Tungsten and Vanadium Bronzes

Emannuel Ramli Literature Seminar April 28, 1987

The term "oxide bronzes" has been commonly used to describe a class of ternary compounds with a general formula $A_xM_yO_z$. In this formula, the range of x is $0 < x < 1$, and A is an electropositive element which includes the alkali metals, alkaline earth metals, Group IIIA elements, lanthanide elements and several low-oxidation-state transition metals. M in M_yO_z is a transition metal, and it is in its highest oxidation state in the binary oxide.

Oxide bronzes possess several common characters [1]. They have a metallic luster and are intensely colored; their colors can vary as x in $A_xM_yO_z$ is varied. They also change their structural phases as x is varied. Upon insertion of xA into M_yO_z, M becomes partially reduced to form a non-stoichiometric $A_xM_yO_z$. Because of this partial reduction, bronzes are semiconductors and metals.

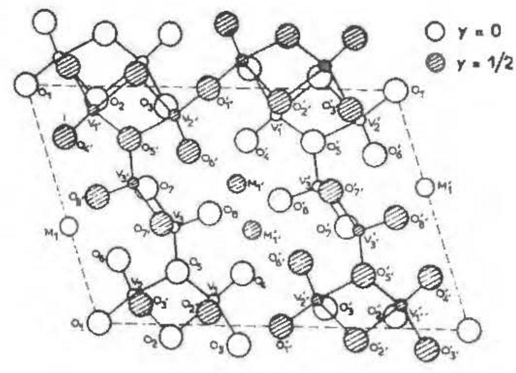
Tungsten and vanadium bronzes have been the two most commonly studied bronzes because of their potential practical applications. They have been tested as electrode materials in secondary lithium batteries [2], as catalysts [3], as materials for electrochromic display [4,5], and as electron emitting cathodes [6].

The general formula for tungsten bronzes is A_xWO_3, and their common structural phases are the orthorhombic, hexgonal, tetragonal and cubic phases [7]. The vanadium bronzes have two general formulas: $A_xV_2O_5$ and $A_{1+x}V_3O_8$. For $A_xV_2O_5$, the common structural phases are the orthorhombic α and monoclinic β phases, and for $A_{1+x}V_3O_8$, the monoclinic phase [8].

Tungsten and vanadium bronzes can be synthesized using two approaches [1]. In one approach two or three solid reactants are reacted at a high temperature (500 - 900°C) without the loss of O_2. In this approach, it is imperative that the combined Gibbs free energies of the reactants are equal to or larger than that of the bronze. In the other approach, two solid reactants are reacted at a high temperature (500 - 900°C) with the loss of O_2. In this approach, the spontaneity of the reaction depends on the partial pressure of O_2 produced.

The two bronzes have different electrical properties: tungsten bronzes are metals [9], while vanadium bronzes are semiconductors [10,11]. To account for the metallic property of tungsten bronzes, Goodenough [12] has developed a useful qualitative model which is still widely used today and which has been applied to other bronzes. According to this model, the conduction band in tungsten bronzes is predominantly W-t_{2g} in character, and conduction electrons are donated by A atoms when they are inserted into M_yO_z.

To account for the semiconductivity of vanadium bronzes, Goodenough [13,10] developed another qualitative model which applies particularly to the β-vanadium bronzes, **1**. β-vanadium bronzes exhibit a quasi-one-dimensional conduction property, and the model indicates that this is due to an electron hopping process assisted by polarons (electron-phonon interactions).



References

1. Dickens, P. G.; Wiseman, P. J., "Oxide Bronzes and Related Phases," Sol. State Chem. Inorg. Chem. Series Two 1975, 10, 211.

2. Liaw, B. Y.; Raistrick, I. D.; Huggins, R. A., "The Thermodynamics and Kinetics of the Gamma-Lithium Vanadium Bronze Structure," Sol. State Ionics 1986, 18 & 19, 828.

3. Kosaka, N.; Sakai, Y.; Tsuda, N., "Metal-Insulator Transition and a Selectivity of a Catalytic Reaction: Propylene over Na_xWO_3," J. Cat. 1986, 98, 95.

4. Kang, K.; Green, M., "Solid State Electrochromic Cells: Optical Properties of the Sodium Tungsten Bronze System," Thin Sol. Films 1984, 113, L29.

5. Joo, S. K.; Raistrick, I. D.; Huggins, R. A., "The Electrochemical Insertion of Lithium into Bleached Potassium Hexatungstate Thin Films: A New Electrochemical Material," Sol. State Ionics 1986, 18 & 19, 592.

6. Zocchi, F., "Thermionic Electron Emission of the Barium Tungsten Bronzes: $Ba_{0.15}WO_3$ and $B_{0.21}WO_3$," Appl. Phys. Lett. 1985, 47, 1276.

7. (a) Hussain, A., "Phase Analyses of Potassium, Rubidium and Cesium Tungsten Bronzes," Acta Chem. Scan. A 1978, 32, 479.
   (b) Michel, C.; Hervieu, M.; Tilley, R.J.D.; Raveau, B., "$Ba_{0.15}WO_3$: a Bronze with an Original Pentagonal Tunnel Structure," J. Sol. State Chem. 1984, 52, 281.

8. (a) Bose, M.; Basu, A., "NMR Studies of the Mixed Conductor $Li_xV_2O_5$," Sol. State Ion. 1986, 18, 902.
   (b) Pistoia, G.; Panero, S.; Tocci, M.; Moshtev, r. V.; Manev, V., "Solid Solutions $Li_{1+x}V_3O_8$ as Cathodes for High Rate Secondary Li Batteries," Sol. State Ion. 1984, 13, 311.

9. Cadwell, L. H.; Morris, R. C.; Moulton, W. G., "Normal and Superconducting Properties of K_xWO_3," Phys. Rev. B. 1981, 23, 2219.

10 Curelaru, I. M.; Din, K. S., "Localization vs. Delocalization of Orbitals in the Quasi-One-Dimensional Conductor $Na_{0.33}V_2O_5$," Sol. State Ion. 1986, 18, 245.

11. Strobel, P., "Crystal Growth, Structural and Electrical Properties of Rubidium and Cesium Vanadium Oxide Bronzes," J. Sol. State Chem. 1987, 66, 95.

12. (a) Goodenough, J. B., "Mettalic Oxides," Prog. Sol. State Chem. 1971, 5, 145.
(b) Bullett, D. W., "A Theoretical Study of the x-Dependence of the Conduction-Band Density of States in Metallic Sodium tungsten Bronzes Na_xWO_3," Sol. State Comm. 1983, 46, 575.
(c) Wheeler, R. A.; Whangbo, M. H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A., "Symmetric vs. Asymmetric Linear M-X-M Linkages in Molecules, Polymers and Extended Networks," J. Am. Chem. Soc. 1986. 108, 2222.

13. (a) Goodenough, J. B., "Interpretation of $M_xV_2O_5$-β and $M_xV_{2-y}T_yO_5$-β Phases," J. Sol. State Chem. 1970, 1, 349.
(b) Cherkashenko, V. M.; Freidman, S. P.; Gubanov, v. A.; Kurmaev, E. Z., Volkov, V. L.; Fotiev, A. A., "Electronic Structure and Anisotropy of X-Ray Emission Spectra of NaV_6O_{15} Monocrystal," J. Sol. State Chem. 1980, 32, 377.