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LETTER TO THE EDITOR

A New Route for the Synthesis of Tungsten Oxide Bronzes

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A novel method involving ambient temperature reduction of aqueous solutions has been developed for the synthesis of tungsten oxide bronzes. Addition of aqueous sodium borohydride solution into aqueous sodium tungstate solution at pH ≈ 6.5 results in the formation of a reduced sodium tungsten oxide gel. The gel crystallizes sharply at around 440°C to yield the crystalline sodium tungsten oxide bronze, Na_xWO_3. The products are characterized by X-ray powder diffraction and Differential Scanning Calorimetry.

Low-temperature preparative techniques such as sol–gel processing are becoming increasingly important in the synthesis of complex metal oxides, as they offer several advantages over the conventional ceramic techniques. An intimate mixing of the molecular precursors in solutions leads not only to a better homogeneity in the resulting products, but also to lower processing temperatures and higher densities. The lower processing temperatures, in some cases, may also allow stabilization of unusual valence states or metastable phases with unusual atomic arrangements that are otherwise inaccessible by conventional high-temperature procedures. In addition, the rheological properties of sols and gels might provide important advantages in the formation of films or fibers by spinning, dip-coating, or impregnation techniques (1).

Oxide bronzes with general chemical formula A_xMO_n (A = electropositive metals such as alkali or alkaline earth metals and M = transition metals) exhibit rich crystal chemistry and a wide range of electronic properties (2, 3). In addition, they play an important role in technological applications such as electrochromic display and battery electrodes. Among the known oxide bronzes, the tungsten oxide bronzes were the first to be reported, as early as 1823 (4). Sodium tungsten oxide bronzes, Na_xWO_3, are generally synthesized by high-temperature reactions (2): (i) reaction between required quantities of Na_2WO_4, WO_3, and W metal, (ii) chemical or electrochemical reduction of a mixture of sodium tungstate and WO_3, or (iii) reaction of sodium vapor with WO_3. More recently, they have also been made by a high-temperature reduction of WO_3 with NaI (5). We have developed a novel method in which addition of an aqueous solution of sodium borohydride into a solution of sodium tungstate at ambient temperature results in the formation of a reduced sodium tungsten oxide gel, which crystallizes sharply at around 440°C to yield crystalline sodium tungsten oxide bronze, Na_xWO_3. Our preliminary results are reported in this communication.

Sodium borohydride was recognized 40 years ago as an effective reducing agent for metal ions in aqueous solutions (6). Use of sodium borohydride to generate metallic particles has gained enhanced interest in recent years in relation to the formation of nanophase magnetic particles. For example, ultrafine metallic magnetic particles such as Fe, Co, or Ni with boron can be generated by a reduction of aqueous solutions of Fe^{2+}, Co^{2+}, or Ni^{2+} with sodium borohydride (7–9). The nature of the reaction products, the boron content, and the particle size seem to depend strongly on the solution concentrations, the pH, and the method and rate of mixing (8, 9). We have used sodium borohydride to generate, for the first time, a reduced sodium tungsten oxide gel, which converts at higher temperatures to crystalline Na_xWO_3. Our experimental procedure and results are given below.

Drops of dilute NaOH were added to 200 ml of distilled water in a 500-ml beaker until the pH rose to about 10. Sodium borohydride (1.9 g) was dissolved in this pH = 10 solution to obtain a 0.25 M solution of $NaBH_4$. The initial pH was maintained around 10 in order to suppress the rate of evolution of hydrogen from $NaBH_4$. A 0.25 M $Na_2WO_4 \cdot 2H_2O$ solution (200 ml) was prepared by dissolving 16.5 g of $Na_2WO_4 \cdot 2H_2O$ in water in another 500-ml beaker. Drops of dilute HCl were added to the sodium tungstate solution until the pH dropped to about 6.5. The sodium tungstate solution was then kept under constant stirring on a magnetic stirrer. To this constantly stirred

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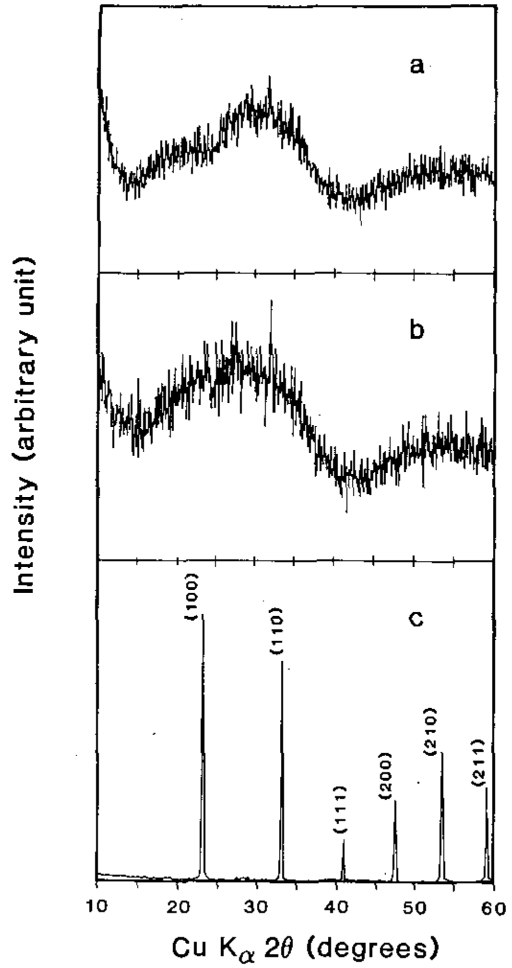

FIG. 1. X-ray powder diffraction patterns of the reduced sodium tungsten oxide (a) as prepared gel, (b) after heating the gel in N_2 atm in DSC at 350°C for 2 hr, and (c) after heating the gel in an evacuated sealed silica tube at 700°C for 7 hr.

solution, the $NaBH_4$ solution was added from a burette while the pH was maintained at 6.5 ± 0.2 by adding drops of dilute HCl. Immediately after the addition of sodium borohydride, the solution turned blue, indicating the reduction of W^{6+}. Continued addition of the 200 ml of sodium borohydride solution (within about 15 min) resulted in the formation of a dark brown gel in a dark blue sol medium. The gel was allowed to settle for about 2 hr and then filtered through a sintered glass funnel. The gel was finally washed with acetone. Extra care was exercised during filtration to avoid the passage of the fine gelatinous particles through the sintered glass into the filtrate. The gel was then allowed to dry in the sintered glass funnel at ambient temperature for about 1 hr and stored in a sample bottle.

The X-ray powder diffraction pattern recorded with the gel is shown in Fig. 1a. It shows only a very broad hump around $2\theta = 30°$ without any Bragg reflection, indicating the noncrystalline nature of the sample. The powder diffraction pattern did not show any significant change even after the gel was dried overnight in an air-oven at around 100°C or was heated in N_2 atm at 350°C for 2 hr (Fig. 1b). A small portion of the gel was then loosely wrapped in a silver foil and loaded into a 13-mm-diameter quartz tube. The quartz tube was then evacuated to a vacuum of 1×10^{-5} Torr, gently heated with a flame to remove water and other volatile residues, and sealed under vacuum. The quartz tube with the sample was then heated in a furnace at 700°C for 7 hr and cooled to room temperature. The X-ray pattern of the annealed sample is shown in Fig. 1c. The pattern shows sharp reflections corresponding to cubic Na_xWO_3. The very weak unindexed peaks ($<2\%$ intensity) correspond to the impurity phase $Na_2W_2O_7$. The impurity reflections increase in intensity as the pH of the gel preparation increases from 6.5. Decrease of pH below 6 does not give any gel formation.

Indexing of the X-ray pattern in Fig. 1c gave a cubic cell parameter $a = 3.831$ Å. The cell parameter in cubic Na_xWO_3 has been shown (2, 10) to vary with the sodium content x as

$$a = (3.7845 + 0.082x)\ \text{Å}. \qquad [1]$$

Substitution of the observed lattice parameter into Eq. 1 yields a value of $x = 0.57$ in our sample of Na_xWO_3. The value of x may, however, depend on the concentrations and the quantities of the solutions employed as well as the pH. Experiments to clarify this aspect are currently in progress.

In order to understand the temperature of crystallization of the gel, we carried out differential scanning calorimetric (DSC) experiments in N_2 atm at a heating rate of 10°C/min with a Perkin-Elmer Series 7 Thermal Analysis System. The DSC plot is shown in Fig. 2a. We see a broad, strong endothermic peak centered around 375°C, a moderate exothermic peak around 440°C, and a weak exothermic peak around 520°C. In order to understand the nature of the transformations associated with each DSC peak, we heated a portion of the gel for a constant time of 2 hr in DSC at various temperatures and examined the product by room-temperature X-ray powder diffraction. The gel heated at 350°C did not show any reflections (Fig. 1b), indicating the noncrystalline nature up to this temperature. On the other hand, the gel heated at 475°C showed sharp reflections—similar to that found in Fig. 1c—that could be indexed on a cubic unit cell. These observations suggest that the endothermic peak observed around 440°C corresponds to crystallization of the gel, while the exothermic peak observed around 375°C may correspond to loss of water and other volatile residues present in the gel. This conclusion is also supported by the following DSC experiment. The gel was preheated at

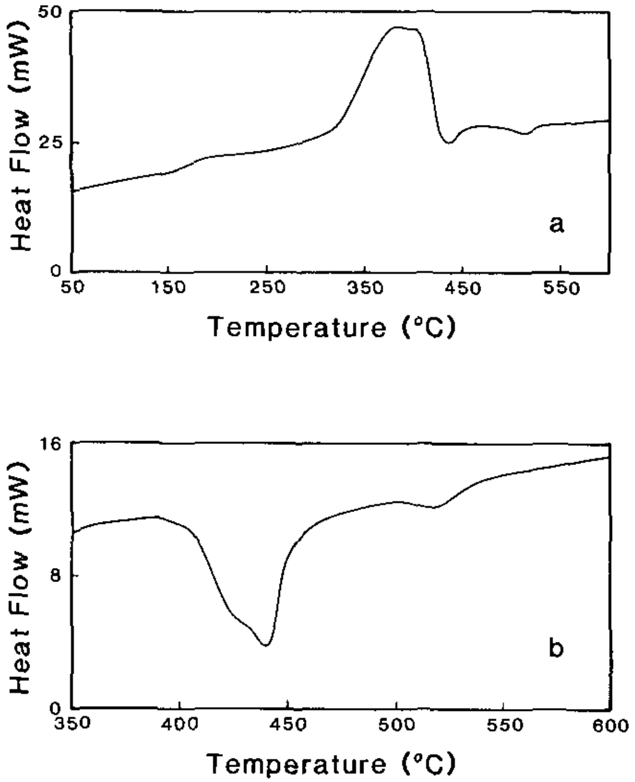

FIG. 2. DSC curve of the reduced sodium tungsten oxide gel recorded in N_2 atm with a heating rate of 10°C/min (a) as prepared gel, and (b) as prepared gel after holding at 350°C for 2 hr.

350°C for 2 hr in DSC, and then the DSC curve was recorded (Fig. 2b). The endothermic peak around 375°C is now absent, and only the crystallization peak around 440°C and the other unassigned weak peak around 520°C are found. We presume that most of the volatiles are lost in 2 hr at 350°C and, therefore, the endothermic peak around 375°C is absent.

Glavee *et al.* (9) have recently found that the chemistry of borohydride reduction is quite complex, and the nature of the reaction products depends on the synthesis procedures. For instance, rapid mixing (~45 sec) of 0.01 *M* $CoCl_2$ solution with solid $NaBH_4$ gives Co_2B under anaerobic conditions and metallic Co under aerobic conditions along with $B(OH)_3$ or B_2O_3. On the other hand, addition of about 10% of the $CoCl_2$ solution to $NaBH_4$ and allowing 8–15 min before adding the remainder of the $CoCl_2$ solution results in the formation of an additional product $Co(BO_2)_2$, which can react with Co_2B at higher temperatures to give metallic Co and B_2O_3. B_2O_3 and $B(OH)_3$ can be removed during washing with water. No attempt is made at this time to clarify whether or not boron is present in our reaction product. However, X-ray powder diffraction did not indicate the presence of any boron-containing phases in the final crystalline product (Fig. 1c). The very weak unindexed lines could all be assigned to $Na_2W_2O_7$ impurity.

In conclusion, we have developed a novel method to produce at ambient temperatures sodium tungsten oxide gel, which upon crystallization can yield crystalline tungsten oxide bronzes, Na_xWO_3. We believe this method can be applied to other oxide bronze systems containing V or Mo and such experiments are currently in progress in our laboratory.

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