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Electrochemical Crystal Growth in the Cesium Molybdate–Molybdenum Trioxide System

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A systematic investigation of crystal growth in the cesium molybdate/molybdenum trioxide system is described. A previously unknown blue cesium molybdenum bronze phase has been prepared as well as the known red bronze, $Cs_{0.33}MoO_3$, and high-quality crystals of the Magneli-phase compound, γ-Mo_4O_{11}. This new blue bronze, with empirical formula, $Cs_{0.19}MoO_{2.85}$, is monoclinic with cell constants, $a = 19.198(4)$ Å, $b = 5.519(2)$ Å, $c = 12.213(2)$ Å, and $\beta = 119.44(2)°$. Measurements of the susceptibility and of the resistivity vs temperature are reported. As is the case for other alkali molybdenum bronzes, the product formed is determined by the molar ratio of alkali molybdate to molybdenum trioxide and the melt temperature. © 1984 Academic Press, Inc.

Introduction

Interesting phenomena, including superconductivity (*1*), charge-density wave (CDW)-driven phase transitions (*2*), and sliding CDW conduction (*3*), are exhibited by various of the molybdenum bronzes. In particular, the ismorphous compounds, $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$, have been the subject of much study since they were found to exhibit a set of remarkable phenomena believed associated with sliding CDW conduction (*3*). These and other alkali molybdenum oxide bronzes have been prepared by electrolytic reduction of molten MoO_3/alkali molybdate mixtures (*4–6*). In the MoO_3–Cs_2MoO_4 system, however, only the red bronze, $Cs_{0.33}MoO_3$ (a semiconductor), had previously been reported (*7, 8*). This paper describes a systematic investigation of crystal growth in the molybdenum trioxide/cesium molybdate system and characterization of resulting phases. A previously unknown blue cesium molybdenum bronze phase has been prepared as well as the known red bronze $Cs_{0.33}MoO_3$ and high-quality crystals of the Magneli-phase compound, γ-Mo_4O_{11}. As is the case for other alkali molybdenum bronzes, the molar ratio of alkali molybdate to molybdenum trioxide and the melt temperature determine the product formed.

Experimental

The apparatus used for the electrochemical crystal growth has been described previously (*9*). A typical charge of approximately 40 g of 99.9% Cs_2MoO_4 and MoO_3 (Cerac) mixture was vacuum-dried before use. The melt was contained in a high-purity recrystallized alumina crucible (Coors) which was seated in a graphite support. Crucibles were used only once, although no

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evidence of crucible attack nor of aluminum incorporation into products was observed. The crucible-support assembly was contained under inert atmosphere within a quartz vessel itself inside a crucible furnace. In all runs, a Pt-foil electrode served as the anode and 1-mm Pt wire as the cathode. A Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a Model 179 digital coulometer was used for crystal growth experiments. All electrolyses were carried out under galvanostatic control. Following deposition, traces of melt were removed by gently heating product in 12 *M* HCl.

Products were identified from powder X-ray diffraction data collected on a diffractometer using Cu$K\alpha$ radiation. Tungsten was used as an internal standard. Precession photographs, made with unfiltered Mo radiation, were used to determine lattice symmetry and approximate lattice parameters.

Electrical resistivities were measured along the monoclinic *b* axis of $Cs_{0.19}MoO_{2.85}$ and the *b* axis of γ-Mo_4O_{11}. Colinear four-probe measurements were made as described elsewhere (*10*). Contacts were made using ultrasonically soldered indium. In the case of $Cs_{0.19}MoO_{2.85}$, contacts were difficult to form and contact resistances were, at best, no less than several ohms at room temperature. Alternatives such as silver paint yielded much higher resistance contacts. In all cases, the contact resistance increased rapidly when the temperature was lowered, limiting the range over which measurements could be made. Magnetic susceptibilities were measured using the Faraday method as described previously (*1*). Elemental analyses were performed by Schwartzkopf Analytical Laboratories for the metals only.

Results

Table I summarizes the products obtained as a function of melt composition, temperature, and current density. This data is schematically represented on the phase diagram (*2*) in Fig. 1. MoO_2 is the sole product resulting from electrolyses of melts containing less than ~70 mole% MoO_3.

At melt compositions from 70 to 80 mole% MoO_3, the red bronze, $Cs_{0.33}MoO_3$, is formed. $Cs_{0.33}MoO_3$ was first prepared by Reid and Watts (*7*) by the electrolysis of a 30 mole% Cs_2MoO_4–70 mole% MoO_3 melt at 530°C. This material is a diamagnetic semiconductor at all temperatures below its

TABLE I

RESULTS OF ELECTROLYTIC CRYSTAL GROWTH

No.	Melt composition (mole %) MoO_3	Cs_2MoO_4	Temp. (°C)	Current (mA)	Coulombs passed	Product
1	70	30	552	3	37	MoO_2 only
2	72	28	556	10	530	MoO_2 only
3	77.8	22.2	553	25	108	$Cs_{0.33}MoO_3$ (Good yield)
4	79.8	20.2	552	30	73	Mostly $Cs_{0.19}MoO_{2.85}$ + traces $Cs_{0.33}MoO_3$
5	84.6	15.4	593	20	210	$Cs_{0.19}MoO_{2.85}$ (Good yield)
6	85.2	14.8	611	50	112	Small amount Mo_4O_{11}
7	86.2	13.8	615	60	240	Mo_4O_{11} (Good yield)
8	89.4	10.6	680	60	132	Small amount Mo_4O_{11}

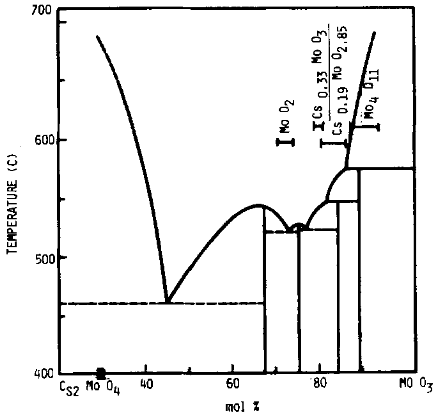

FIG. 1. Electrolytic growth conditions in the cesium molybdate–molybdenum trioxide system. Phase diagram taken from Ref. (12).

~540°C decomposition temperature. We found that raising the MoO_3 concentration in the melt by a small amount improved the yield of crystals of this phase. However, when the melt reaches ~80 mole% in MoO_3, the melting point equals the temperature at which $Cs_{0.33}MoO_3$ decomposes and this phase no longer forms.

Large crystals of a new cesium molybdenum oxide were obtained from melts containing ~80 to ~85 mole% MoO_3. These crystals are blue–black in color and grow as clumps of thick platelets adhering to the cathode. The crystal habit is layered, and the crystals are quite fragile and splinter easily. Precession photographs reveal monoclinic symmetry. Lattice parameters are a = 19.198(4) Å, b = 5.519(2) Å, c = 12.213(2) Å, and β = 119.44(2)° based on a least-squares fit of 30 powder lines with $2\theta < 75°$. Figure 2 shows a plot of log ρ vs $1/T$ along the monoclinic b axis. The figure is a composite of data from two crystals. The aforementioned contact problems limited the temperature range over which data was obtained from any sample. The material is a semiconductor at all temperatures investigated, with a room-temperature resistivity of 0.2 Ω-cm. The plot of log ρ vs $1/T$ is linear above ~220 K, with an activation energy of 0.14 eV. A change in slope occurs near ~220 K, upon which the activation energy increases to 0.27 eV.

Anomalous behavior is observed in the magnetic susceptibility (Fig. 3) of this blue cesium molybdenum oxide bronze. From 200 K to room temperature, the susceptibility is paramagnetic and displays a weak temperature dependence. Near 200 K, a sharp decline in the susceptibility is observed. A Curie tail which is observed at low temperature arises from magnetic impurities in the sample.

In electrolyses of melts containing greater than approximately 85 mole% MoO_3, purple crystals of composition Mo_4O_{11} were obtained. The best yield was from a 86.2 mole% MoO_3 : 13.8 mole% Cs_2MoO_4 mixture with a melting temperature of 615°C. Crystals up to 0.5 cm in length were grown. Precession photographs match those of the known orthorhombic phase, γ-

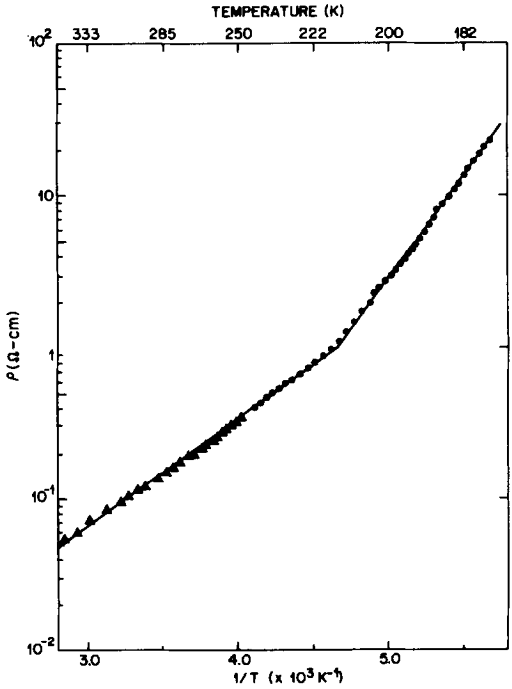

FIG. 2. Log ρ vs $1/T$ for $Cs_{0.19}MoO_{2.85}$. ▲, Sample 1; ●, Sample 2.

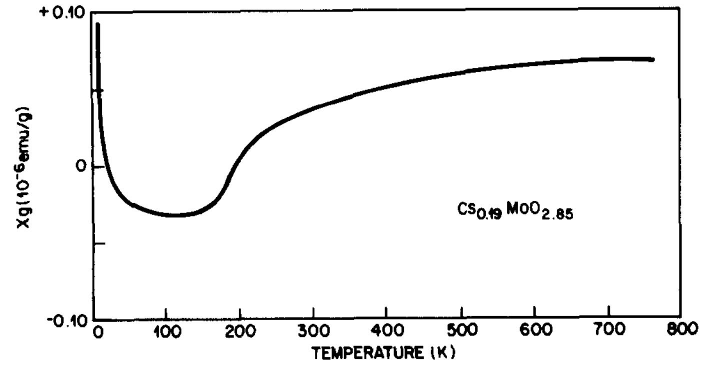

FIG. 3. Gram susceptibility vs temperature for $Cs_{0.19}MoO_{2.85}$.

Mo_4O_{11}, with a = 24.4 Å, b = 5.45 Å, and c = 6.70 Å (*13*).

The magnetic susceptibility of an electrolytic γ-Mo_4O_{11} sample was measured between 4.2 and 300 K. The data is shown in Fig. 4. The solid line is the measured susceptibility uncorrected for the core diamagnetism. A Curie tail due to magnetic impurities is also evident at low temperature. In the dashed curve, this Curie component has been subtracted out as previously described (*11*). Above 110 K, the susceptibility is paramagnetic with a weak temperature dependence. Below 110 K there is a sharp decline in the susceptibility.

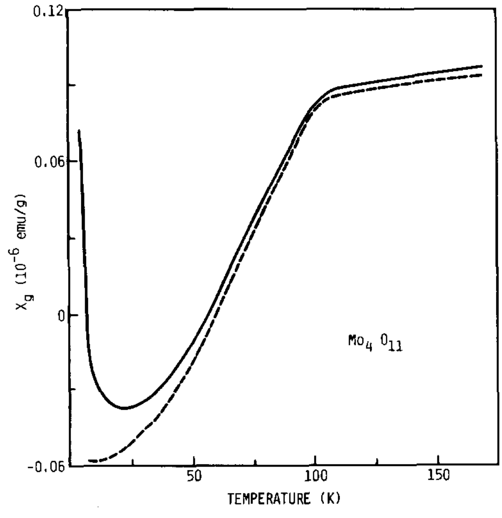

FIG. 4. Gram susceptibility vs temperature for electrolytic γ-Mo_4O_{11}.

Figure 5a shows the resistivity of an electrochemically grown γ-Mo_4O_{11} crystal as a function of temperature. From 110 K to room temperature, metallic behavior is observed. An upturn occurs at 110 K, the same temperature at which an anomaly is observed in the magnetic susceptibility. Below this temperature the resistivity slowly increases as the temperature decreases. Below 50 K the resistivity increases more steeply. For comparison, the resistivity vs temperature of a γ-Mo_4O_{11} platelet grown by iodine vapor transport is shown in Fig. 5b. Again, metallic behavior is observed at high temperature, but the low-temperature increase begins at a lower temperature and no further abrupt changes in slope occur.

Discussion

The preparation of alkali molybdenum oxide bronzes requires precise control of melt composition and temperature. High temperatures or cesium-rich melts favor the formation of MoO_2. From low-melting eutectics containing between 70 and 77 mole% MoO_3, the known red bronze, $Cs_{0.33}MoO_3$, is obtained. This phase undergoes an irreversible phase transition upon grinding to an unknown blue phase (*5*).

A new blue cesium molybdenum bronze

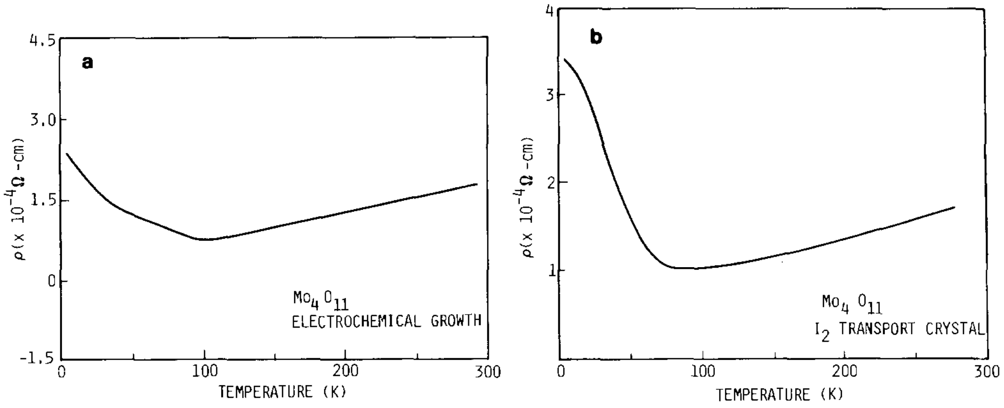

FIG. 5. Resistivity vs temperature for (a) electrolytic γ-Mo_4O_{11} (b) I_2 vapor transport-grown γ-Mo_4O_{11}.

is prepared by electrolyzing melts containing between 79.8 and 84.6 mole% MoO_3. The empirical formula determined from analysis is $Cs_{0.19}MoO_{2.85}$. This phase is monoclinic with a unit cell that bears no obvious relationship to the unit cells of other alkali molybdenum bronzes. A single crystal X-ray diffraction study is in progress (*14*). The anomalies in the susceptibility and the resistivity vs temperature suggest that this material undergoes a phase transition near 200 K. The chemically related compounds, $K_{0.30}MoO_3$ and $Rb_{0.30}$ MoO_3, show susceptibility anomalies similar in shape and even the temperature at which they occur to the anomaly observed in $Cs_{0.19}MoO_{2.85}$. These anomalies in the potassium and rubidium phases are associated with a CDW-driven phase transition (*3*) from a metallic state to a semiconducting state at low temperatures. However, the magnitude of the susceptibility decrease in this cesium molybdenum bronze is only about a third of that observed in $K_{0.30}MoO_3$. Further, the resistivity of $Cs_{0.19}MoO_{2.85}$ is semiconducting above as well as below the anomaly. Consequently, if the sample is single phase, this transition cannot be due to a CDW. Such behavior could, in principle, however, be observed in a two-phase sample. The structure of the second phase would have to be such that domains were coherently interfaced with the primary phase, as would be the case if some regions differed slightly in cesium ion occupancy, since X-ray studies suggest that "single crystals" are prepared. If one phase is semiconducting while the other is metallic but occurs as microdomains dispersed through the sample, any phase transition affecting the metallic phase could produce an anomaly in the susceptibility of an apparently semiconducting sample. A similar argument has been used to explain susceptibility and resistivity anomalies observed in $(NbSe_4)_3I$ (*15*). The sources of the anomalies in both $(NbSe_4)_3I$ and $Cs_{0.19}MoO_{2.85}$ and relationships to anomalies due to CDW-driven phase transitions occurring in structurally and chemically similar materials are under investigation.

In other alkali molybdenum bronze systems, a phase of approximate composition $M'_{0.9}Mo_6O_{17}$ can be grown from MoO_3-rich melts (*6*). In the case of the cesium molybdenum oxide system, however, the large size of the cesium ion apparently precludes the formation of such a phase. Still, conditions are such that the molybdate is not fully reduced to MoO_2 and Mo_4O_{11} is the resulting product.

Measurements of the susceptibility and of the resistivity vs temperature for γ-Mo_4O_{11} also reveal anomalies indicative of a phase transition occurring near 110 K. Similar anomalies in susceptibility were recently reported in this and related Magneli-phase molybdenum oxides in measurements above 77 K (*16*). Such anomalies in the electrical resistivity, thermopower, and specific heat of η-Mo_4O_{11} single crystals grown by vapor-phase transport have been attributed to CDW instabilities (*17*). It seems possible that the anomalies observed in γ-Mo_4O_{11} are also due to CDW's. A sample of γ-Mo_4O_{11} was examined by high-resolution powder X-ray diffraction at temperatures above and below 110 K. Results indicate that the structure is perturbed only weakly (*18*), consistent with the CDW explanation for the anomalies in the transport data. However, diffraction experiments must still be carried out to show the weak incommensurate superlattices that would verify the existence of CDW's in these Mo_4O_{11} phases.

Comparing the behavior of the Mo_4O_{11} grown electrochemically to that prepared by I_2 vapor transport is interesting. The transition from metallic conductivity to increasing resistivity is broadened and occurs at lower temperature in the transport crystal. Since defects and impurities usually lower and broaden a phase-transition temperature, we conclude that electrochemically grown γ-Mo_4O_{11} is of higher quality than transport-grown crystals.

Summary

We have systematically examined the products obtained as a function of melt composition, temperature, and current density in the MoO_3–Cs_2MoO_4 system. At melt compositions from 70–80 mole% MoO_3, the red bronze, $Cs_{0.33}MoO_3$, a diamagnetic semiconductor at all temperatures, is obtained. From melts containing 79.8–8.46 mole% MoO_3, a new blue bronze, $Cs_{0.19}MoO_{2.85}$, is obtained. Although also a semiconductor, a anomaly is observed in the magnetic susceptibility of this compound at 200 K suggesting a phase transition of unknown origin. Crystals of the Magneli-phase compound, γ-Mo_4O_{11}, are obtained from melts containing >85 mole% MoO_3. Measurements of the susceptibility and of the resistivity vs temperature for γ-Mo_4O_{11} also reveal anomalies indicative of a phase transition occurring near 110 K.

Acknowledgments

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References

1. M. Greenblatt and W. C. McCarroll, presented at the 186th National ACS Meeting, Washington, D.C., Aug. 28–Sept. 2, 1983.
2. R. Brusetti, B. K. Chakraverty, J. Devenyi, J. Dumas, and C. Schlenker, "Recent Developments in Condensed Matter Physics," Vol. 2, p. 181, Plenum, New York (1981).
3. J. Dumas, C. Schlenker, J. Marcus, and R. Buder, *Phys. Rev. Lett.* **50,** 757 (1983).
4. A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.* **3,** 545 (1964).
5. P. Strobel and M. Greenblatt, *J. Solid State Chem.* **36,** 331 (1981).
6. R. Buder, J. Devenyi, J. Dumas, J. Marcus, J. Mercier, and C. Schlenker, *J. Phys. Lett.* **43,** L-59 (1982).
7. A. F. Reid and J. A. Watts, *J. Solid State Chem.* **1,** 310 (1970).
8. W. G. Mumme and J. A. Watts, *J. Solid State Chem.* **2,** 16 (1970).
9. L. F. Schneemeyer and V. Tierney, *J. Electrochem. Soc.* **131,** 351 (1984).
10. F. J. DiSalvo, D. E. Moncton, and J. V. Waszczak, *Phys. Rev. B* **14,** 4321 (1976).
11. F. J. DiSalvo and J. V. Waszczak, *Phys. Rev. B* **23,** 457 (1981).
12. E. M. Levin, C. R. Robbins, and H. F. McMurdie, "Phase Diagrams for Ceramists," p. 86, Amer. Ceramic Soc., Columbus, Ohio (1964).

13. A. MAGNELI, *Acta Chem. Scand.* **2,** 861 (1948).

14. S. C. ABRAHAMS, P. MARSH, S. E. SPENGLER, C. E. RICE, AND L. F. SCHNEEMEYER, in press.

15. P. GRESSIER, A. MEERSCHAUT, L. GUEMAS, J. ROUXEL, AND P. MONCEAU, *J. Solid State Chem.* **51,** 141 (1984).

16. H. GRUBER, H. HASELMAIR, AND H. P. FRITZER, *J. Solid State Chem.* **47,** 84 (1983).

17. H. GUYOT, C. ESCRIBE-FILIPPINI, G. FOURCAUDOT, K. KONATE, AND C. SCHLENKER, *J. Phys. C. Solid State Lett.* **16,** L1227 (1983).

18. R. M. FLEMING AND R. G. DUNN, private communication.