (a) Zn and HCl, (b) Mo powder in the presence of water, (c) atomic hydrogen, and (d) by using $LiAlH_4$. Some samples were also made by dehydrogenation of $H_{2.0}MoO_3$ by heating at 110°C under a vacuum or by treatment of $H_{1.68}MoO_3$ with an aqueous slurry of MoO_3 in a sealed tube at 80°C and heating up to 5 days followed by a careful washing under nitrogen (7). These materials have potential application in electrochemical systems or in catalysis.

Hydrogen-inserted compounds H_xMoO_3 are deeply colored: they are mixed ionic/electronic conductors of interest for electrochemical systems (8) in accordance with

$$MoO_3 + xH^+ + xe^- = H_xMoO_3.$$

Octahedral-site Mo^{6+} and Mo^{5+} ions are displaced alternately up and down perpendicular to the layers in this structure, each toward a terminal oxygen to form oxomolybdenum ions $(Mo{=}O)^{4+}$ and $(Mo{=}O)^{3+}$. The hydrogen is associated with the bridging of oxide ions O_2 of Fig. 6 (9). This hydrogen distribution illustrates that the O^{2-} ion toward which a Mo ion moves becomes more acidic; the one from which it moves becomes more basic; but the O_2 oxygen that bridges two Mo is more basic than the O_1 oxygen that is coordinated to three Mo atoms. The ability to change the acid/base character of a surface anion by a simple cation displacement is significant for the role of Mo^{6+} in heterogeneous catalysis (10). In this, paper, we provide a simple, solution-based chemical method to synthesize such hydrogen–molybdenum bronzes. As an example, we describe the synthesis and characterization of a bronze $MoO_{3-x}(OH)_x$ with $x \cong 1$ corresponding to H_xMoO_3.

EXPERIMENTAL

A 0.1 M solution of hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) was prepared by dissolving 1.737 g of the salt in 100 ml of water; the pH of this solution was adjusted to be around 10 by dissolving pellets of NaOH. A 0.1 M ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution was prepared by dissolving 2.784 g of the salt in 100 ml of water in another beaker. Drops of dilute HCl were added to the ammonium molybdate solution until the pH reached about 7. The molybdate solution was kept under continuous stirring on a magnetic stirrer. To this constantly stirred

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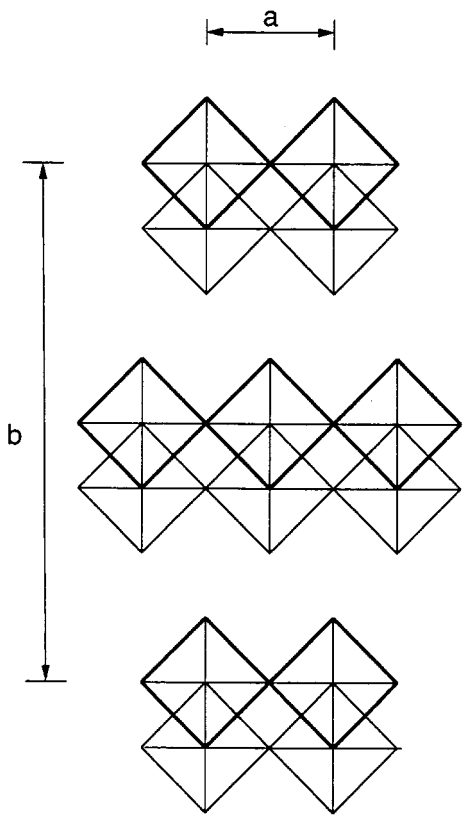

FIG. 1. Crystal structure of MoO_3 represented in terms of the octahedra, which are obtained by joining the centers of the oxygen atoms coordinated with each metal atom. Octahedra indicated by heavy lines are located at a higher level than those drawn within thin lines.

solution, hydroxylamine hydrochloride solution was added dropwise from a burette while the pH of the solution was maintained at 7 ± 0.2. Immediately after the addition of hydroxylamine hydrochloride, the solution turned dark in color, signaling the decomposition of ammonium molybdate. Further addition of the 100 ml of hydroxylamine hydrochloride within a period of 15 min resulted in a dark sol medium. It was allowed to settle overnight, whereupon the gel precipitated. The gel was then carefully filtered, washed with a minimal amount of water, and allowed to dry overnight.

Powder X-ray diffraction (XRD) of the samples was recorded with a Philips PW 1729 diffractometer and Cu$K\alpha$ radiation in the 2θ range 10°–60°. Differential scanning calorimetry (DSC) of the sample was performed in a flowing N_2 atmosphere at a heating rate of 10°C/min in the temperature range 30–500°C with a Perkin–Elmer Series 7 thermal analysis system. A JEOL JEM-200CX transmission electron microscope (TEM) with 200 keV energy was used to investigate particle morphology. A scanning electron microscope equipped with energy dispersive spectroscopic analysis was used to detect qualitatively the elements in the samples. The TEM specimens were made by dispersing the sample in methanol and adding a few drops of the suspension on a carbon-coated grid. IR spectra were recorded at room temperature with a Nicolet Magna-550 spectrometer, which has a resolution of about 2.5 cm^{-1}. Thin, transparent pellets were made by compacting an intimate mixture obtained by shaking *ca.* 5 mg of the sample in *ca.* 100 mg of KBr. Electrochemical characterization was performed with an Arbin Battery Tester System. The samples were mixed with 25 wt % fine carbon and 5 wt % polytetrafluroethylene binder and made into circular electrodes of ca. 2 cm^2 area. The electrode performance was studied with coin-type cells having metallic Li anodes and $LiClO_4$ in (PC)/1,2-dimethoxyethane electrolyte. The cells were tested at a current density of 0.5 mA/cm^2 unless otherwise stated.

RESULTS AND DISCUSSION

The as-prepared sample of $MoO_3 \cdot nH_2O$ ($n = 1.75$) was amorphous as indicated by the absence of any Bragg reflections in the XRD (Fig. 2). This sample was dried in an oven at 110°C, and subsequent XRD showed the sample was still amorphous (Fig. 2). The amorphous nature of both samples was also confirmed by the absence of diffraction spots or ring patterns in a TEM study. EDS showed the presence of only Mo; no other elements were detected (within our instrument limitations). DSC in a flowing N_2 atmosphere showed an exothermic peak around 300°C, signaling the temperature of crystallization. Crystalline $Mo_{1-\delta}O_2$ and

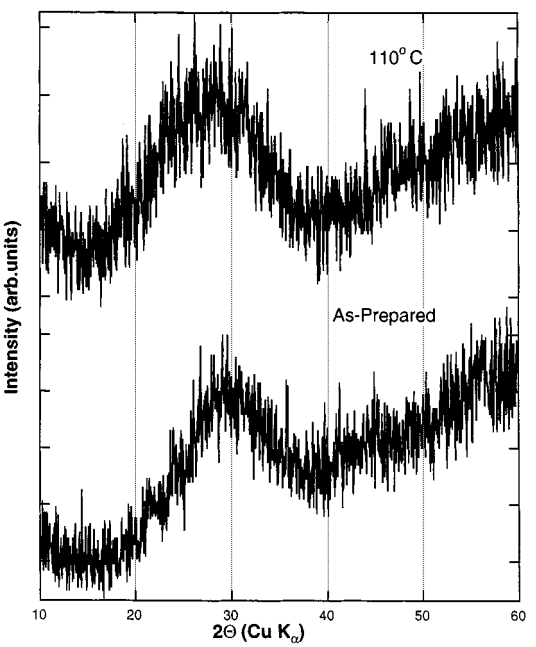

FIG. 2. XRD patterns of amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$): bottom, as-prepared; top, dried at 110°C.

H_xMoO_3 (bronze) were synthesized from amorphous MoO_3 as per the conditions in Table 1. The corresponding XRD spectra are given in Fig. 3.

The as-prepared, amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$) is yellow in color. Heating this sample in air up to 300°C gave a gray, metallic product (crystalline H_xMoO_3). TGA (Fig. 4) also showed a weight loss of $\approx 10\%$ up to 110°C and a further loss of $\approx 8\%$ up to ≈ 280°C, indicating the loss of free H_2O in the first stage and bound water in the second stage. When the as-prepared sample was vacuum heated at 300°C, it transformed to a blue crystalline bronze H_xMoO_3. Also, the same amorphous sample, when heated in an evacuated quartz tube at 600°C for 24 h, transformed to $Mo_{1-\delta}O_2$ (black color and crystalline). Electrochemical characterization of these samples in the range 3 to 1.5 V versus lithium (Fig. 5) indicates that ≈ 1.5 lithium per formula unit can react with the amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$) materials up to ≈ 0.5 lithium per formula unit with both the crystalline $Mo_{1-\delta}O_2$ and H_xMoO_3 bronze materials. Discharge–charge curves also showed access to both $Mo^{6+/5+}$, $Mo^{5+/4+}$ couples for the amorphous MoO_3, but access to only the $Mo^{5+/4+}$ couple for crystalline $Mo_{1-\delta}O_2$ and H_xMoO_3 bronze.

The as-prepared $MoO_3 \cdot nH_2O$ ($n = 1.75$) contains, in addition to free water, a considerable amount of water bound directly to Mo as terminal OH^- or, opposite to a Mo=O bond, as terminal OH_2. On heating in air to 300°C, the crystallization reactions

$$2OH^-/_t - - - - - - O^{2-}/_b + H_2O\uparrow \qquad [1]$$

$$OH_{2/t} + OH^-/_t - - - - - - OH^-/_b + H_2O\uparrow \qquad [2]$$

would normally occur, where the subscripts t and b refer to terminal and bridging oxo groups, respectively. When the amorphous sample is heated at an elevated temperature in an evacuated quartz tube at 10^{-6} Torr pressure for a long period of time, it loses O_2 in addition to water to become $Mo_{1-\delta}O_2$. When the sample is vacuum heated at 300°C for a short period of time, like 2 h, there is loss of water with some retention of OH^- bridging units, Eq. [2]. The product is the crystalline, blue bronze H_xMoO_3 (with minor impurity). Such an observation is in total agreement with the blue bronze H_xMoO_3 obtained by Birtill and Dickens (7) with H_2 reduction in the presence of Pt. On heating in air at 300°C, some of the bridging OH^- groups are replaced by bridging O^{2-}, which oxidizes the bronze to small x.

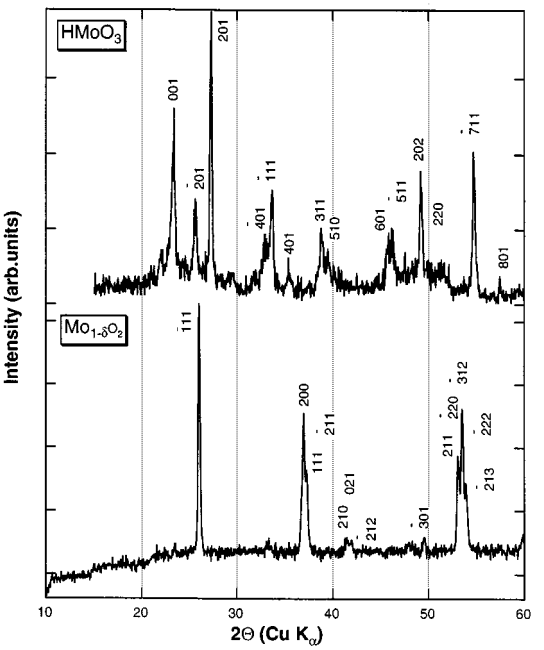

FIG. 3. XRD patterns of (bottom) crystalline $Mo_{1-\delta}O_2$ and (top) H_xMoO_3 ($x \cong 1$) (bronze).

TABLE 1
Synthesis of Crystalline $HMoO_3$ (Bronze) and $Mo_{1-\delta}O_2$ from Amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$) (Yellow)

Synthesis condition	Product	Reference	Unit-cell	Structure type
600°C, evacuated quartz tube, 24 h and cooled	$Mo_{1-\delta}O_2$ Black MoO_2	JCPDS[a] 32-0671	Monoclinic 5.607, 4.859 5.537, 119.37° $P21/c$, $z = 4$	Distorted-rutile
300°C, vacuum-dried, 2 h	$MoO_{3-x}(OH)_x$ $x \sim 1$ Blue	JCPDS[a] 05-0508 MoO_3	Monoclinic 14.51, 3.788 3.868, 93.72° $Cmcm$, $z = 4$	Layered

[a] Joint Committee on Powder Diffraction Standards, Swarthmore, PA.

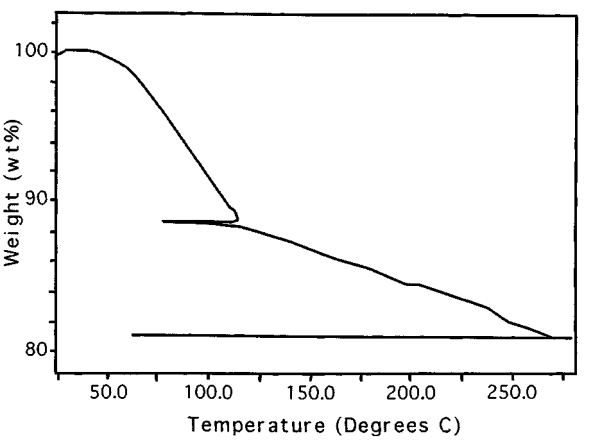

FIG. 4. TGA plot of the amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$) heated up to 300°C in air.

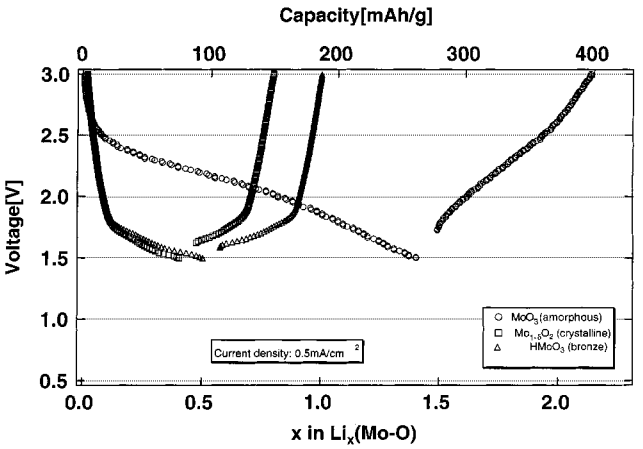

FIG. 5. Electrochemical behavior of (a) amorphous MoO_3, (b) $Mo_{1-\delta}O_2$, and (c) H_xMoO_3 ($x \cong 1$) at 0.5 mA/cm^2 versus a lithium anode.

The electrochemical data demonstrate the presence of Mo^{5+} in both $Mo_{1-\delta}O_2$ and the H_xMoO_3 bronze. The XRD pattern of H_xMoO_3 is analogous to $Mo_2O_4(OH)_2$ or $HMoO_3$ reported earlier (1) (cell-parameters were not given). Least-squares refinement of the powder pattern showed that $Mo_2O_4(OH)_2$ had crystallized in a monoclinic system with *Cmcm* space group; $a = 14.515(5)$ Å, $b = 3.788(7)$ Å, $c = 3.868(3)$ Å, and $\beta = 93.72(6)^\circ$. These values are in agreement with the values reported by Birtill and Dickens (7) and lie in the range $0.93 \leq x \leq 1.04$ (Table 2) for the blue monoclinic H_xMoO_3 bronze phase having the structure of Fig. 6. The change in the lattice parameter for the entire range $0 < x < 2$ is within 5% for the *a* and *b* axes and within 10% for the *c* axis from the cell-parameters for MoO_3 (12).

In the amorphous material, water between the $MoO_{3-x}(OH)_x$ layers allows Li^+ ions access to most of the Mo atoms as though they were at internal surfaces, and the potential versus *x* resembles the curve of an electrochemical faradaic capacitor more than that of a battery cathode. On discharge, the Li^+ ions form surface Li–O bonds attached to a reduced Mo atom, but surface OH^- ions block formation of a Li–O bond, which limits the capacity. The mobility of a hydrated Li^+ ion is too low for a practical faradaic capacitor. The crystalline materials, on the other hand, have a much smaller surface area and intercalate Li^+ into their interstitial space only slowly and incompletely, which limits their capacity.

TABLE 2
Lattice Parameters of Blue Bronze H_xMoO_3 from Various Studies

H_xMoO_3	Space group	*a*(Å)	*b*(Å)	*c*(Å)
$x = 0$	*Pbnm*	3.9628(7)	13.855(3)	3.6964(6)
$x = 0.5$, Single-crystal X-ray	*Cmcm*	3.888	14.082	3.734
$x = 0.5$, Neutron diffraction	*Cmcm*	3.8812(4)	14.0657(14)	3.7280(4)
P. G. Dickens *et al.*				
$x = 0.85$	*Cmcm*	14.54	3.794	3.860, 93.67°
$x = 1.04$	*Cmcm*	14.42	3.784	3.911, 93.62°
$x \sim 1$ this study	*Cmcm*	14.51	3.788	3.868, 93.72°

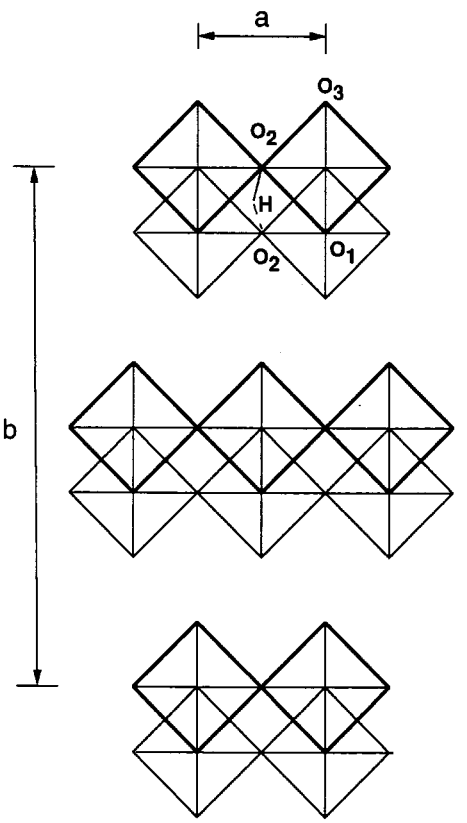

FIG. 6. Crystal structure of H_xMoO_3 ($x \cong 1$) showing the location of protons in the (100) mirror plane attached to the bridging O_2 atoms.

In hydrogen-insertion compounds, hydrogen may bond either to the metal directly to form a hydride bond (M–H) or to oxygen as an isolated OH^- group or as an OH_2 group. For compounds containing OH_2 groups, IR spectroscopy shows that absorption bands occur in the regions 1630–1600 and 3500–3000 cm^{-1} due to the H–O–H bending vibration of the OH_2 group. Absorption bands are found at 3500–3000 and 1200–900 cm^{-1} in the spectra of OH^--containing compounds corresponding to O–H stretching and bending vibrations, respectively. The presence of protons in $HMoO_3$ is evidenced by the occurrence of absorption bands around 1000 cm^{-1} (bending mode) and 3000 cm^{-1} (stretching mode) in the IR spectrum. A similar band, which has been attributed to a V–O–H deformation, is seen in the IR spectrum of $H_{0.33}V_2O_5$ (11).

It is of importance to locate the position of hydrogen in the bronze material. MoO_3 crystallizes in the *Pbnm* (No. 62)

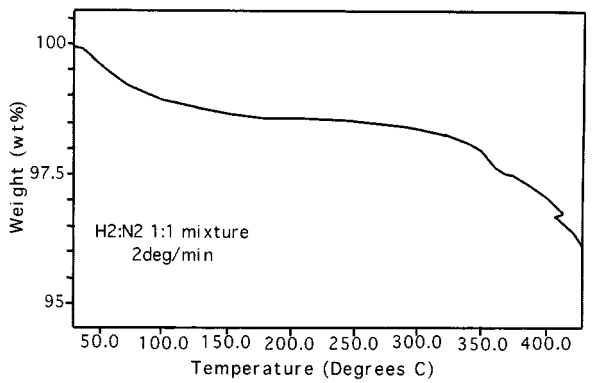

FIG. 7. TGA plot of the hydrogen bronze $HMoO_3$ ($x \cong 1$) heated in a $H_2:N_2$ gas mixture at the heating rate of 2°C/min.

space group with all the atoms in four-fold positions (4c). As the oxide ions in the structure of MoO_3 are replaced by OH^- groups, there is a slight change in the lattice parameter, but the intensity distribution in the powder patterns of the hydrogenated material is similar to that of MoO_3 (preferred orientation has equal influence on both the compounds) with the exception that all reflections with $h + k = 2n + 1$ are missing. The missing reflections suggest a C-centering of the lattice, which can be achieved if the four x coordinates in *Pbnm* are put equal to zero resulting in the *Cmcm* space group. X-ray structure analysis of a single crystal of H_xMoO_3 with nominal composition $x = 0.5$ (12) showed that the Mo atoms in the bronze are displaced toward the apical oxygen. However, the hydrogens were assumed incorrectly to be associated with the apical oxygen.

Neutron diffraction, which was employed on the same composition to determine the location of the protons, showed the actual value of x in that composition to be 0.31 with the protons attached statistically to the bridging O_2 atoms and lying in the (100) mirror plane (13). Hydrogen bonding between nearest-neighbor O_2 oxygen gives an O–H bond length at 1.31 Å and an O–H bond length at 1.9 Å with an OHO bond angle of 155° (Fig. 6). We assume that the hydrogens are similarly located for all $x \leq 1$.

When a sample of crystalline blue bronze $HMoO_3$ was subjected to TGA in a flowing gas mixture of 1:1 $H_2:N_2$ in the temperature range 30–400°C at 2°C/min, a constant plateau (Fig. 7) was observed. From the weight loss, this plateau would correspond to the loss of 0.13 H_2O per formula unit. The reduced samples are still colored deep blue, and IR measurements confirm the retention of OH^- groups in the sample.

CONCLUSION

Amorphous $MoO_3 \cdot nH_2O$ ($n = 1.75$) was prepared from ammonium molybdate by a novel solution-based low-temperature route. Crystalline hydrogen–molybdenum bronzes H_xMoO_3 with $0 < x \leq 1$ can be prepared by heating the amorphous product at 300°C under different partial pressures of oxygen. Crystalline $Mo_{1-\delta}O_2$ with a distorted rutile structure was obtained from the amorphous material by heating at 600°C. Heating the hydrogen bronze in a 1:1 $H_2:N_2$ gas mixture gave an initial loss of *ca.* 13 H_2O per formula unit, the residual hydrogen remaining as OH^- anions to 300°C.

ACKNOWLEDGMENT

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