growth, and thin platelet crystals are formed. Under slow growth conditions, in a few cases the sample thickness is comparable to its width, and the crystal morphology appears to favor blocks (entry 1).

All the crystals listed in Table I have been surveyed by use of ESR spectroscopy at arbitrary orientations, and the peak-to-peak line widths all fall within the range 60–80 G, which is consistent with the reported values for κ-(ET)$_2$Cu[N(CN)$_2$]Br.[1,14]

Listed in the last column of Table I are the T_c's of different samples as determined from rf (radio frequency) penetration depth measurements.[15] In this method, superconductivity is exhibited by an increase in resonant frequency over that of the empty coil caused by the exclusion of the rf field from the sample by the persistent shielding currents. Both the onset temperatures and the signal saturation temperatures are listed. All samples show similar onset temperatures (11.4–11.6 K), indicating that the crystals are of comparable high quality. Entries 1, 2, 4 and 5 all give narrow superconducting transition widths (2.6 K) while entry 3 shows a broader transition width (3.4 K). The slightly broader transition width indicates increased inhomogeneity in the samples.

In summary, all five synthetic routes give high-quality crystals of κ-(ET)$_2$Cu[N(CN)$_2$]Br. The in situ preparations are the most straightforward syntheses. On the basis of Scheme I, anionic species **1**–**3** are in equilibrium in solution. The anions **2** and **3** are isolated as PPh_4^+ salts, while anion **1** is stabilized as an ET salt. The title superconductor can be reached by use of in situ preparations (entries 2–4) or from compounds **2** and **3**. This study indicates that the crystal morphology can be modified from thin platelets to chunky blocks by varying the applied current density. A low current density favors slow crystal growth and thicker crystals elongated along the *b* axis. The anionic rearrangements, as seen in this study, have been postulated in the synthesis of nonsuperconducting (ET)$_3$Ag$_{6.4}$I$_8$ from either [K(18-crown-6)]$_2$Ag$_4$I$_6$ or [K(18-crown-6)]AgI$_2$.[5,14] It is encouraging that five synthetic routes, from different starting materials, all lead to the same organic superconducting compound with the highest T_c reported to date.

Note Added in Proof.

We have discovered[16] that κ-(ET)$_2$Cu[N(CN)$_2$]Cl, isostructural to the Br salt reported herein, can be prepared by the same routes. The Cl salt is superconducting (T_c = 12.8 K, 0.3 kbar)[16] and superconductivity can be stabilized at "ambient pressure" by simply coating the crystals with G. E. varnish or Apiezon N grease prior to cooling.

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Registry No. 1, 128164-16-9; [κ-(ET)$_2$] **1**, 127793-44-6; 3, 129215-60-7; (PPh$_4$) **3**, 129215-62-9; ET, 66946-48-3; TCE, 79-00-5; CuBr, 7787-70-4; N(CN)$_2^-$, 17997-40-9; CuN(CN)$_2$, 21962-69-6; Br$^-$, 24959-67-9; EtOH, 64-17-5; (PPh$_4$)[N(CN)$_2$], 51501-04-3; Na[N(CN)$_2$], 1934-75-4; N(*n*-Bu)$_4$Br, 1643-19-2; 18-crown-6, 17455-13-9.

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Electrochromic Molybdenum Trioxide Thin Film Preparation and Characterization

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Molybdenum trioxide is a very interesting material because it has applications in catalysis,[1] in lithium batteries as cathode material,[2] and in electrochromic devices.[3,4] Techniques that have been used to prepare molybdenum trioxide include chemical vapor deposition,[5] vacuum evaporation,[6] and sol-gel.[7] Moreover, molybdenum trioxide has recently been prepared by electrodeposition from hexavalent molybdate solution (Li$_6$Mo$_7$O$_{24}$)[8] and molybdenum–hydrogen peroxide solution.[9]

Our laboratory has recently been interested in molybdenum trisulfide thin films obtained by electrodeposition from an aqueous solution of ammonium tetrathiomolybdate.[10,11] It is well-known that thermal oxidation of molybdenum trisulfide yields molybdenum trioxide.[12] With this in mind, we have decided to prepare molybdenum trioxide thin film coated tin oxide electrode from molybdenum sulfide thin film by thermal oxidation in air. This paper deals with the preparation of molybdenum trioxide thin films and their characterization by X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, cyclic voltammetry, and UV–visible spectroscopy.

The preparation of molybdenum trioxide thin films comprises two steps. In the first step, a molybdenum trisulfide thin film is electrodeposited at a potential of 0.6 V vs SCE on a conducting substrate such as tin oxide coated glass electrode from a 10 mM aqueous ammonium tetrathiomolybdate solution.[10,11] The thickness of the molybdenum sulfide film can be varied by changing the deposition time. In the second step, the electrodeposited

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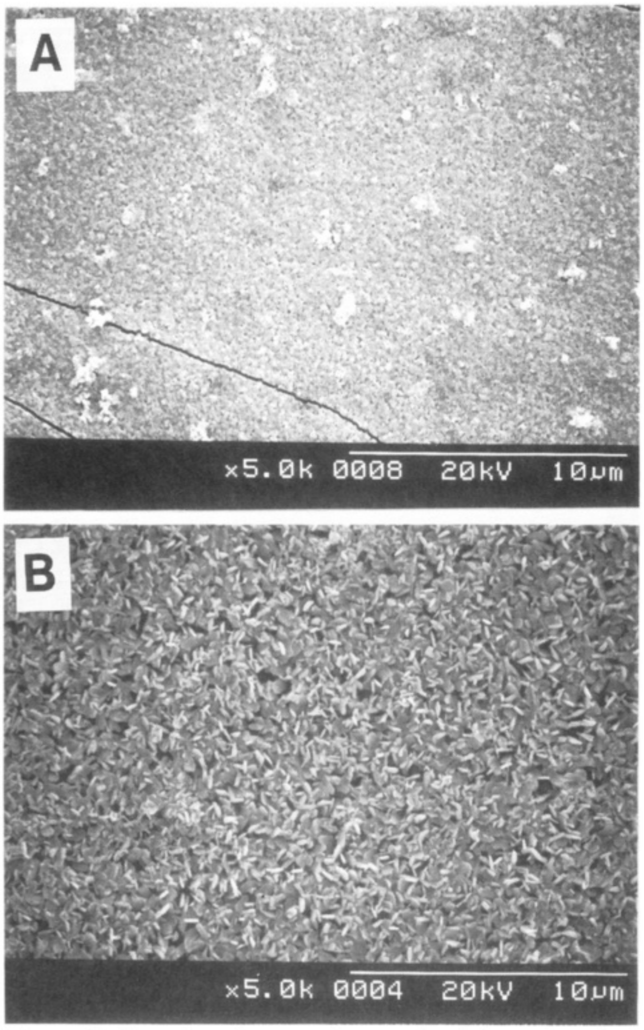

Figure 1. Scanning electron micrographs of electrodeposited molybdenum sulfide thin film on a tin oxide substrate (A) freshly prepared and (B) after thermal oxidation in air at 400 °C for 15 min. Magnification ×5000.

film is heated in air at a temperature sufficient to effect the oxidation of the sulfide.[12] In the present study, temperatures ranging from 400 to 550 °C have been used to prepare the molybdenum trioxide film. Previous investigators have shown that when MoS_3 is heated in air a rapid loss of weight occurred between 390 and 430 °C, which was attributed to the formation of MoO_3.[12]

X-ray photoelectron spectroscopy (XPS) was used to characterize the molybdenum trioxide thin film. The spectrometer was calibrated to the C(1s) (284.5 eV) level. XPS core level Mo(3d) spectra of MoO_3 exhibit a doublet at binding energies of 236 eV ($3d_{3/2}$) and 232.9 eV ($3d_{5/2}$) with an intensity ratio of 2:3. The MoO_3 doublet is separated by 3.1 eV. These features are characteristic of Mo^{6+} ions in MoO_3.[13] In addition the O(1s) binding energy (530.5 eV) is also in good agreement with that reported in the literature for vacuum-evaporated MoO_3.[13]

The effect of thermal treatment in air of molybdenum sulfide thin film on the morphology of the resulting film was studied by scanning electron microscopy. Figure 1 shows scanning electron micrographs of a freshly deposited molybdenum sulfide film (A) and a film that now consists of MoO_3 after heating at 400 °C for 15 min (B), at the same magnification. The molybdenum sulfide film is rather smooth in comparison to MoO_3, which shows a platelike structure. From micrographs obtained at higher magnification (not shown), the dimensions of the plates has been estimated to be ~0.15 µm thick and ~0.5 µm wide. We have also observed that heating at higher temperature resulted in an increase of the size and the number of the plates. This increase is related to the enhancement of MoO_3 crystallization at higher temperature.

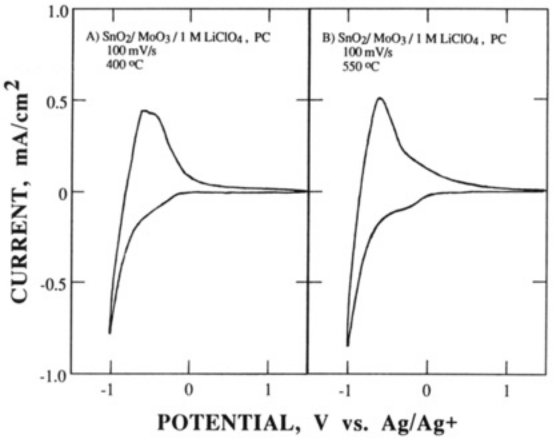

Figure 2. Cyclic voltammetry of SnO_2/MoO_3 electrodes in 1 M $LiClO_4$, polypropylene carbonate (PC) for electrodes prepared by heat treatment in air at (A) 400 °C and (B) 550 °C. Scan rate = 100 mV/s.

X-ray diffraction measurements were made on freshly deposited molybdenum sulfide and molybdenum trioxide powders. Our molybdenum sulfide deposits are amorphous, as already reported for both thermally[14] and electrochemically[10] prepared molybdenum sulfide. On the other hand, the X-ray diffractogram showed that molybdenum trioxide produced on heating at 400 and 550 °C are polycrystalline, in agreement with SEM data. The X-ray diffraction data of MoO_3 indicate crystallization in the orthorhombic structure with a = 3.963 Å, b = 13.855 Å, and c = 3.696 Å[15] as was the case for MoO_3 thin films prepared by annealing of black molybdenum thin films.[5] X-ray diffraction data, obtained by using the Co Kα radiation, also show peaks at 2θ = 14.9° (6.9 Å), 30° (3.456 Å), and 45.7° (2.306 Å), corresponding to (020), (040), and (060) reflections of MoO_3 respectively.

The molybdenum trioxide thin films were also characterized by cyclic voltammetry in 1 M $LiClO_4$/polypropylene carbonate (PC) solution. Figure 2 shows cyclic voltammograms at a scan rate of 100 mV/s for films that were thermally oxidized at 400 and 550 °C, respectively. A platinum flag electrode was used as counterelectrode in a one-compartment electrochemical cell with $Ag/AgClO_4$ (20 mM) in PC as reference electrode. The cyclic voltammograms show a cathodic current starting at −0.2 and 0 V for the electrodes prepared at 400 and 550 °C, respectively, but no well-defined cathodic wave. On the anodic scan, a well-defined wave is observed for both electrodes. These cyclic voltammograms are similar in shape to those previously reported for MoO_3.[9] The reduction process, accompanied by the coloration of MoO_3 (vide infra), involves the injection of lithium cation and electron into MoO_3 according to[16]

$$MoO_3 + xLi^+ + xe^- \rightarrow Li_xMoO_3 \qquad (1)$$

The redox potential of this reaction has been evaluated to be 2.85 V vs Li/Li^+,[17] which corresponds to −0.9 V vs Ag/Ag^+ and the potential for which significant cathodic current is recorded for our MoO_3 electrodes (Figure 2).

Typical optical absorption spectra of molybdenum oxide

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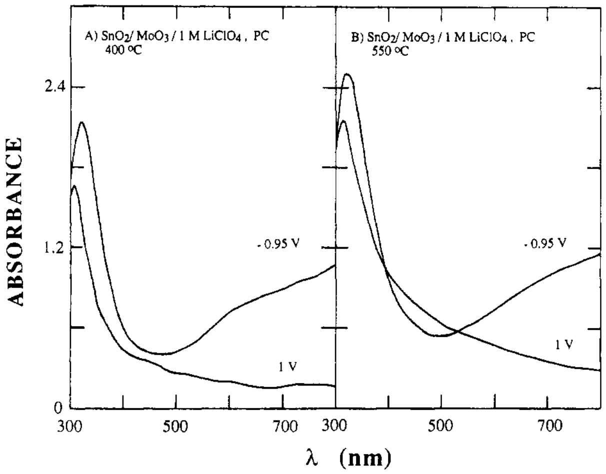

Figure 3. Absorption spectra of SnO_2/MoO_3 electrodes bleached at 1 V and colored at −0.95 V vs Ag/Ag^+ in 1 M $LiClO_4$, PC. Electrode prepared at 400 °C (A) and 550 °C (B).

films prepared at 400 and 550 °C are shown in Figure 3. The films are colorless when potential positive of 1 V vs Ag/Ag^+ is applied to the MoO_3 electrode. Reduction of the film at negative potential such as −0.95 V vs Ag/Ag^+ resulted in the formation of deep blue Li_xMoO_3. The evaluation of the electrochromic performance of a material involves the determination of the coloration efficiency and the switching time. The coloration efficiency, evaluated from the slope of the graph of the optical density versus the charge injected,[18] has been measured at 634 nm. For 0.15-μm-thick film, coloration efficiencies of about 30 and 10 $cm^2\ C^{-1}$ have been obtained for films heated at 400 and 550 °C, respectively. The coloration effiency of the film prepared at 400 °C is slightly lower than the values reported in the literature for molybdenum trioxide obtained by annealing of molybdenum black.[19] However, it should be noted that a different electrolyte was used in the latter study. The switching time, defined as the time necessary to record a variation of 0.3 unit of optical density,[19] for MoO_3 films prepared at 400 and 550 °C are in the order of 50 and 500 s, respectively. The data presented above and in Figure 3 indicates that the films prepared at 400 °C show a better bleaching and better electrochromic performances than those prepared at 550 °C. This is presumably related to an enhancement of reflected light at higher temperature due to increasing crystallization. Further, the films prepared at 550 °C have a white powder appearance, while films heated at 400 °C are clearly more transparent.

This paper has described the preparation of molybdenum trioxide thin film by an electrochemical/thermal process. Our preliminary results on the characterization of these deposits are also given. Current work in our laboratory aimed at a more detailed characterization of the MoO_3 thin films is underway and will be reported elsewhere. Future work will also be directed toward a comparison of the electrochromic properties of molybdenum trioxide prepared by various methods to identify the more efficient material and toward the enhancement of the electrochromic switching characteristics of our MoO_3 thin films. Since it is well-known that the electrochromic properties of a material are related to the preparation technique,[20] it is worthwhile to evaluate this new preparation technique for the preparation of MoO_3 thin films.

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Registry No. MoO_3, 1313-27-5; MoS_3, 12033-29-3.

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Reviews

Landau Theory of Symmetry-Breaking Transitions: A Basis for Clarification of Diffraction Studies of Phase Behavior

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The appliation of the Landau theory of symmetry and phase transitions is reviewed. A number of recent applications that resulted in clarifications of confused or mistaken heterogeneous equilibria and structures are presented.

Introduction

There is a type of problem that arises in the study of the structure of materials for which the usual diffraction methods of structure determination are not well suited. The problem arises because a crystalline solid that occurs either in principle or in practice in some high-symmetry space group in some of its range of existence exists in a form of broken symmetry under the conditions of the

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