Tungsten Bronzes: Electrochromic properties and Metal Insulator Transitions.

Alan Kleiman

MATR 286 G

November 28th 2005

Outline

- Application of Tungsten Bronzes
- What are Tungsten Bronzes?
- Electrochromic Materials
- Metal to Insulator Transition
- Conclusions

Application of Tungsten Bronzes.

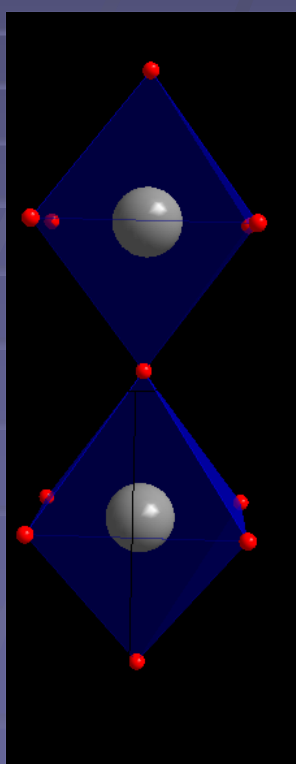
- Piezoelectric($Pb_{1-x}Ba_xNb_2O_6$, $Sr_{1-x}Ba_xNb_2O_6$)
- Gas Sensors
- Catalysis (Bronsted Acid)
- Ion Exchange Compounds
- Chromic Devices (electro, photo, thermo)
- Metal to Insulator Transitions

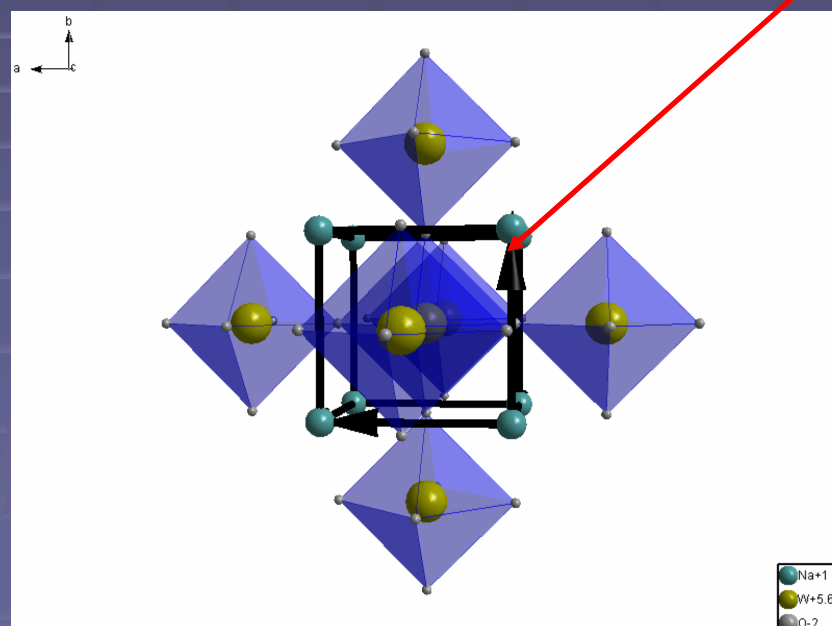
What are Tungsten Bronzes?

- Tungsten Bronzes are compounds with the general formula

$$A_xMO_{3-y}$$ M=W, Mo, Nb

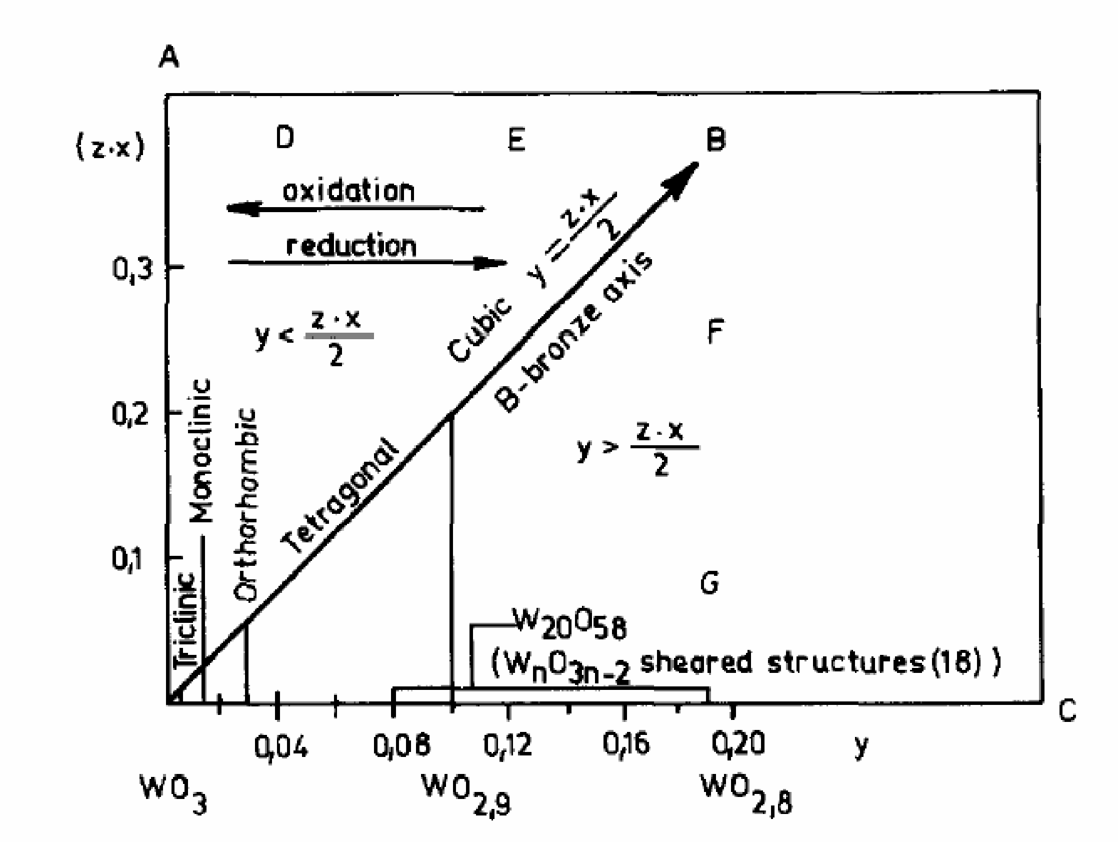
- composed of MO_6 shared octahedra. Bronze forming atom A



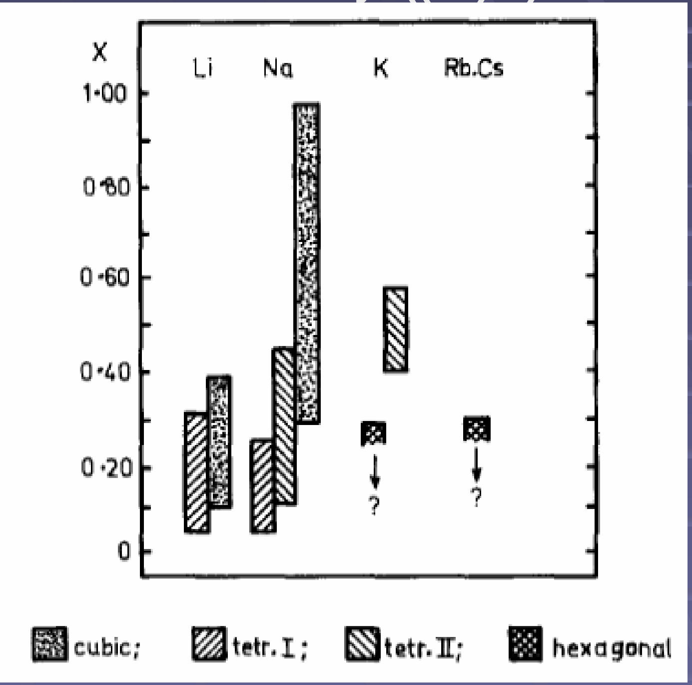


$Na_{0.39}WO_3$ P m -3 m (221) – cubic
a=3.8160 Å V=55.57 Å3 Z=1

Phases of Tungsten Bronzes



$A_x{}^zWO_{3-y+((zx)/2)}$

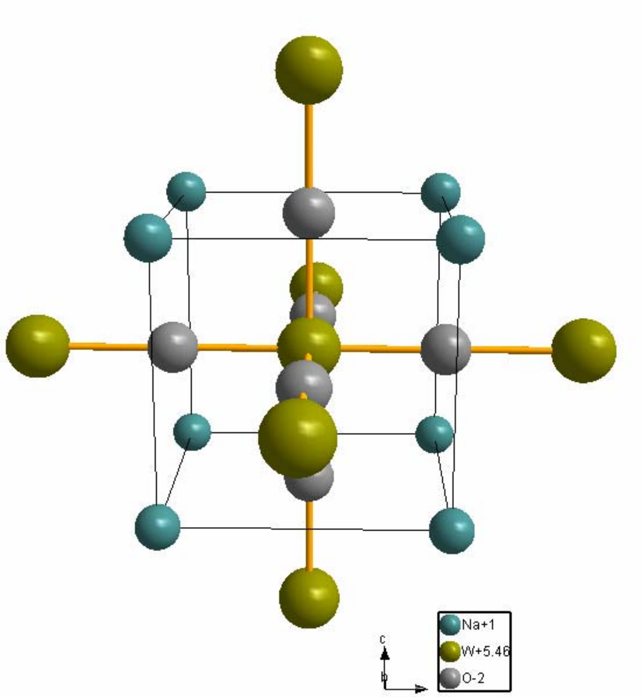


A) Monotungstates and polytungstates
B) Oxide and bronzes of ideal comp.
C) Oxygen deficient oxides
D) Reduced polytungstates
E) OB with cation excess
F) OB with cation deficiency
G) Oxygen deficient oxides with cation contamination

L. Barth, *Int, J, if Refractory Metals and Hard Metals*, ***13***, *1995, 77-91.*

Cubic Tungsten Bronzes

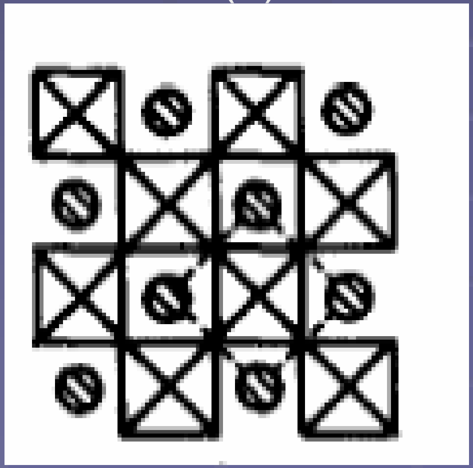
A_xWO3, A=Li, Na, D Li$^+$=0.68 Å, Na$^+$=0.96 Å



Compound: $Na_{0.5}WO_3$

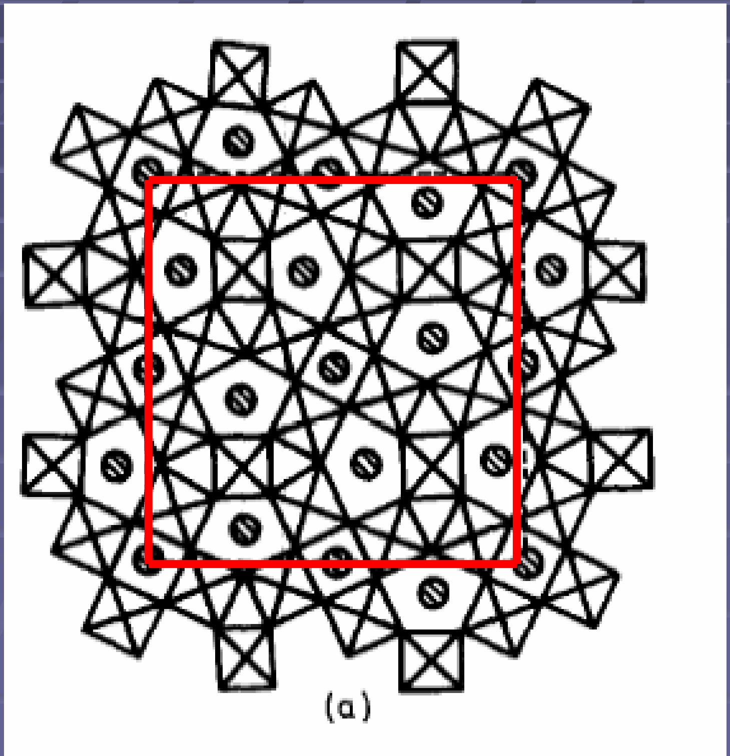
Space Group: P m -3 m (221) – cubic

Cell a=3.829(1) Å



L. Barth, *Int, J, if Refractory Metals and Hard Metals,* ***13****, 1995, 77-91.*

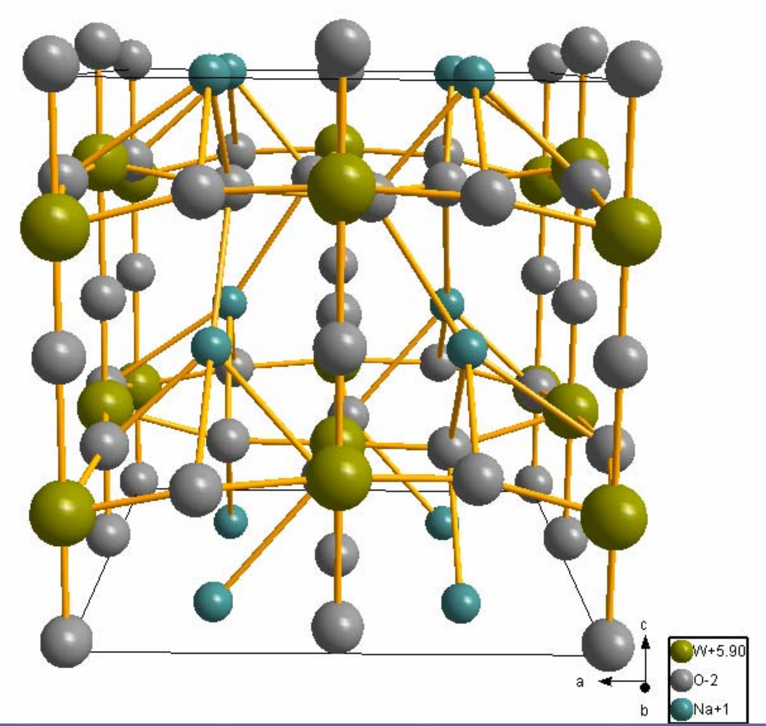
Tetragonal Tungsten Bronzes



Compound: $Na_{0.1}WO_3$

Space Group: P 4 (75) - tetragonal

Cell a=7.423(3) Å c=7.791(1) Å c/a=1.0496



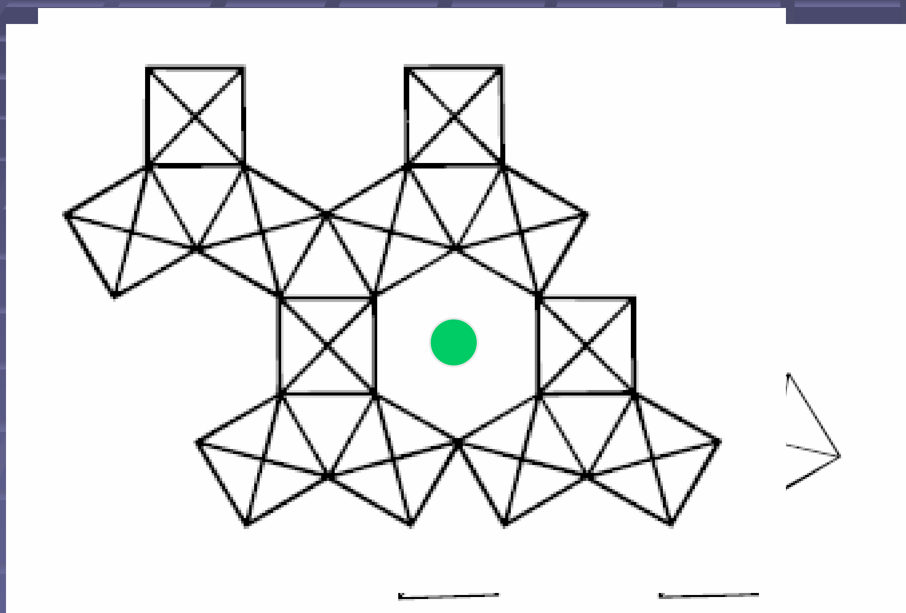
L. Barth, *Int, J, if Refractory Metals and Hard Metals,* ***13****, 1995, 77-91.*

Hexagonal Tungsten Bronzes

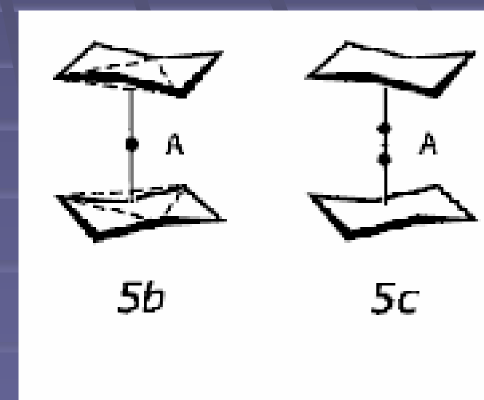
A_xWO_3 A=K,Rb,Cs x<0.33

For X=0.33 all the hexagonal Tunnels are occupied (ideal lattice). 5a

For X<0.33 the W atoms shift into the octahedra: 5b for big cations (Rb^+=1.52 Å, Cs^+=1.67 Å) and 5c for small cations (K^+=1.37 Å)



001 Projection



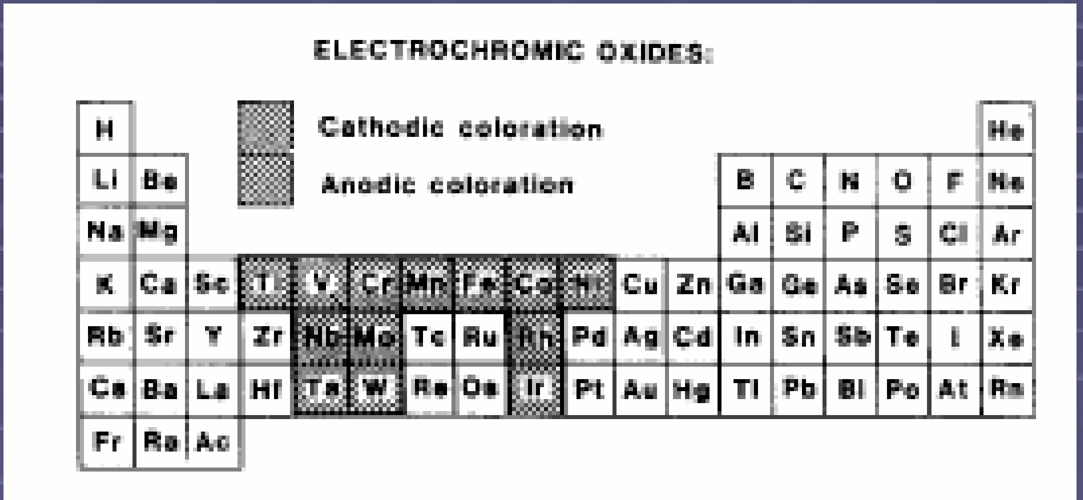
With larger A+ cations in the hexagonal tunnel, the vibrational motion of the Oxygen atoms is more restricted and the WO_3 lattice becomes stiffer. The stiffness also increases as the A+ occupancy increases.

Lee, *J. Am. Chem Soc.*,**119**, 1997, 4043-4049

Outline

- Application of Tungsten Bronzes.
- What are Tungsten Bronzes?
- Electrochromic Materials
- Metal to Insulator Transition
- Conclusions

Electrochromism



C.G. Granqvist et al. / Journal of Non-Crystalline Solids 218 (1997) 273–279

bleached → coloured

cathodic: $MO_x + yA^+ + ye^- \rightleftharpoons A_yMO_x,$

$A^+ = H^+, Li^+, Na^+, Ag^+,$

bleached → coloured

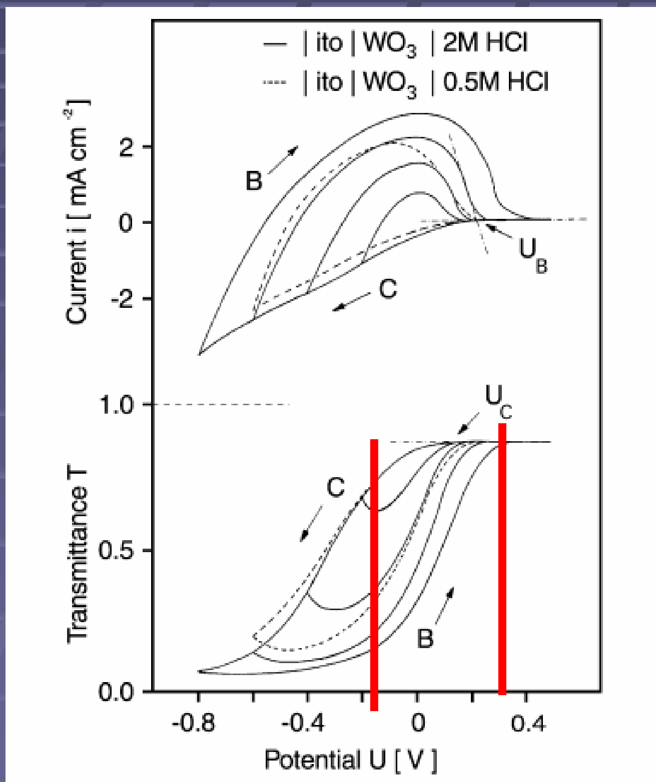
anodic: $MO_x + yA^- + yh^+ \rightleftharpoons A_yMO_x,$

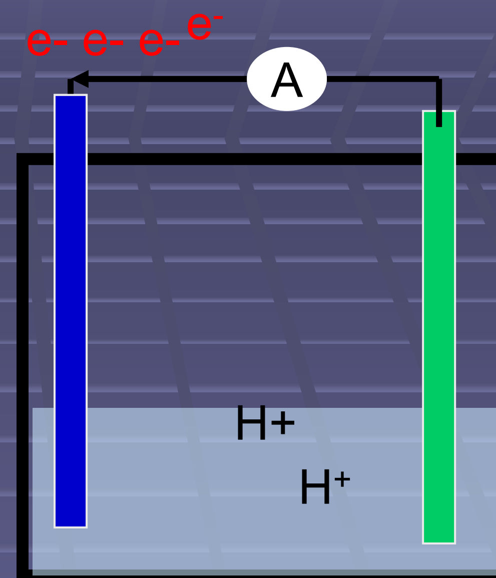
$A^- = F^-, CN^-, OH^-, H^+; \quad 0 < y < 0.3.$

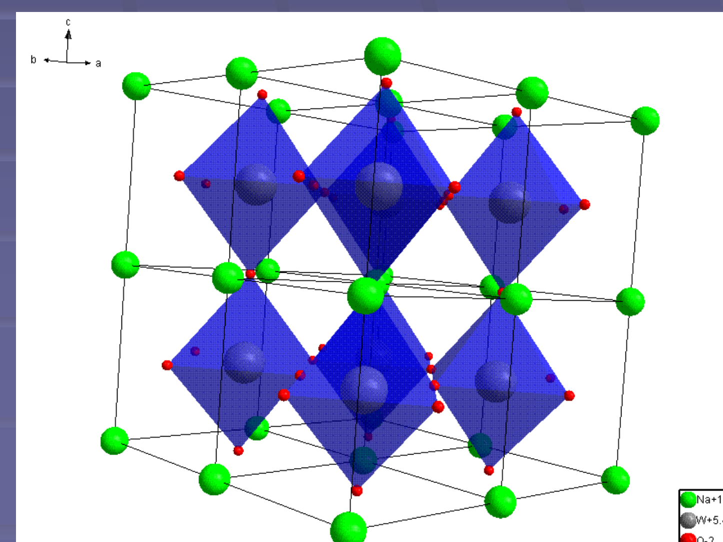
K. Bange, *Sol. Energ, Materials & Solar Cells,* **58**,1999,1-131

Electrocromism

$\lambda = 543$ nm.





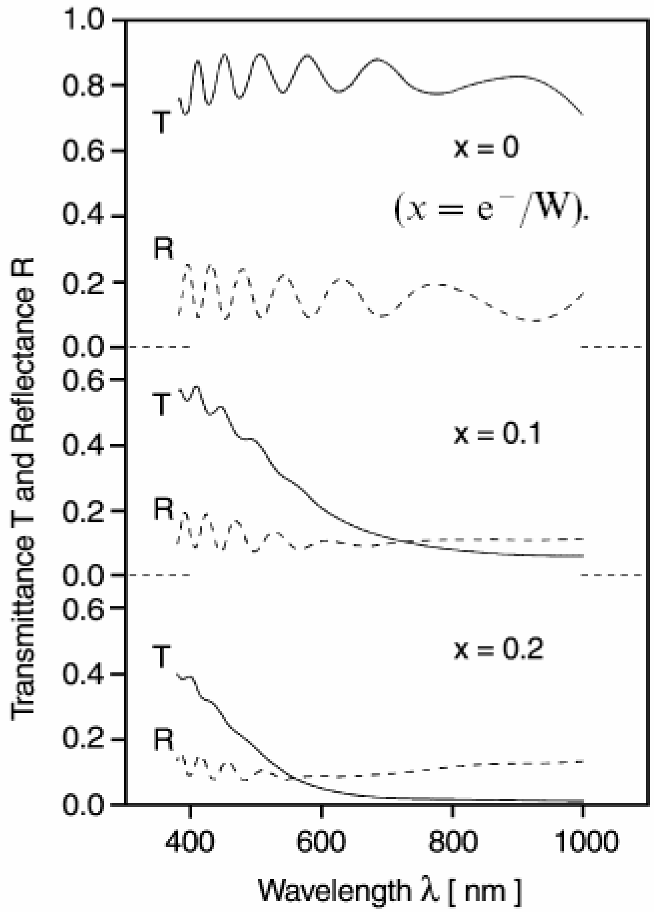


K. Bange, *Sol. Energ, Materials & Solar Cells,* **58**,1999,1-131

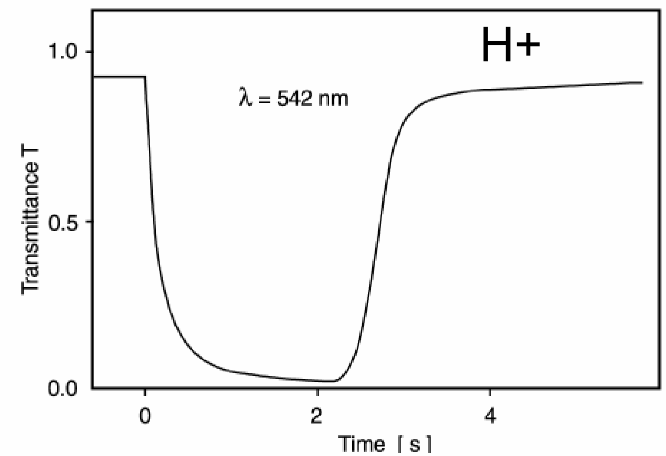
Electocromic Response

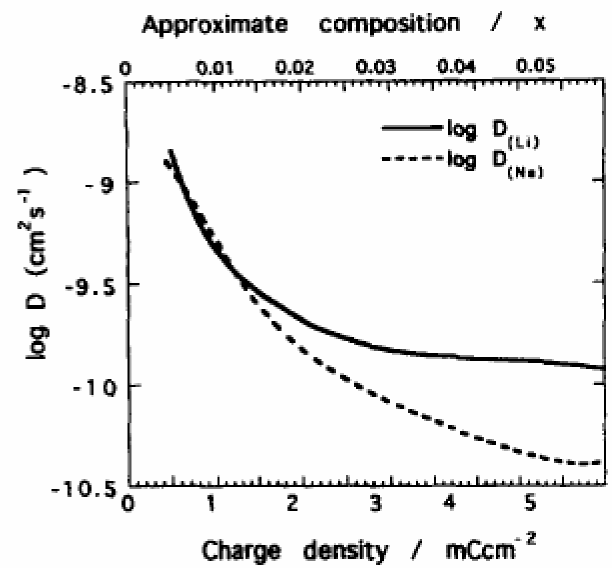
Time Response

Optical response



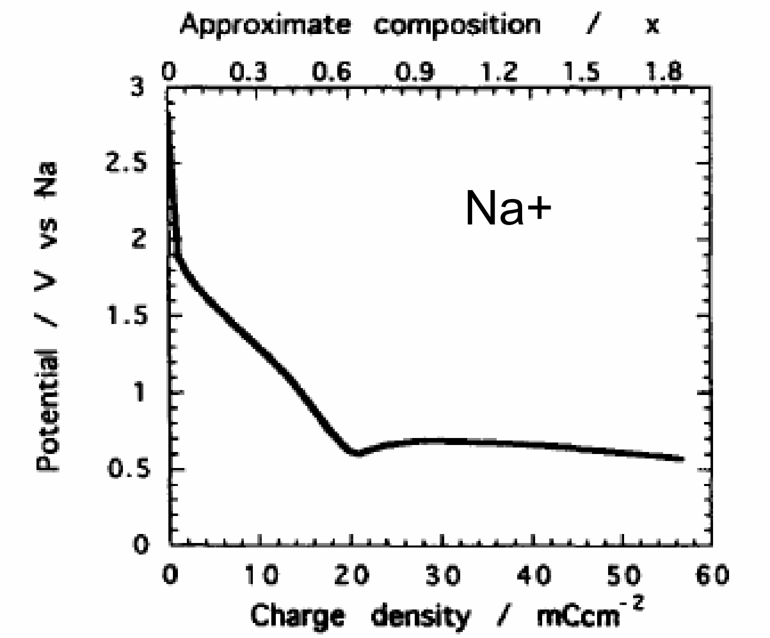
K. Bange / Solar Energy Materials & Solar Cells 58 (1999) 1–131





E. Masetti et al. / Solar Energy Materials and Solar Cells 39 (1995) 301–307

Intercalation Stability

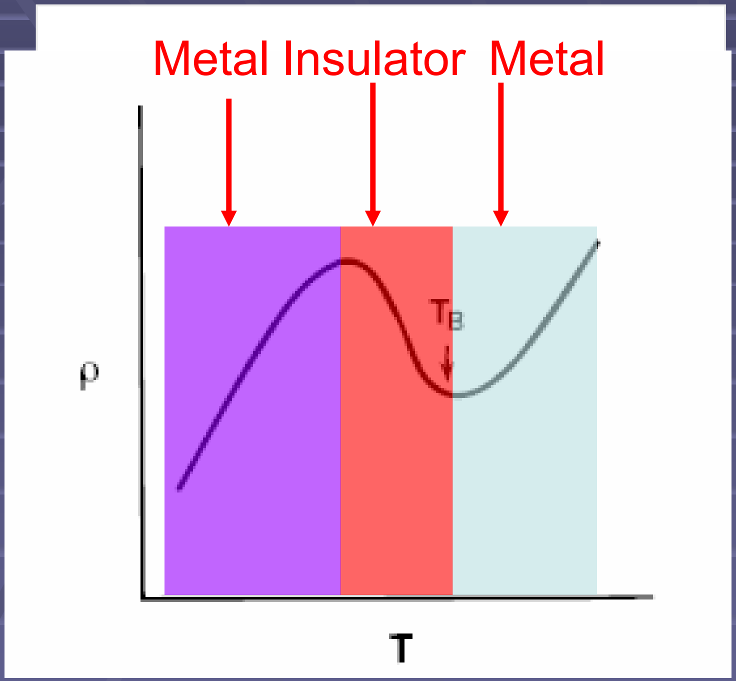


The Intercalation introduced irreversible changes in the optical properties.
Ion accumulation on the surface can induce phase transformation in the surface.

"surface accumulation of the alkali ions can occur if the insertion rate (i.e., current) is comparable with the diffusion rate of the ion…The cation accumulation effect could be interpreted as a new phase formation."

E. Masetti et al. / Solar Energy Materials and Solar Cells 39 (1995) 301–307

Metal to Insulator Transition



Metal to Insulator Transition are caused by Charged Density Wave Instabilities (CDW)

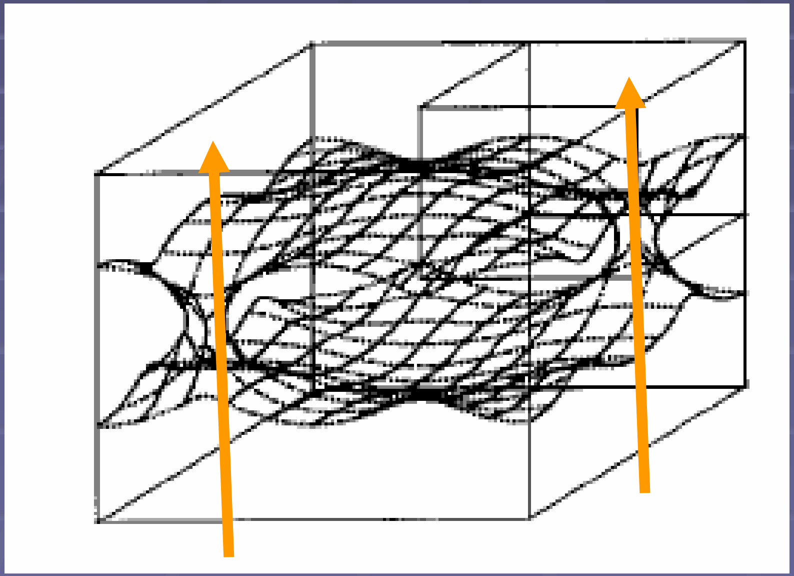
Variables that modify the Metal to Insulator Transition

- **The size of the alkali metal**
- **The amount of the alkali metal**
- **The amount of Oxygen**

Lee, *J. Am. Chem Soc.*,**119**, 1997, 4043-4049

Charged Density Wave Instability

- CDW arises when a part of two fermi surfaces are nested (overlap) and undergo a lattice distortion that lowers the electronic energy and opens a band gap.

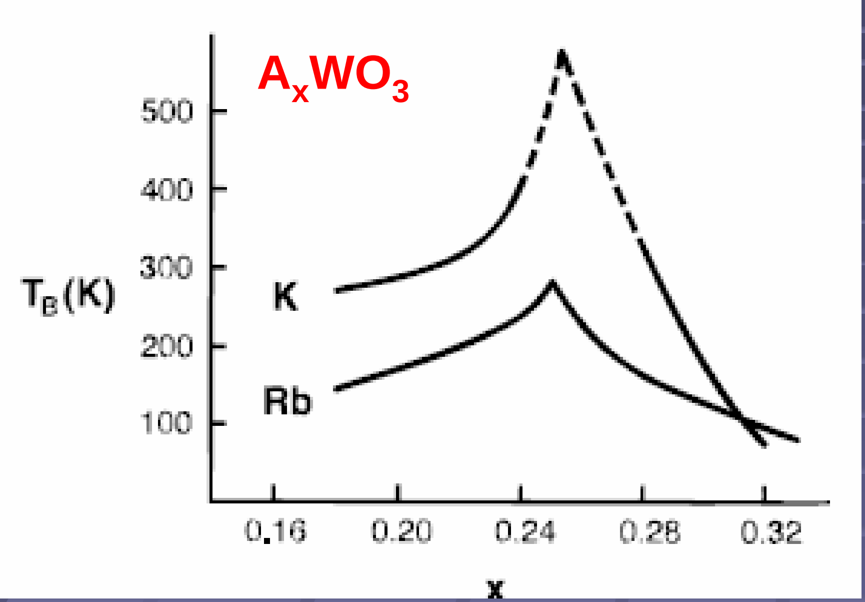


1D Metallic character along the c-direction

1D Fermi Surface for $K_{0.18}WO_3$

“the metal to semiconductor phase transition reduces the density of the carriers responsible for the electrical conductivity along the c direction”[2]

The amount and size of the alkali metal in HTB



Cs doesn't show a CDW transition.
$Cs^+ > Rb^+ > K^+$

Since a CDW transition distortions the lattice creating strains and destabilizing it. A CDW transition will only ocurre when:
$E_{gainDistortion} > E_{destabilization}$

In the case of Cs_XWO_3 the lattice is more rigid since the Cs+ is 1.67 A (as compared to the 2.0 channel radius).
Cs+>Rb+>K+
As the radiai of the Ions decereses TB increases.

Why are Metal to Insulator Transitions important.

- Unexpected changes in material properties.
- Guéry et al have shown that the increase in the electronic conductivity (IMT) of the sample is accompanied by a decrease of its reflectivity.

Summary

- The electrochromic properties of Tungsten Bronzes are dependant to the phase and tungsten bronze compound (Li_xWO_3,H_xWO_3).
- MIT should be taken in acount when Intercalating Ions into the tungsten bronze, since the electronic properties can change dramatically.
- Higher lifetimes of electrochromic materials and efficiencies are needed if TOB wille be used for smart Windows.

Thermochromic/UV coloration

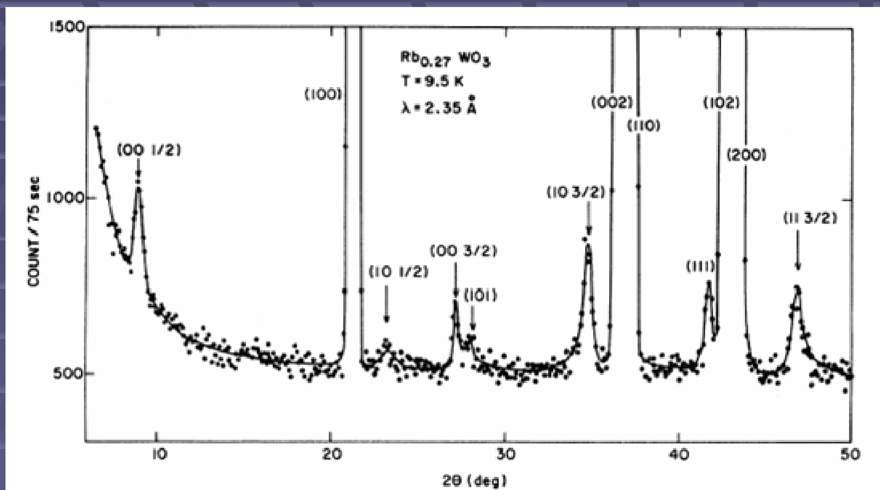
$$WO_{3-z} \cdot pH_2O \xrightarrow{Ta} WO_{3-z-r} \cdot pH_2O + \frac{r}{2} O_{2+}\uparrow,$$

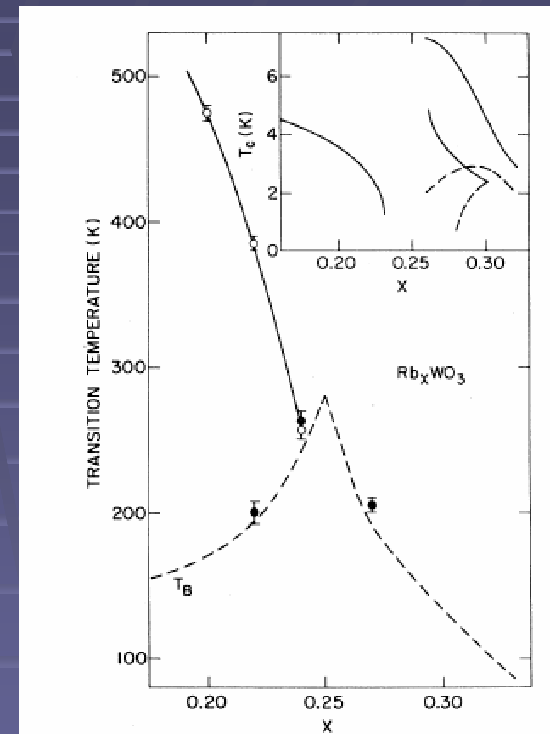
- "Thermochromic colouration of the tungsten oxide occurs as a result of heating in vacuum, while bleaching is obtained when the films are annealed in air."

$$WO_{3-z} \cdot pH_2O \overset{h\nu}{\leftrightarrow} H_{2p}WO_{3-z} + \frac{p}{2} O_2\uparrow$$

K. Bange/Solar Energy Materials & Solar Cells 58 (1999) 1–131

Metal to Insulator Transition: change in unit cell





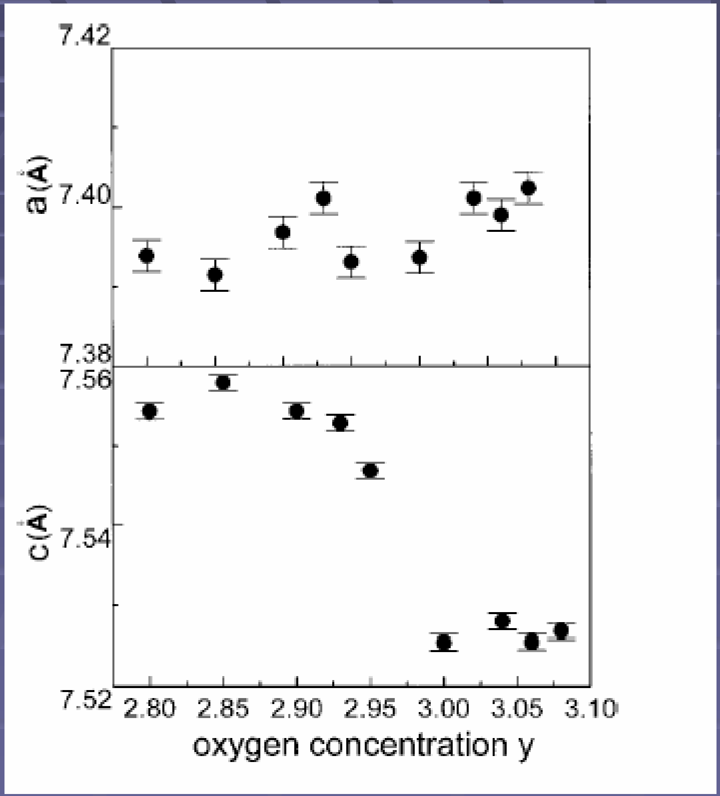
At T<205 K the superlatice reflection are present which indicates a doubling of the unit cell in the c-direction. The formation of the superlatice arises from the Rb ordering in the hexagonal tunnels.

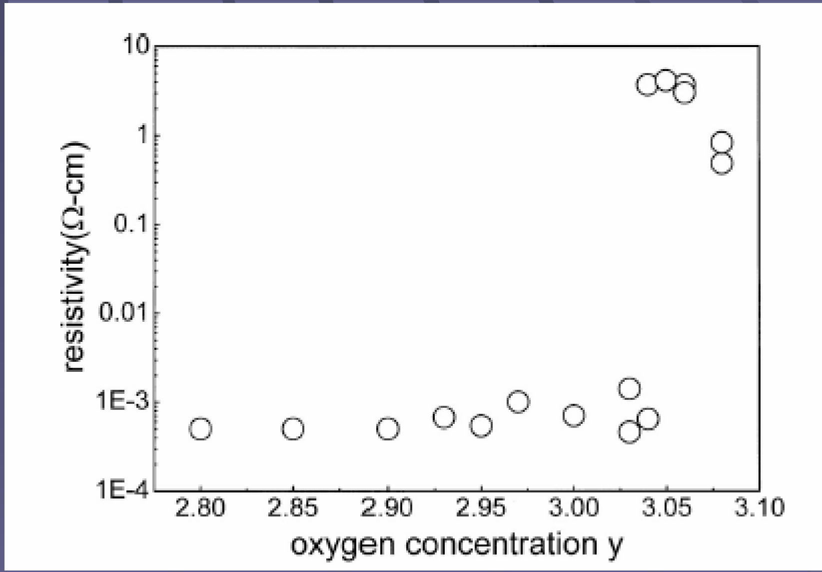
M. Sato, *Phys Rev B*, **25**,1,1982, 501

2)Lee, *J. Am. Chem Soc.*,**119**, 1997, 4043-404

The amount of Oxygen

$Rb_{0.27}WO_y$





Journal of Superconductivity: Incorporating Novel Magnetism, Vol. 15, No. 6, December 2002 (© 2002)