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LETTER TO THE EDITOR

Low-Temperature Synthesis of Novel Layered Alkali Metal–MoO_3 Bronzes and Hexagonal Bronzes of the Type $K_yW_{1-x}Mo_xO_3$*

A. K. GANGULI, L. GANAPATHI, J. GOPALAKRISHNAN,
AND C. N. R. RAO†

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India*

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A new class of layered alkali metal–MoO_3 bronzes, A_xMoO_3 (A = Li, Na, K, Rb), with nearly the same unit cell parameters as the host oxide has been synthesized by the solid-state reaction of MoO_3 with alkali metal iodides around 575 K; Li_xMoO_3 absorbs H_2O causing an increase in the b parameter of the unit cell. Hexagonal potassium bronzes of $W_{1-x}Mo_xO_3$ are synthesized for the first time.

Hexagonal, tetragonal, cubic, and intergrowth bronzes formed by WO_3 with alkali metals are well-documented in the literature (*1–4*). MoO_3 forms blue bronzes of the formula $A_{0.3}MoO_3$ (A = K, Rb, or Tl) and red bronzes of the composition $A_{0.33}MoO_3$; these bronzes are described adequately in the literature (*1, 5–7*). The blue bronzes show metal–nonmetal transition, while the red bronzes are semiconducting at all temperatures (*8*). We have explored the use of the solid-state reaction between MoO_3 and alkali metal iodides (*9*) to synthesize novel, metastable bronzes by carrying out the reaction at relatively low temperatures. In this communication, we report, for the first time, the synthesis of a class of layered alkali metal–MoO_3 bronzes, with little or no change in the unit cell parameters compared to those of the parent MoO_3. In addition we investigated the bronzes formed by the $W_{1-x}Mo_xO_3$ solid solutions (*10*) for the first time, their synthesis becoming possible because of the low-temperature method employed by us.

The procedure for the synthesis of the bronzes of MoO_3 was as follows. MoO_3 (0.025 mole) and the anhydrous alkali metal iodide (0.025 mole) were mixed and heated in a silica tube at ca. 575 K *in vacuo* (ca. 10^{-3} Torr) for periods ranging from 3 to 6 hr. Intermediate grinding and reheatings were required to ensure completion of the reaction. The liberated iodine, condensed in a liquid nitrogen trap, was dissolved in cyclohexane and quantitatively estimated by the thiosulfate titration. The iodine thus estimated directly gave the extent of insertion of the alkali metal. The bronzes were independently analyzed for the Mo^{5+} content, by dissolving a weighed amount of solid in a known quantity of Ce^{4+} (0.05 M)

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* Contribution No. 442 from the Solid State and Structural Chemistry Unit.

† To whom all correspondence should be addressed.

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TABLE I

LAYERED MOLYBDENUM BRONZES A_xMoO_3

A	x	Lattice parameters[a] (Å)		
		a	b	c
Li	0.06–0.50	3.97–3.99	13.90–13.91	3.70–3.74
Na	0.10–0.36	3.96–3.98	13.87–13.92	3.70–3.71
K[b]	0.02–0.17	3.96–3.97	13.87	3.70
Rb[b]	0.03–0.16	3.97–4.01	13.87–13.89	3.71

[a] Lattice parameters of MoO_3 are $a = 3.962$, $b = 13.860$, $c = 3.696$ Å.

[b] The blue bronze appears as impurity phase (5–10%) when $x \geq 0.15$.

solution and titrating the excess Ce^{4+} with 0.05 M Fe^{2+} solution potentiometrically. The alkali metal content in the bronzes was also ascertained by atomic absorption spectroscopy. The presence of Mo^{5+} in the bronzes was determined by employing X-ray photoelectron and ESR spectroscopy. Three compositions of $W_{1-x}Mo_xO_3$ (x = 0.3, 0.5, 0.7) were prepared by the topochemical dehydration of their monohydrates (*10*). The procedure for the synthesis of the potassium bronzes of $W_{1-x}Mo_xO_3$ (x = 0.3, 0.5, 0.7) was essentially the same as that described earlier for the layered MoO_3 bronzes.

Layered MoO_3 Bronzes

In Table I, the composition ranges of the layered alkali metal bronzes of MoO_3 synthesized by us are listed along with the lattice parameters. Figure 1 shows the X-ray diffraction patterns of some of these bronzes. While we could prepare pure layered MoO_3 bronzes of Li and Na by carrying out the reaction at 575 K, the layered bronzes of K and Rb almost always had some blue bronze as impurity at high levels of insertion (Figs. 1d and 1e). If the reaction with K or Rb iodide is carried out at 800 K, the blue bronze is formed. The absence of any significant lattice expansion in the layered bronzes in spite of the insertion of a large proportion of the alkali metal is noteworthy. In oxide bronzes, one generally obtains a new structure (compared to the host oxide) after insertion of the guest metal as in the blue and red molybdenum bronzes; in layered materials, on the other hand, insertion of metal atoms results in an increase in the interlayer separation and hence lattice expansion (*11*).

Since there is almost no lattice expansion in the alkali metal–MoO_3 bronzes prepared in the present study, it is likely that the inserted alkali metal atoms are present within layers of MoO_3 (Fig. 2a). In such a case, the alkali metal atom would have a ninefold coordination. The layered alkali metal–MoO_3

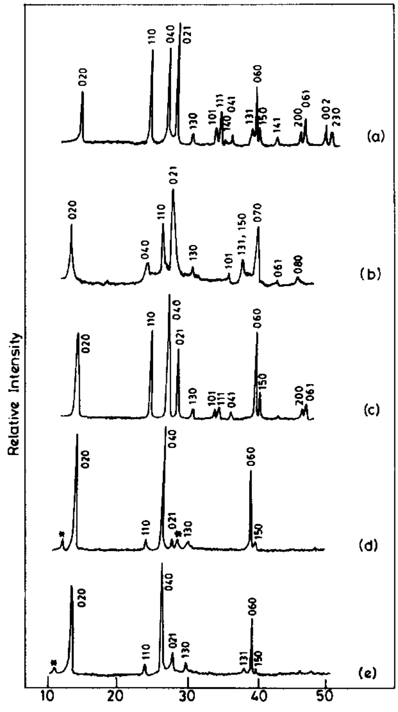

FIG. 1. X-ray diffraction patterns of (a) $Li_{0.5}MoO_3$, (b) $Li_{0.5}MoO_3 \cdot 0.5H_2O$, (c) $Na_{0.36}MoO_3$, (d) $K_{0.17}MoO_3$, and (e) $Rb_{0.16}MoO_3$. Asterisks in (d) and (e) denote the lines due to the corresponding blue bronzes appearing as impurity phase. The relative intensity of the (0k0) lines are quite high in (d) and (e) as compared to those in (a) or (c); this may be due to the preferred orientation effects.

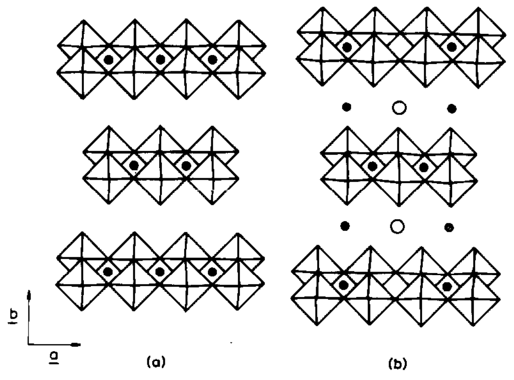

FIG. 2. Possible model for the structure of layered alkali metal–MoO_3 bronzes; (a) A_xMoO_3 (A = Li, Na, K, Rb) and (b) $Li_{0.5}MoO_3 \cdot 0.5H_2O$. In (a), filled circles denote alkali metal atoms and in (b), hatched circles denote lithium atoms and open circles, water molecules.

bronzes are different from the purple bronzes (*12, 13*) of the type $A_{0.9}Mo_6O_{17}$ (A = Li, Na, K, Tl). The structures of purple bronzes have little resemblance to the parent MoO_3 structure and are made up of slabs of corner-sharing MoO_6 octahedra and MoO_4 tetrahedra.

We have examined the infrared and electronic spectra as well as the electrical resistivity of the layered MoO_3 bronzes. The charge-transfer band of MoO_3 at 360 nm (*14*) progressively diminishes in intensity on insertion of the alkali metal, accompanied by a shift to lower wavelengths. The characteristic IR absorption bands of MoO_3 in the region 1000–350 cm^{-1} decrease in intensity with increase in the alkali metal content of the bronze and disappear at high values of x. Thus, when $x = 0.17$ for K or 0.5 for Li, we do not see any characteristic IR bands of MoO_3. Electrical resistivities of the layered bronzes are higher than those of the blue bronzes of MoO_3, but lower than those of the red bronzes; the purple bronzes are quasi-two-dimensional metals. For example, the resistivities of $Na_{0.36}MoO_3$, $K_{0.17}MoO_3$, and $Rb_{0.16}MoO_3$ are of the order of 10^2 ohm cm at room temperature.

The layered lithium bronze, Li_xMoO_3, on exposure to moist air, absorbs water (as revealed by thermogravimetry) accompanied by an increase in the b parameter of the unit cell. Accordingly, the hydrated bronze, $Li_{0.5}MoO_3 \cdot 0.5H_2O$, has the lattice parameters $a = 3.67$ Å, $b = 16.23$ Å, and $c = 3.74$ Å with a nearly constant resistivity of ~ 6 ohm cm between 300 and 20 K. The lattice expansion of the hydrated bronze is likely to be due to the presence of hydrated Li^+ between the layers (Fig. 2b). This bronze is somewhat similar to the layered alkali metal molybdenum bronze hydrates recently reported by Thomas and McCarron (*15*). We could not however obtain similar hydrated bronzes of sodium, potassium, and rubidium even after refluxing the layered A_xMoO_3 with water.

$K_yW_{1-x}Mo_xO_3$

The reaction of KI with $W_{1-x}Mo_xO_3$ (x = 0.7, 0.5, and 0.3) carried out close to 570 K has yielded hexagonal tungsten bronzes of the general formula $K_yW_{1-x}Mo_xO_3$. In Fig. 3 we show the X-ray diffraction patterns of the potassium bronzes of $W_{1-x}Mo_xO_3$ studied by us to demonstrate that the bronzes are indeed formed in the reaction. With $W_{0.3}Mo_{0.7}O_3$ the HTB phase obtained was $K_{0.15}W_{0.3}Mo_{0.7}O_3$ with $a = 7.314$ Å and $c = 7.732$ Å. The space group of this HTB is probably $P6_3$ since the (101) reflection is present in the X-ray diffraction pattern. Electron diffraction patterns do not, however, reveal the presence of any superstructure. It is indeed noteworthy that the HTB structure is stabilized at such a low potassium concentration ($y = 0.15$) in this system. Normally in K_yWO_3 bronzes, the HTB phase is stable in the range $0.2 \leq y \leq 0.33$ (*16*). Insertion of a larger proportion of potassium destroys the HTB structure in $K_yW_{0.3}Mo_{0.7}O_3$; instead, a blue molybdenum bronze-like phase is formed.

$W_{0.5}Mo_{0.5}O_3$ and $W_{0.7}Mo_{0.3}O_3$ form HTB

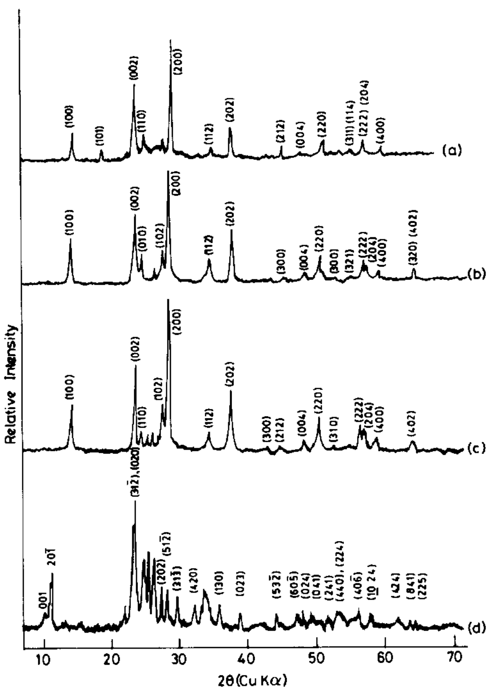

FIG. 3. X-ray diffraction patterns of (a) $K_{0.15}W_{0.3}Mo_{0.7}O_3$, (b) $K_{0.2}W_{0.5}Mo_{0.5}O_3$, (c) $K_{0.33}W_{0.7}Mo_{0.3}O_3$, and (d) $K_{0.4}W_{0.3}Mo_{0.7}O_3$. In (d), the major phase is the blue bronze with a = 18.16 Å, b = 7.44 Å, c = 9.93 Å, and β = 117.8°.

phases with potassium in the y range $0.2 \leq y \leq 0.33$. Thus, $K_{0.2}W_{0.5}Mo_{0.5}O_3$ (a = 7.333 Å, c = 7.628 Å) and $K_{0.33}W_{0.7}Mo_{0.3}O_3$ (a = 7.357, c = 7.636 Å) are clearly HTB's (Fig. 2). A certain degree of disorder seems to be present in these bronzes as suggested by streaking in the a^* direction of the electron diffraction patterns; clear evidence for doubling of the a-axis is seen in the patterns. Such supercells have been found in A_xMoO_3 and A_xWO_3 (*17, 18*). No evidence for intergrowth bronzes (*4, 19*) was found in the lattice images, but some of them showed the presence of a WO_3-like phase with the HTB phase. The absorption edge of the HTB phase of $K_yW_{1-x}Mo_xO_3$ is shifted progressively to lower wavelengths with increase in y. XPS studies show that Mo^{5+} is formed in these bronzes.

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