being sufficient to produce the characteristic lines of the compound in less than 1 min. Oxygen containing 0.6% water vapor produced NaOH as the only reaction product visible on the surface, and even carbon dioxide containing 0.6% water vapor gave NaOH as the only product on surfaces when the reaction was not extensive.

The initial reaction product of sodium with dry oxygen is crystalline Na_2O, and the clear, sharp patterns from these surfaces would seem to preclude any appreciable amounts of noncrystalline materials on the metal surface. No trace of Na_2O_2 or higher sodium oxides was ever observed. The residual water vapor present under the driest conditions was revealed by small amounts of NaOH present on the surface, and it was probably variation in the trace of water vapor present which caused the variation in the extent of the reaction of the surface with oxygen. Dried air produced about the effect which would be expected from its oxygen content, and the trace of CO_2 present did not affect the course of the reaction. Moist laboratory air, however, produced no oxide at all, only NaOH appearing in patterns from the surface. The formation of a crystalline carbonate is a very late stage in the surface reaction, even in the presence of an overwhelming excess of CO_2, and Na_2CO_3 was observed only on surfaces where extensive reaction had taken place. No trace of crystalline $NaHCO_3$ was observed.

Acknowledgment.—L. G. M. wishes to acknowledge the financial support of the National Science Foundation and of the Graduate School of the University of Michigan. He also wishes to thank the Department of Chemistry of the University of Michigan for numerous fellowships and scholarships.

CONTRIBUTION NO. 1200 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Synthesis of Molybdenum and Tungsten Bronzes at High Pressure

BY T. A. BITHER, J. L. GILLSON, AND H. S. YOUNG

Received March 30, 1966

Molybdenum bronzes $Na_{0.90-0.97}MoO_3$ (cubic), $K_{0.89-0.93}MoO_3$ (cubic), $K_{\sim 0.5}MoO_3$ (tetragonal I), and $Rb_{0.27}MoO_3$ (hexagonal), isotypic with known tungsten bronzes, have been prepared at 65 kbars pressure. The cubic and tetragonal phases are metallic conductors like their tungsten analogs, but the hexagonal bronze shows semiconductor behavior. In addition, an orthorhombic $Rb_{0.41-0.44}MoO_3$ (semiconductor) and the previously unreported cubic K_xWO_3 have also been made under the same conditions, as well as a monoclinic $Na_2Cr_3O_9$ phase (insulator).

Introduction

Although early workers[1,2] have indicated the preparation of nonstoichiometric alkali metal molybdenum bronze-type compounds M_xMoO_3, the first authenticated examples of these have only recently been reported by Wold, *et al.*,[3] who used an electrolytic reduction technique for their preparation. Products low in sodium or potassium ($x < 0.3$) with structures[4] not related to those observed in the tungsten bronzes were formed.

Molybdenum bronze phases with sodium, potassium, and rubidium, some of which are isotypic with known cubic, tetragonal I, and hexagonal tungsten bronzes, have now been prepared by reaction of alkali molybdate with molybdenum trioxide and molybdenum metal under high pressure. A monoclinic sodium and the heretofore unreported cubic potassium tungsten bronze have also been isolated. Extension to alkaline earth tungstates has given the previously reported tetragonal I Ba_xWO_3 and Sr_xWO_3[5] and hexagonal Ca_xWO_3[6] phases. In the chromium system, a monoclinic $Na_2Cr_3O_9$ phase has been prepared.

Experimental Section

Preparation of Materials.—Syntheses were effected in a tetrahedral anvil press of National Bureau of Standards design[7] at pressures of 60–65 kbars, unless otherwise indicated. Pressure was calibrated on the basis of the electrical transitions for Bi (25.4 and 26.9 kbars), Tl (36.7 kbars), and Ba (59.0 kbars).[7] Temperatures were measured with Pt–Rh thermocouples uncorrected for pressure effects. The syntheses were carried out in cylindrical platinum containers (0.14 cm^3 volume) inserted into pyrophyllite tetrahedra. The platinum containers also served as heaters, and the thermocouples were adjacent thereto. An almost instantaneous quench to room temperature from the elevated reaction temperature was achieved by power cut off.

Mixtures of reagent grade alkali metal molybdate, molybdenum trioxide, and powdered molybdenum metal were blended according to the stoichiometry

$$xM_2MoO_4 + \frac{6-4x}{3}MoO_3 + \frac{x}{3}Mo \longrightarrow 2M_xMoO_3$$

---

[1] A. Stavenhagen and E. Engels, *Ber.*, **28**, 2280 (1895).

[2] G. Canneri, *Gazz. Chim. Ital.*, **60**, 113 (1930).

[3] A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.*, **3**, 545 (1964).

[4] N. C. Stephenson and A. D. Wadsley, *Acta Cryst.*, **19**, 241 (1965); N. C. Stephenson, *ibid.*, **20**, 59 (1966); J. Graham and A. D. Wadsley, *ibid.*, **20**, 93 (1966).

[5] L. E. Conroy and T. Yokokawa, *Inorg. Chem.*, **4**, 994 (1965).

[6] P. E. Bierstedt, T. A. Bither, and F. J. Darnell, *Solid State Commun.*, **4**, 25 (1966).

[7] E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **C63**, 59 (1959).

with $0 < x \leq 1$ and were then ground together. Excess M_2MoO_4 was sometimes used for greater fluxing action. No effort was made to obtain anhydrous materials; for example, the dihydrate of Na_2MoO_4 was used. Reactants were pelleted at 40 tons/in.[2] to give a cylinder that fit snugly into the platinum container. In the Na system, mixtures calculated to give $x = 0.4–1.0$ were heated in the temperature range 500–1000° for 3–16 hr, followed by a quench, while in the K system, the same ratios of reactants were heated at 400–700° for 14 hr and quenched. In the Rb system, a wider ratio of starting materials calculated to give $x = 0.2–1.0$ was used, and reactions were run at 600–700° for 14 hr before quenching. Reaction products were digested for several hours in fresh lots of hot water to remove unreacted M_2MoO_4 and MoO_3 from the resultant bronze phases. Ultrasonic vibration of the slurry speeded up this process.

The Ba, Sr, and Ca tungsten bronzes were formed at 1200°, 6 hr followed by quench from reactants mixed in the mole ratio $3MWO_4:2WO_3:W$. In the Cr system, $CrO_3:Na_2CrO_4$ in the mole ratio 1:1.25 was heated in the temperature range 500–800° for 3–8 hr, followed by slow cooling to 100° over 3.5–12 hr. Unreacted Na_2CrO_4 was removed from these reaction products by hot water extraction, and CrO_2 was eliminated by magnetic separation in aqueous slurry, leaving the water-insoluble $Na_2Cr_3O_9$ phase.

Chemical Analysis.—The Na, K, and Rb bronze phases M_xMoO_3 were decomposed in aqua regia, and their alkali metal content was determined by flame photometry. The Mo content of one of the Rb bronzes was also determined spectrophotometrically. *Anal.* Calcd for $Rb_{0.44}MoO_3$: Rb, 20.71; Mo, 52.85. Found: Rb, 20.3, 20.5; Mo, 52.56, 52.70. The Ba_xWO_3 bronze was fused in Na_2CO_3 and the resultant $BaCO_3$ was filtered off after leaching the fusion mixture in water. The $BaCO_3$ was acidified with dilute hydrochloric acid, traces of WO_3 were filtered out, and Ba was determined as $BaSO_4$. The composition $Na_2Cr_3O_9$ was decomposed in perchloric acid. Sodium was then determined by flame photometry and Cr by iodimetry. *Anal.* Calcd for $Na_2Cr_3O_9$: Na, 13.29; Cr, 45.09. Found: Na, 12.94; Cr, 44.53.

X-Ray Data.—Debye–Scherrer X-ray diffraction powder data were obtained on all materials. Space group determinations on single crystals were carried out in some instances by the Weissenberg and in others by the precession technique.

Electrical Measurements.—Resistance measurements were carried out on reasonably well shaped crystals using a four-probe procedure in which a known current was passed through the sample and the voltage drop across a pair of intermediate contacts was measured with a high impedance (10^{14} ohms) voltmeter. Current contacts at the crystal ends were applied by soldering leads in place with indium metal. Voltage contacts across the crystal were made with conducting silver paste. Crystals were mounted on quartz plates by soldering the four leads into small mounds of indium stuck to the quartz. External leads were then run from the lumps of indium, leaving the crystal mounting undisturbed by handling stresses.

Results

Na_xMoO_3.—Two new Na_xMoO_3 bronze phases have been identified. At 65 kbars pressure, wide variations of both reactant ratios and temperatures gave bright red crystals, some having edge lengths up to 1–2 mm, of Na_xMoO_3 having the cubic perovskite structure with x in the limited range 0.90–0.97 and cell dimensions from 3.847 to 3.853 A. This result is in contrast to cubic Na_xWO_3, which can be obtained with x from approximately 0.3 to 0.9 in colors ranging from blue through red to gold by proper adjustment of starting stoichiometries. Molybdenum dioxide in variable amounts always formed simultaneously as well as traces of other blue-black Na_xMoO_3 phases. One of these was demonstrated to have monoclinic symmetry in the space group $P2_1/n$ with cell dimensions $a = 7.76$, $b = 15.03$, $c = 5.05$ A, $\beta = 130.9°$, but low yields and difficulty of isolation in pure form precluded analysis.

Maintenance of high pressure during synthesis appears to be essential to the formation of cubic Na_xMoO_3. Thus, reaction at 20 kbars and 700° gave but a minor amount of red cubic Na_xMoO_3 admixed with MoO_2, and in separate hydrothermal experiments carried out at 3 kbars pressure, only MoO_2 was formed. The failure of previous workers[8] to obtain this cubic bronze at atmospheric pressure is thus explained. Its chemical stability is markedly less than that of Na_xWO_3, for it is slowly attacked by warm, concentrated HCl, H_2SO_4, and H_3PO_4 and rapidly destroyed by dilute HNO_3. This bronze also becomes coated with MoO_2 after standing in air for a few weeks. After long-term storage, a fresh red surface, even on very small crystallites, can be obtained by ultrasonic cleaning in warm water, but MoO_2 is still present in the bulk product, as evidenced by X-ray diffraction data. Resistivity measurements on single crystals showed cubic Na_xMoO_3 to have the same high conductivity and metallic-type behavior observed for the tungsten bronzes.

K_xMoO_3.—Three K_xMoO_3 bronze phases have been identified. In the presence of excess K_2MoO_4, the cubic perovskite form of K_xMoO_3 was obtained as bright, raspberry-red crystals, some with edge lengths up to 1–2 mm. Again, x was in the limited range 0.89–0.93, and cell dimensions were from 3.917 to 3.920 A. These products were usually free from MoO_2. The stability was similar to that of cubic Na_xMoO_3, both toward acids and in the tendency to become coated with MoO_2. Resistivity measurements on single crystals also indicated a high conductivity coupled with metallic-type behavior.

When the K_2MoO_4 content was lowered to give calculated x values in the range 0.8–1.0, the red cubic K_xMoO_3 phase was obtained admixed with a second blue phase of small crystallite size. This proved to be the tetragonal I-type bronze K_xMoO_3, with cell dimensions $a = 12.32$, $c = 3.859$ A, the structure of which was initially determined by Magnéli[9] for $K_{0.48-0.57}WO_3$. Isolation of sufficient material as a single phase for analysis proved difficult, but an approximate x value of 0.5 was obtained. Again, the stability toward acids was similar to that of the cubic Mo bronzes, but the rate of formation of MoO_2 was slower. Single-crystal resistivity measurements were suggestive of metallic-type behavior, although very little change was observed from liquid helium to room temperature.

At a still lower K_2MoO_4 content (calculated x of 0.4), a mixture of red cubic (trace), blue tetragonal I, and a third bronze-colored K_xMoO_3 phase was formed. Single-crystal work demonstrated this latter phase to be monoclinic in space group Cm, C2, or C2/m with $a = 14.31$, $b = 7.71$, $c = 6.38$ A, $\beta = 92.33°$. This is the $K_{0.26}MoO_3$ phase reported by Wold.[3]

---

(8) M. E. Straumanis and K. K. Irani, *J. Am. Chem. Soc.*, **74**, 2114 (1952).
(9) A. Magnéli, *Arkiv Kemi*, **1**, 213 (1949).

Rb_xMoO_3.—Two Rb_xMoO_3 bronze phases were obtained. Either a mixture of irregularly shaped purple crystals plus blue-black rods (some up to 2 mm in length) or the blue-black phase alone was isolated. Variable amounts of MoO_2 were also present. The purple phase had the composition $Rb_{0.27}MoO_3$, and single-crystal data indicated the hexagonal-type bronze structure with cell dimensions $a = 7.321$, $c = 7.683$ A. This structure was initially determined by Magnéli[10] for $Rb_{0.29}WO_3$. The stability was markedly greater than that of the Na or K molybdenum bronzes, and aqua regia was required for rapid decomposition. No coating of MoO_2 was observed to form on these crystals. In contrast to the metallic conduction of Rb_xWO_3,[11] resistivity measurements on single crystals of hexagonal $Rb_{0.27}MoO_3$ showed a semiconductor-type of behavior.

Several lots of the blue-black phase, when prepared in the presence of a high concentration of Rb_2MoO_4, had the range of composition $Rb_{0.41-0.44}MoO_3$. Single-crystal work indicated that this material had undergone a distortion of the hexagonal Rb_xMoO_3 network to orthorhombic symmetry in the space group Pmnm. Precession photographs showed an extensive sixfold superlattice in the b direction, the cell dimensions being $a = 7.724$ A ($\sim c_{\text{hex}}$), $b = 37.624$ A ($\sim 6(\sqrt{3}/2)a_{\text{hex}}$), and $c = 7.385$ A ($\sim a_{\text{hex}}$). Structural studies are now in progress on this orthorhombic phase. Its stability is like that of hexagonal Rb_xMoO_3, and it also shows semiconductor-type behavior. A phase $Rb_{0.17}MoO_3$, with a powder pattern similar to that of the orthorhombic material, was obtained when the initial Rb_2MoO_4 content was lowered to give a calculated x value of 0.33.

Na_xWO_3.—In the tungsten system, with an Na_2WO_4 charge calculated to give an x value of 0.8, the known, red, cubic $Na_{0.6}WO_3$ was obtained (3 hr at 900°, 3 hr to 600°, quench) interspersed with blue crystals. Single-crystal work showed this latter phase to have monoclinic symmetry in space group Cm, C2, or C2/m, with cell dimensions $a = 9.103$, $b = 5.741$, $c = 4.554$ A, $\beta = 92.33°$. A low yield, coupled with difficulty of isolation, made a meaningful Na analysis impossible. Comparison of the Debye–Scherrer powder pattern of the blue crystals with that calculated from the monoclinic cell dimensions showed excellent agreement, except for an extra ten lines, some of moderate intensity. These extra lines could be indexed on the basis of a hexagonal cell with dimensions $a = 7.38$, $c = 7.55$ A. This suggests that the Na_xWO_3 analog of hexagonal $K_{0.27-0.31}WO_3$ was admixed in the blue phase. In support of this, the ionic radii of Na and Ca are almost identical, and hexagonal $Ca_{0.10}WO_3$ has been prepared in hydrothermal experiments.[6]

K_xWO_3.—In the tungsten system, with a K_2WO_4 charge calculated to give an x value of 0.8, red-purple crystals of the known tetragonal I-type K_xWO_3 bronze were obtained (3 hr at 1000°, 3 hr to 700°, quench) plus an extremely thin layer of bright yellow crystals at each end of the reaction zone. These had the cubic perovskite type of structure with cell dimension $a = 3.926$ A, indicating formation of the previously unknown cubic form of potassium tungsten bronze. The use of excess K_2WO_4 (14 hr at 1000°, quench) failed to increase the yield of cubic K_xWO_3, and insufficient material was isolated to determine the potassium content. An x value close to 0.9 is indicated, however, from data on the cubic sodium and potassium molybdenum and sodium tungsten bronzes.

$M^{II}_xWO_3$.—Group II-A tungsten bronzes of Ba, Sr, and Ca were obtained in low yield mixed with their respective tungstates. Orange crystals isolated from the Ba system by removal of $BaWO_4$ in warm ammoniacal EDTA solution were found in single-crystal studies to have the tetragonal I-type bronze structure with $a = 12.27$, $c = 3.855$ A, and the approximate composition $Ba_{0.3}WO_3$. This bronze, with the stoichiometry $Ba_{0.12}WO_3$ and the correspondingly smaller cell dimensions $a = 12.16$, $c = 3.843$ A, has recently been prepared by Conroy and Yokokawa[5] using a low-pressure technique. Red crystals of Sr_xWO_3 having the same tetragonal structure with $a = 12.14$, $c = 3.77$ A were also obtained. In the Ca system, blue crystals present were demonstrated by single-crystal studies to be the same hexagonal Ca_xWO_3 bronze phase, $a = 7.37$, $c = 7.53$ A, prepared hydrothermally.[6]

$Na_2Cr_3O_9$.—Chromium bronzes have not been reported in the literature. Deep red-black crystals (red in powder form) isolated from the reaction of Na_2CrO_4 with CrO_3 had the composition $Na_2Cr_3O_9$, and single-crystal, X-ray studies indicated monoclinic symmetry in space group $P2_1$ or $P2_1/m$ with $a = 8.46$, $b = 5.99$, $c = 7.54$ A, $\beta = 111.1°$. Although the color and stoichiometry suggest a bronze $Na_{0.67}CrO_3$, single crystals were insulators with a room temperature resistivity of 10^{10} ohm cm. The $NaCr_3O_8$ phase described by Ward[12] appears to be a similar composition.

Discussion

Young and Schwartz[13] have commented on the failure of a number of small cation molybdates to form at atmospheric pressure in the wolframite structure characteristic of the analogous tungstates in spite of the close correspondence of Mo^{6+} and W^{6+}. They obtained the molybdates in this structure, however, by synthesis at 60 kbars pressure.

The use of high pressure to form new compounds isotypic with known series one level below in the periodic table is again demonstrated in this work. Comparison of cell dimensions of the alkali metal Mo and W bronzes is given in Table I. The chemical stability of the Mo bronzes, which increases with decreasing alkali metal content, is markedly lower than that of their W analogs. Resistivity measurements on the Mo bronzes are typical of metallic-type conduction, as with W compounds, for high alkali metal content, but indicate semicon-

---

(10) A. Magnéli, *Acta Chem. Scand.*, **7**, 315 (1953).

(11) M. J. Sienko and S. M. Morehouse, *Inorg. Chem.*, **2**, 485 (1963).

(12) L. Suchow, I. Fankuchen, and R. Ward, *J. Am. Chem. Soc.*, **74**, 1678 (1952).

(13) A. P. Young and C. M. Schwartz, *Science*, **141**, 348 (1963).

TABLE I

CELL DIMENSIONS OF ISOTYPIC ALKALI METAL Mo AND W BRONZES

	Mo	W
Cubic	$Na_{0.90-0.97}MoO_3$, a = 3.847–3.853 A	$Na_{0.30-0.85}WO_3$,[a] a = 3.810–3.854 A
	$K_{0.89-0.93}MoO_3$, a = 3.917–3.920 A	$K_{\sim 0.9}WO_3$, a = 3.926 A
Tetragonal I	. . .	$Na_{0.28-0.38}WO_3$,[b] a = 12.094–12.102, c = 3.748–3.752 A
	$K_{\sim 0.5}MoO_3$, a = 12.32, c = 3.859 A	$K_{0.40-0.57}WO_3$,[9,11] a = 12.25–12.317, c = 3.81–3.841 A
Hexagonal	. . .	Na_xWO_3, a = 7.38, c = 7.55 A
	. . .	$K_{0.27-0.31}WO_3$,[10] a = 7.40–7.37, c = 7.56–7.54 A
	$Rb_{0.27}MoO_3$, a = 7.321, c = 7.683 A	$Rb_{0.27-0.32}WO_3$,[10,11] a = 7.38–7.386, c = 7.56–7.54 A

[a] B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76,** 963 (1954).
[b] A. Magnéli and B. Blomberg, *Acta Chem. Scand.*, **5,** 375 (1951).

ductor behavior at lower x values in Rb_xMoO_3. These data are shown in Figure 1. Cubic $K_{0.9}MoO_3$ had a low Seebeck voltage of −4 μv/deg, typical of a metallic-type conductor, while the semiconductors $Rb_{0.27}MoO_3$ and $Rb_{0.44}MoO_3$ had values of −20 and −44 μv/deg, respectively.

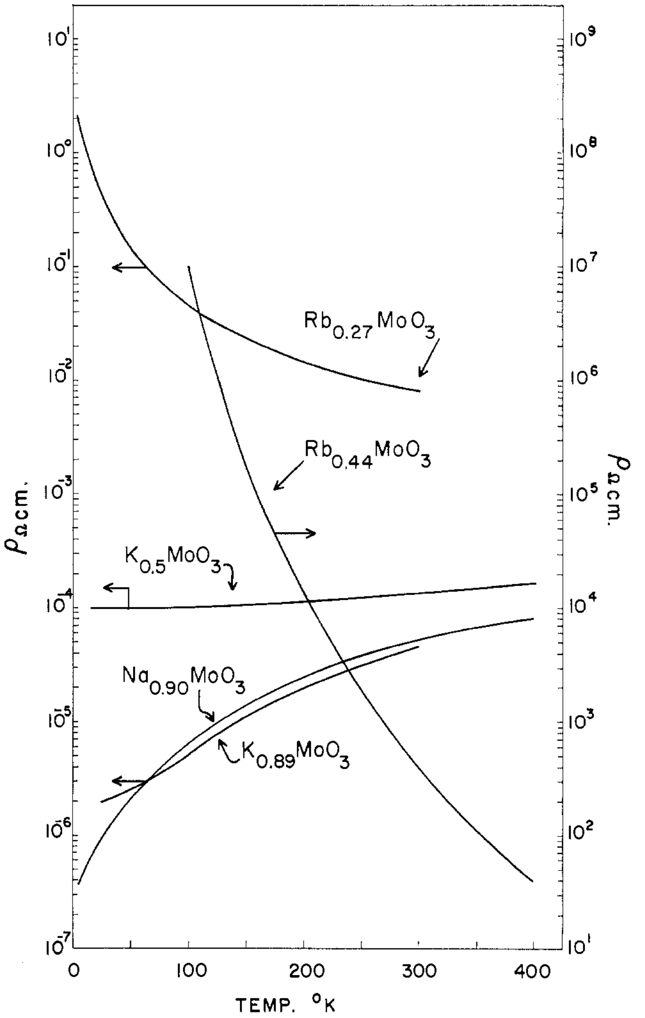

Figure 1.—Resistivity of Mo bronzes.

This shift from metallic-type conduction to semiconductor behavior is of interest in regard to the Goodenough[14] mechanism of conduction in certain oxides including the W bronzes. The model, based upon a critical distance between cations, proposes in this case delocalized molecular orbital formation through overlap of the tungsten 5d (t_{2g}) wave functions with the p wave functions of the oxygen atoms. At low x values in M_xWO_3, distortions of the tungsten octahedra occur, leading to a permanent electric moment and the quenching of metallic conduction. In the case of the Mo bronzes, the 4d orbitals would be involved, and Wold[15] has suggested that increases observed in resistivity may in part arise from a smaller overlap of these orbitals as compared to that of the 5d tungsten orbitals. The character of the resistivity curve for hexagonal $Rb_{0.27}MoO_3$ may thus reflect this smaller orbital overlap, while for the orthorhombic semiconductor $Rb_{0.44}MoO_3$, the effect of distortion of the molybdenum octahedra from their basic positions in the hexagonal structure may also pertain. On the same basis, for the insulator $Na_2Cr_3O_9$ there would be no contribution of the 3d chromium orbitals to the formation of a conduction band.

Acknowledgments.—The authors wish to thank Mr. C. L. Hoover for supervision of the high-pressure experiments, Drs. J. F. Whitney and C. T. Prewitt for single-crystal determinations, and Dr. A. W. Sleight for many helpful discussions.

---

(14) J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).
(15) A. Wold, *ibid.*, 1051 (1965).