Single-Crystal Conductivity Measurements of Hydrogen Molybdenum Bronzes: H_xMoO_3

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This work reports single-crystal conductivity measurements for the hydrogen molybdenum bronzes $H_{0.5}MoO_3$ and $H_{1.7}MoO_3$ from room temperature to 130 and 65 K, respectively. Both bronzes show thermally activated conduction characteristic of semiconductors, with activation energies of 0.4 and 0.2 eV. © 1988 Academic Press, Inc.

Introduction

The so-called hydrogen molybdenum bronzes, H_xMoO_3, formed by gentle reduction of solid MoO_3, have attracted the interest of many research groups due to their unusual and rich behavior. Following the pioneering work of Glemser and co-workers (1, 2), four phases have been identified and characterized by Birtill and Dickens (3, 4) as blue orthorhombic ($x \sim 0.3$), blue monoclinic ($x \sim 1$), red monoclinic ($x \sim 1.7$), and green monoclinic ($x \sim 2$). X-ray and neutron scattering measurements show the reduction to proceed without disrupting the gross overall features of the parent orthorhombic MoO_3 lattice (4–6).

It is well known that the hydrogen bronzes are good conductors. On the basis of magnetic susceptibility, ESR, and XPS measurements, Tinet et al. (7) suggest that $H_{1.7}MoO_3$ is metallic in character and is similar to the sodium bronzes Na_xMoO_3 and Na_xWO_3. In contrast to the alkali metal bronzes, no temperature- and phase-depen-

dent conductivity measurements have been reported for the hydrogen molybdenum bronzes.

We report here the first single-crystal conductivity measurements on two of the hydrogen molybdenum bronzes, $H_{0.5}MoO_3$ and $H_{1.7}MoO_3$, from room temperature to 130 and 65 K, respectively. Both bronzes show thermally activated conduction characteristic of semiconductors, with activation energy gaps of 0.4 and 0.2 eV.

Experimental

A. Preparation of Materials

Single crystals of MoO_3 were grown by high-temperature transport using Cl_2 as a transporting agent in the following manner: 5 g of MoO_3 powder (Aldrich Chemicals) was placed in a 25-cm-long quartz tube which beforehand was dried under vacuum at 800°C to remove adsorbed water. Chlorine gas of laboratory quality was purified further by washing with sulfuric acid. The

washed gas was then dried over P_2O_5 prior to condensation in a dry ice/acetone trap. The liquid chlorine was finally distilled under vacuum into a gas storage bulb. Roughly 0.2 atm of gas was then transferred to the evacuated transport tube.

Transport took place in a tubular furnace with two independent heating elements that provided temperatures of 800 and 700°C at the ends of the sample tube with a gradient of approximately 4°C/cm between them. The initial charge of MoO_3 was fully transported after 24 hr, yielding long, flat single crystals with the characteristic orthorhombic habit described by Bursill (8) and Volpe and Boudart (9). Typical crystal dimensions were about 5–10 × 1–2 × 0.1–0.2 mm along the [001], [100], and [010] directions, respectively, although crystals as large as 30 × 10 × 1 mm were also produced. The slightly yellow, transparent crystals were subjected to elemental analysis which showed the presence of Cl_2 impurities at 0.1 to 0.2% by weight.

Selected crystals were reduced following the methods of Glemser et al. (1, 2). Both Zn and $SnCl_2$ were tried as reducing agents for crystals immersed in a 1 M HCl solution. The reaction with Zn proved unsuitable for reducing single crystals as the reaction required intimate contact with the zinc granules, a condition difficult to maintain due to the strong evolution of hydrogen. In contrast, the homogeneous $SnCl_2$/HCl solution provided a smooth reaction rate. The crystals were observed to react in the manner described by Schollhorn (10). A concentration of 1 g $SnCl_2 \cdot 2H_2O$/100 ml 1 M HCl was used to ensure a slow reaction rate. Typically the crystals became dark blue in color after 24 hr, transforming to metallic red after an additional day. This method of producing single crystals of $H_x MoO_3$ can only yield compositions approximating those determined for pure phases. Some care is also required in producing highly reduced (red) crystals since pro-

longed reaction leads to exfoliation and disintegration of the crystal. The following procedure was therefore adopted: One batch of crystals was allowed to react until the red phase was formed on the surface. The crystals were then allowed to stand in aerated water for 12 hr, thereby oxidizing the material back to a blue color. Since reoxidation of the higher bronzes is kinetically hindered beyond $x \sim 0.4$ (10), these crystals should have compositions close to this value. For preparation of single crystals of the red phase, $H_{1.7}MoO_3$ crystals were allowed to continue reacting until exfoliation appeared imminent. They were then washed with distilled water in a nitrogen atmosphere and dried under vacuum.

B. Conductivity Measurements

Electrical contact was made to the crystals by using silver paste contacts located on the ends of the crystal in a standard two-probe configuration. Measurements were made along the [001] direction. Four probe measurements using platinum paste verified that contact resistance and ionic conductivity effects were negligible. $H_{1.7}MoO_3$ crystals were reacted, stored, and mounted in a nitrogen atmosphere since the crystal resistance was found to change by as much as 13% in the first 10 min of exposure to air. This was not necessary for crystals of $H_{0.5}MoO_3$ since similar percentage changes required 24 hr.

Crystals were mounted onto an alumina microstrip which was heat sunk to a copper block. Cooling power was derived from the cold finger of an Air Products Displex closed cycle refrigerator. Temperatures were regulated using Lakeshore Cryotronics and Air Products controllers, providing a stability of ±0.05 K. The dc biases were obtained from a Keithley 220 current source and a Keithley 192 digital multimeter was used for dc voltage measurements. All temperature control and data acquisi-

tion functions were automated using an IBM AT computer.

Results and Discussion

Temperature-dependent conductivity measurements for both the blue and red bronze exhibit thermal behavior character-istic of a semiconductor as illustrated in Figs. 1 and 2. The activation energy gap for H$_{0.5}$MoO$_3$ was found to be 0.4 eV, whereas H$_{1.7}$MoO$_3$ has a gap of approximately half that at 0.19 eV. The gap for both bronzes was found to decrease slowly with tempera-ture, indicative of possible disorder in this system. Exact values of the room tempera-ture conductivity were difficult to deter-mine due to uncertainties in the thickness of the crystals. Destructive microscopic ex-amination after completion of the conduc-tivity measurements revealed an unreacted or partially reacted center for the blue bronzes, and in both bronzes some amount of exfoliation occurred such that the crys-tals easily split into loosely connected lay-ers. Gross estimates of the room tempera-ture conductivity are from 9–20 (Ω cm)$^{-1}$ for H$_{1.7}$MoO$_3$ and from 2 (Ω cm)$^{-1}$ and less
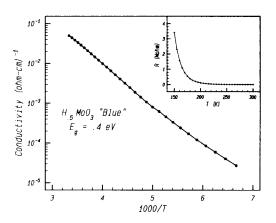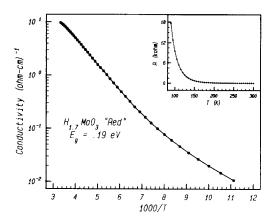

FIG. 2. Conductivity of H$_{1.7}$MoO$_3$ as a function of inverse temperature for a crystal of dimensions 2.1 × 1.4 × 0.08 mm. Inset shows experimental resistance versus temperature.

for H$_{0.5}$MoO$_3$. The values for the conductiv-ities given in the figures are therefore cer-tain only to within a factor of two or three. Measurements made on a number of differ-ent crystals gave nearly identical tempera-ture profiles for the conductivity, indicating that crystal inhomogeneity contributed only to uncertainties in cross-sectional ar-eas. Our single-crystal data are also in qual-itative agreement with earlier, unpublished measurements on polycrystalline samples of H$_{0.3}$MoO$_3$ and H$_{1.7}$MoO$_3$ (11). Undoped MoO$_3$ was found to have a conductivity of less than 10^{-10} (Ω cm)$^{-1}$. Thermopower measurements yield $S = -35$ μV/K at an average temperature of 260.5 K indicating that the majority of carriers are electrons.

Room temperature conductivity mea-surements were also performed as a func-tion of time on crystals exposed to air. As shown in Fig. 3, the red bronze resistance rapidly increases with time, with a nearly linear dependence for long times. Similar measurements for the blue bronze show lin-ear kinetics with a much reduced reaction rate as given in Fig. 4. After exposure to air for a few days, the red bronze becomes dark purple in color and has conductivity behavior similar to H$_{1.7}$MoO$_3$ but with a

FIG. 1. Conductivity of H$_{0.5}$MoO$_3$ as a function of inverse temperature for a crystal of dimensions 2.6 × 1.85 × 0.15 mm. Inset shows experimental resistance versus temperature.
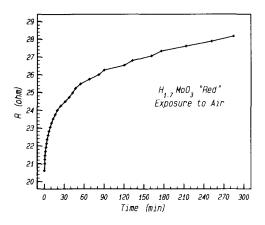
FIG. 3. Room temperature resistance of $H_{1.7}MoO_3$ as a function of time after exposure to air.

slightly higher energy gap of 0.25 eV. These data suggest that we have not reached the maximum conductivity, or the minimum band gap possible with hydrogen bronzes. The fully reduced bronze $H_{2.0}MoO_3$ may exhibit metallic conduction, but due to the instability of this phase at room temperature, no conductivity measurements were attempted. Single-crystal measurements for the fully reduced bronze are clearly ruled out since crystals reacted to completion disintegrate entirely. The observed increase in conductivity with reduction is similar to indirect results found for H_xWO_3 (12) as well as the behavior observed for precise conductivity measurements on $Li_x WO_3$ (13). In general, it is expected that a transition from semiconducting to metallic behavior will occur for sufficiently high reduction (14). In addition, both metallic and semiconductor properties have been observed for the alkali metal bronzes of MoO_3 and WO_3 (15–17). Crandall and Faughnan (18) performed conductivity measurements on amorphous films of H_xWO_3. For low values of x, the temperature dependence follows the form expected for a variable range hopping model (19). At high x and high temperatures, H_xWO_3 is observed to be a semiconductor with a small bandgap of about

0.01 eV, and undergoes an insulator-to-metal transition at 20 K. The hydrogen bronzes of MoO_3 are observed here to have significantly larger gand baps. A gap of 0.4 eV for the blue $H_{0.5}MoO_3$ phase is in agreement with the X-ray electron spectroscopy measurements on substoichiometric MoO_3 made by Rabalais et al. (20). Although the measurements were performed on nominally substoichiometric material ($MoO_{2.96}$), the method of producing color centers by application of UV radiation or an electric field, in the presence of atmospheric or adsorbed water, probably induces hydrogen insertion as well.

The agreement between our conductivity measurements and the XPS results suggest that the activation energy gaps determined from the conductivity are indeed actual band gaps for these materials, at least for $H_{0.5}MoO_3$. XPS results on the valence band for $H_{1.7}MoO_3$ (7) are qualitatively similar to those for $H_{0.5}MoO_3$, but no quantitative measurement of the gap was made. This gap is presumably between the conduction band and "impurity" or "defect" bands, created by hydrogen insertion and lying within the large (~3 eV) insulating gap of unreacted MoO_3. Nevertheless, the conductivity results cannot provide unequivocal measurements of band gaps, and cor-
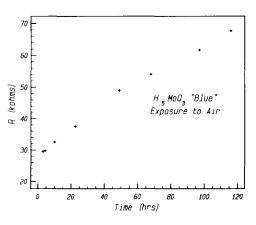

FIG. 4. Room temperature resistance of $H_{0.5}MoO_3$ as a function of time after exposure to air.

roborative optical and photoconductive experiments would be useful extensions of this work.

Following models proposed by Goodenough (21), it has recently been suggested that the metallic and semiconductor behavior for the blue and red potassium bronzes, $K_{0.3}MoO_3$ and $K_{0.33}MoO_3$, represent a formal Mott transition (22). In this scheme, a conduction band is formed from covalently mixed Mo $d(t_{2g})$ and oxygen $P\pi$ orbitals, resulting in delocalized states for Mo–O bond distances under roughly 2 Å. For the blue hydrogen bronze, $H_{0.33}MoO_3$, neutron scattering data give a Mo–O bond length of 1.95 Å (4). An even shorter length of 1.89 Å has been determined for $H_{1.7}MoO_3$ (23). That H_xMoO_3 is semiconducting in spite of these short distances is probably due, in part, to hydrogen as the electron donor to the MoO_3 lattice. Hydrogen forms covalent bonds to the oxygen atoms, thereby introducing electron traps. Recent deuterium solid-state NMR measurements show that the electric field gradient at deuterium in $D_{1.7}MoO_3$ is within the range expected of normal O–D covalent bonds (24).

Acknowledgments

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