A New Method for the Synthesis of Oxide Bronzes of Tungsten, Molybdenum, and Vanadium

Vasudeva Bhat and J. Gopalakrishnan

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

A novel method for the synthesis of oxide bronzes of tungsten, molybdenum, and vanadium, based on the reaction of WO_3, MoO_3, or V_2O_5 with the iodides of electropositive metals, is reported.

Oxide bronzes formed by the insertion of electropositive metal atoms into transition metal oxide hosts such as WO_3, MoO_3, and V_2O_5 constitute an important class of inorganic solids exhibiting a wide variety of structures and electronic properties.[1] Tungsten bronzes are generally prepared by reacting a mixture of WO_3, WO_2, and a tungstate *in vacuo* at high temperatures or by reducing tungstate–WO_3 mixtures chemically or electrochemically.[1] Direct reaction of metal vapours with WO_3 has also been employed for the synthesis of some tungsten bronzes,[2—4] but the method does not always yield single-phase products. Alkali metal molybdenum bronzes are generally prepared by electrolytic reduction.[5,6] In this communication, we describe a novel method for the synthesis of some of the oxide bronzes of tungsten, molybdenum, and vanadium. The method is based on the reaction of WO_3, MoO_3, or V_2O_5 with electropositive metal iodides, MI_n, involving reductive insertion of M into the oxide host accompanied by quantitative liberation of iodine; for example, $WO_3 + 0.25KI \rightarrow K_{0.25}WO_3 + 0.125I_2$.

We list in Table 1 the bronzes synthesized. We first standardized the method by synthesizing some of the known

Figure 1. Powder X-ray diffraction patterns of (a) $Ba_{0.15}WO_3$–HTB, (b) $Ba_{0.15}WO_3$–PC, (c) $Ba_{0.25}WO_3$–TTB, and (d) $K_{0.21}Nb_{0.5}W_{0.5}O_{2.75}$. HTB = Hexagonal tungsten bronze, PC = orthorhombic pentagonal column bronze, TTB = tetragonal tungsten bronze.

bronzes of tungsten. For example, hexagonal potassium tungsten bronze (HTB), $K_{0.25}WO_3$, can be readily prepared by heating a mixture of WO_3 and KI at 600 °C *in vacuo* (*ca.* 10^{-4} Torr) under continuous pumping conditions. The reaction is complete in about 2 h and the iodine liberated is quantitative as revealed by chemical analysis,[†] thus providing a means for determining the composition of the bronze formed. Reaction of WO_3 with an excess of KI under similar conditions yielded a mixture of HTB and a tetragonal tungsten bronze (TTB). We could however prepare a single phase TTB in the Ba–WO_3 system by reacting anhydrous BaI_2 and WO_3 at 950 °C (Figure 1). We could prepare a number of interesting bronzes in this system (Table 1). Thus, reaction of BaI_2 with WO_3 yielded a new HTB for $0.15 < x < 0.25$. Ba_xWO_3 in the HTB structure is not known under ambient pressures. We could stabilize this phase under ambient conditions probably because of the relatively low-temperature synthesis conditions employed. It is significant that HTB–Ba_xWO_3 transforms either to a TTB (x *ca.* 0.25) or to the orthorhombic pentagonal column (PC) bronze[7,8] (x *ca.* 0.15) at *ca.* 950 °C, revealing that a HTB structure in the Ba_xWO_3 system is unstable with respect to transformation to PC structures at high temperatures. For $x < 0.05$, we could prepare single-phase intergrowth tungsten bronzes (ITB) in this system. Thus, $Ba_{0.04}WO_3$ obtained by this method is a single-phase orthorhombic ITB. We could also synthesize the phosphorus tungsten bronze,[9] $K_xP_8W_{32}O_{112}$, by this method (Table 1).

We could prepare only the cubic perovskite-like bronze in the Na_xWO_3 system over a wide range of composition $0.1 < x < 0.5$, with cell parameters 3.80—3.82 Å. Attempts to prepare tungsten bronzes of less electropositive metals such as lead and mercury by this method did not succeed because the iodides volatilized at low temperatures before they could react with WO_3.

We explored the possibility of using the iodide method for the synthesis of new oxide bronzes. In the Nb–W–O system, we recently reported[10] the synthesis of a ReO_3-like $HNbWO_6$ by a low-temperature method. Since oxide bronzes containing niobium and tungsten of the type $M_xW_{1-y}Nb_yO_{3-y/2}$ are not known,[‡] we attempted synthesis of such a bronze by the reaction of KI with $HNbWO_6$. Reaction of KI with $HNbWO_6$ yielded a new bronze of composition $K_{0.21}W_{0.5}Nb_{0.5}O_{2.75}$. Powder X-ray diffraction (Figure 1d) revealed that it is a HTB-like phase with the c-axis ill-defined. While the $h00$ and $hk0$ reflections of the HTB structure are well-defined in the pattern, $00l$ reflections are ill-defined. This is further supported by the observation of superstructure spots in the
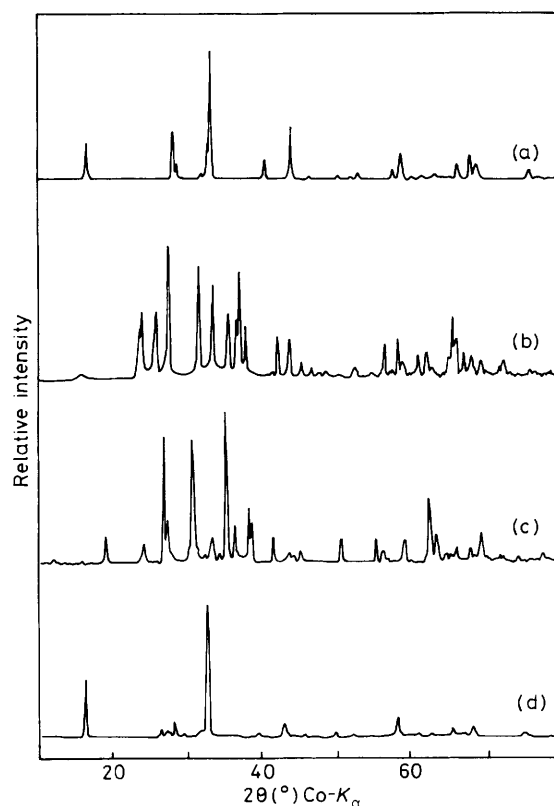
---

† The liberated iodine condensed in a liquid N_2 trap was dissolved in cyclohexane and treated with a known quantity of 0.05 M sodium thiosulphate. The excess of thiosulphate was determined by titration with 0.0083 M $K_2Cr_2O_7$ iodometrically.

‡ Bronzoid phases containing Nb and W of the general formula $M_xNb_xW_{1-x}O_3$ are known however; see, for example, R. Sharma, *Mater. Res. Bull.*, 1985, **20**, 1373; Y. Miyamoto, S. Kume, J-P. Doumerc, and P. Hagenmuller, *ibid.*, 1983, **18**, 1463 for $NaNb_{1-x}$-W_xO_3 bronzes.

Table 1. Synthesis and structural characterization of oxide bronzes.

Reactants	Synthesis conditions °C/h	Products obtained[a]	Lattice parameters (Å)
$0.35NaI + WO_3$	900/2	PTB	Cubic: $a = 3.806$
$0.10KI + WO_3$	850/1	ITB + HTB	ITB–Orthorhombic: $a = 30.92, b = 7.35, c = 7.76$
$0.25KI + WO_3$	600/2	HTB	Hexagonal: $a = 7.365, c = 7.500$
$1.0KI + WO_3$	600/2	HTB + TTB	TTB–Tetragonal: $a = 12.23, c = 3.82$
$0.04BaI_2 + WO_3$	900/4	ITB	Orthorhombic: $a = 28.65, b = 7.32, c = 3.874$
$0.15BaI_2 + WO_3$	750/2	HTB	Hexagonal: $a = 7.32, c = 7.46$
$0.15BaI_2 + WO_3$	900/1	PC	Orthorhombic: $a = 8.84, b = 10.01, c = 3.800$
$0.25BaI_2 + WO_3$	950/1	TTB	Tetragonal: $a = 12.25, c = 3.82$
$1.0KI + (NH_4)_2HPO_4 + 4WO_3$	800/5	Phosphorus–tungsten bronze	Monoclinic: $a = 16.23, b = 3.76, c = 17.03, \beta = 93.9°$
$0.30KI + MoO_3$	520/1	Red and blue Mo bronzes	Red–Monoclinic: $a = 14.26, b = 7.71, c = 6.39, \beta = 92.6°$. Blue–Monoclinic: $a = 18.25, b = 7.56, c = 9.85, \beta = 117.5°$
$0.33NaI + V_2O_5$	500/5	$\beta\text{-Na}_{0.33}V_2O_5$	Monoclinic: $a = 10.12, b = 3.61, c = 15.43, \beta = 109.3°$
$0.5KI + HNbWO_6$	800/2	$K_{0.21}Nb_{0.5}W_{0.5}O_{2.75}$	HTB-type

[a] PTB = perovskite tungsten bronze, ITB = intergrowth tungsten bronze, HTB = hexagonal tungsten bronze, TTB = tetragonal tungsten bronze, PC = orthorhombic pentagonal column bronze.

c^*-direction in electron diffraction patterns. The structure of this new bronze is likely to involve anion vacancy ordering in the $00l$ planes of the HTB structure.

We extended the iodide method to the synthesis of oxide bronzes of molybdenum and vanadium. Thus reaction of KI with MoO_3 at 520 °C yielded a mixture of the blue and the red molybdenum bronzes, $K_{0.3}MoO_3$ and $K_{0.33}MoO_3$ (Table 1). It is possible to prepare nearly pure red bronze by carrying out the reaction at slightly higher temperatures. Reaction of KI with $Mo_{0.75}W_{0.25}O_3$ yielded a blue bronze isostructural with $K_{0.3}MoO_3$. Similarly, we could prepare the well-known β-vanadium bronze, $Na_{0.33}V_2O_5$, by reacting the required quantities of NaI and V_2O_5 at 500 °C. The unit cell parameters of the known bronzes determined from the powder diffraction data (Table 1) agreed with the values reported in the literature. Interestingly, reaction of MoO_3 with an excess of KI yielded MoO_2 according to the reaction, $MoO_3 + 2KI \rightarrow MoO_2 + K_2O + I_2$. KI did not react with TiO_2 and Nb_2O_5 under similar conditions.

The present investigation reveals that iodide ion can reduce W^{6+}, Mo^{6+}, and V^{5+} in the solid state to lower oxidation states, with the simultaneous insertion of electropositive metal atoms into the oxide hosts. From the standard reduction potential data in aqueous solutions, one would expect only V^{5+} to be reduced by I^-. The fact that WO_3 and MoO_3 are also reduced by I^- reveals that oxidation–reduction charac-

teristics of metal ions may be different in the solid state as compared to their behaviour in aqueous solutions.

References

1 P. Hagenmuller, in 'Comprehensive Inorganic Chemistry,' ed. J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, Vol. 4, Pergamon Press, Oxford, 1973; A. Manthiram and J. Gopalakrishnan, *Rev. Inorg. Chem.*, 1984, **6**, 1.
2 M. J. Sienko, *J. Am. Chem. Soc.*, 1959, **81**, 5556.
3 A. Ramanan, J. Gopalakrishnan, M. K. Uppal, D. A. Jefferson, and C. N. R. Rao, *Proc. R. Soc. London, Ser. A*, 1984, **395**, 127.
4 D. A. Rieck and L. Eyring, *Inorg. Chem.*, 1985, **24**, 2461.
5 A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.*, 1964, **3**, 545.
6 P. Strobel and M. Greenblatt, *J. Solid State Chem.*, 1981, **36**, 331.
7 T. Ekström and R. J. D. Tilley, *J. Solid State Chem.*, 1979, **28**, 259.
8 C. Michel, M. Hervieu, R. J. D. Tilley, and B. Raveau, *J. Solid State Chem.*, 1984, **52**, 281.
9 J. P. Giroult, M. Goreaud, P. H. Labbe, and B. Raveau, *Acta Crystallogr., Sect. B*, 1980, **36**, 2570.
10 Vasudeva Bhat and J. Gopalakrishnan, *J. Solid State Chem.*, 1986, **63**, 278.