Indian Journal of Chemical Technology
Vol. 12, May 2005, pp. 304-308

Some properties of sodium tungsten bronzes as a function of sodium concentration

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Received 12 July 2004; revised received 7 March 2005; accepted 21 March 2005

Sodium tungsten bronzes, Na_XWO_3 have been prepared having x = 0.25-0.85 at temperatures between 700 and 850 °C in argon atmosphere. X-ray diffraction and IR absorption spectra were used to characterize the structure of the products. It was found to exist in two distinct phases tetragonal and cubic. The absorption spectra between 300 and 780 nm have been obtained by diffuse reflection method, and the characterized absorption peak wave length shows a slight shift to shorter wave lengths with increasing sodium content. The electrical conductivity (σ) has been measured as a function of sodium concentration and temperature from 300 to 550 °K. The results indicate metallic conduction and the conductivity was found to increase with increasing sodium concentration.

Keywords: Sodium tungsten bronzes, X-ray, IR, electrical conductivity, optical reflectance

IPC Code: C01B19/00; C21B13/00

Tungsten bronzes, M_XWO_3, in which M is a univalent metal and x lies between 0 and 1, represent an unusually interesting series of non-stoichiometric materials with properties ranging from metallic to semi-conducting depending on the univalent metal M. M_XWO_3 is considered to be a solid state defect structure in which holes in a WO_3 network (conceivably greatly distorted from pure WO_3) are randomly occupied by M atoms, with the M atoms more or less dissociated into M^+ ions and free electrons[1]. Tungsten bronze ferroelectric materials have very large electrooptic coefficients which make it possible to produce compact, low-voltage modulation and switching devices for applications in communications, signal processing and sensing[2,3]. In addition, they play an important role in technological applications such as electrochromic display and battery electrodes[4]. Tungsten bronze is chemically inert to all acids and slightly paramagnetic[5]. Although other bronzes have been prepared and investigated, the alkali tungsten bronzes have received the most attention. In particular, extensive data exist on sodium tungsten bronze, Na_xWO_3. The crystal structure of $NaWO_3$ is that of perovskite, in which a tungsten atom is at the center of a cube surrounded octahedrally by six oxygen atoms at the face centers. The corners of the cube are occupied by sodium atoms. In cubic sodium tungsten bronzes with the general formula Na_XWO_3, a fraction (1-x) of sodium atoms is missing from the corner[6]. Several of the properties of Na_XWO_3 were studied such as optical absorption[7], X-ray diffraction[8,9] and electrical resistively[10,11] using definite concentrations of Na. The present study is undertaken to investigate X-ray diffraction, IR absorption, optical reflection and ac conductivity of Na_XWO_3 bronzes (x = 0.25-0.85) as a function of sodium concentration.

Experimental Procedure

Tungsten (99.99%), WO_3 (99.95%) and Na_2WO_4 (99.95%) powders were used to prepare the sodium tungsten bronzes (Na_XWO_3), where x = 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85. The preparation was based on the reaction:

$$\frac{x}{2}Na_2WO_4 + \frac{3-2x}{3}WO_3 + \frac{X}{6}W \rightarrow Na_xWO_3$$

The reactants were weighed accurately, mixed thoroughly in the appropriate proportions and heated for approximately 10 h at 850°C in an alumina boat under purified argon. The samples were left to cool inside the electric furnace.

The prepared samples powder were investigated using X-ray diffraction analysis at room temperature with X-ray diffractometer "Diano Corporation" and

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copper (K_α) radiation with nickel filter. Infrared spectroscopic analysis, using KBr pellets was carried out using a FTIR 300E Fourier transform infrared spectrometer.

For conductivity measurements, the bronzes were crushed to a powder, pressed in a 1.25 cm diameter die without binder at 5 ton and sintered at 750°C for 2 h under purified argon to yield pellets of approximately 1.25 cm diameter and 0.3 cm thickness. Electrical conductivity measurements were made by means of ac two probe method using standard research system model SR 720 LCR meter in a temperature range from 300 to 550°K at frequency 100 KHz and applied 1V.

The optical measurements were carried out using a "Shimadzu" double monochromater recording spectrophotometer Model UV-3101 PC using an integrating sphere attachment for sample pellets. The spectrum was recorded from 300-780 nm against a reference path barium sulphate.

Results and Discussion

The X-ray diffraction patterns of different prepared samples are shown in Fig.1. The data was analyzed with respect to ICDD tables. Two distinct phases are identified in the range $0.25 \leq \times \leq 0.85$. The patterns show sharp reflections corresponding to tetragonal Na_XWO_3 for x = 0.25 and 0.35 and cubic Na_XWO_3 for x = 0.45, 0.55, 0.65, 0.75 and 0.85. This is in accordance with previous studies[8] on Na_XWO_3 which indicate that, in the sodium tungsten bronzes there is a progression of distorted perovskites from x = 0 to $x \cong 0.15$ in the same order as the thermal transitions of WO_3 (monoclinic $\rightarrow$ orthorhombic $\rightarrow$ tetragonal). Between x = 0.15 and 0.38, two tetragonal phases coexist, the second phase having a range of homogeneity from x = 0.28 to 0.38 and followed by a cubic range[8] from x = 0.43 to 0.95. It is also clear from Fig. 1 that, with increasing Na concentration the lines are shifted towards higher d-spacing values. This means that, the lattice parameter increases and there is a lattice expansion[12]. This lattice expansion with increasing Na content is presumably due to the removal of positive charge from W as the sodium ion is added[9].

Infrared spectra of WO_3 as well as Na_XWO_3 samples are shown in Fig. 2. With respect to WO_3 sample, a broad band is observed in the 700-1000 cm^{-1} region and a weak band is observed around 355 cm^{-1}. The broad band covering the range 700-1000 cm^{-1} is in conformity with the bands obtained by

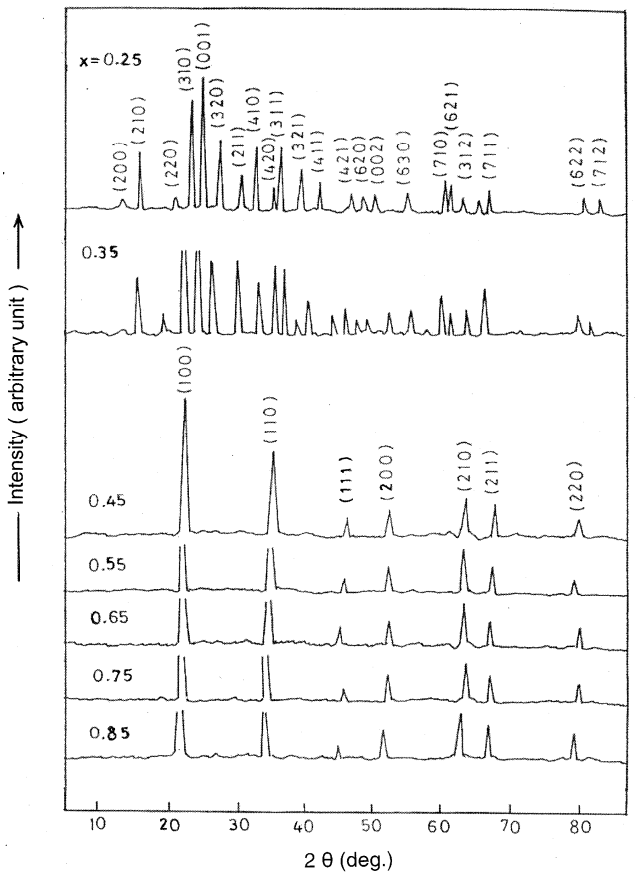

Fig. 1—X-ray diffraction patterns of sodium tungsten bronzes, Na_XWO_3.

previous work[13,14]. They considered the region 650-1000 cm^{-1} to be the region of the tungsten-oxygen bridge vibrations. This is also in agreement with those observed by Yatsenko[15] and Tanisaki[16] at 780 and 870 cm^{-1} for provskite WO_3 powder. These were attributed to inner vibrations of oxygen octahedra. A non well-defined band around 350 cm^{-1} was also observed by Devitt *et al.*[13] for WO_3. With respect to Na_XWO_3 samples, the spectra show a broad band in the range of 630—930 cm^{-1} for the samples with x = 0.25 and 0.35. The spectra of the samples with x content from 0.45 to 0.85 show two absorption bands around 820 and 650 cm^{-1} with a slight shift in bands position to shorter wave length with increasing Na concentration. The appearance of these bands may be due to the change in the crystal structure from tetragonal to cubic structure. The shift in bands position may be attributed to the increase of Na concentration which may affect the polarity of tungsten oxygen bonds[9]. Comparing the IR bands observed in the spectra of the bronze samples, it is clear that the intensities of

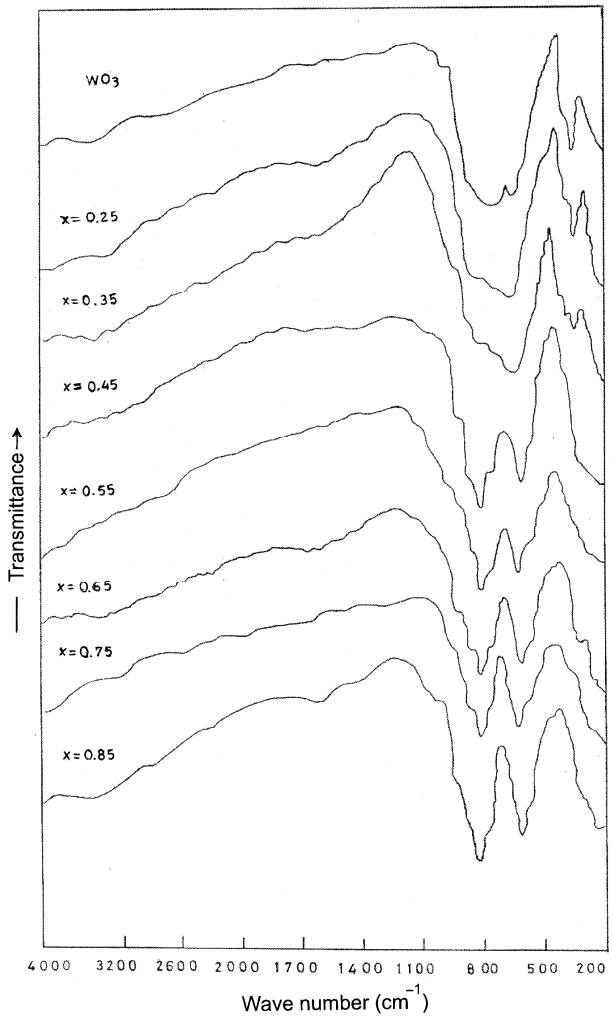

Fig. 2—IR absorption spectra of sodium tungsten bronzes, Na_XWO_3.

absorption bands increase with increasing sodium content. This may be due to the presence of higher free electrons created by increasing the amount of sodium in bronzes[1].

The visual appearance of the prepared bronzes varies from dark blue through yellow to pale yellow as x is increased from 0.25 to 0.85. This means that, there is an optical transition in the sodium bronzes responsible for a pale yellow colouration instead of typical dark blue[17]. The reflectivity change against the wavelength for the prepared samples is represented in Fig. 3. The reflectance curves show a dependence on the composition with an onset in reflectivity at a wavelength of 350 to 400 nm. Curves with Na content from 0.45 to 0.85 in this figure show representative spectra for cubic bronzes and the curves reach higher reflectivities above 70%, while for lower Na content

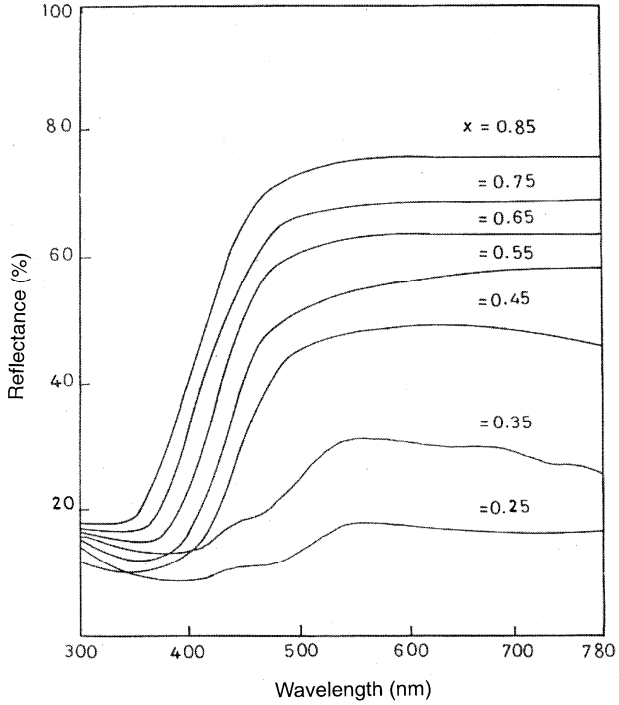

Fig. 3—Reflectance as a function of wavelength for sodium tungsten bronzes, Na_XWO_3.

the curves indicate lower reflectance. Fig. 3 also shows a slight shift of reflectance curves to longer wave lengths with decrease in Na content. The range of colours and metallic luster of the bronzes are the result of high IR reflectivity (due to free electron interband transitions, as in a metal), with a sharp drop in reflectivity at the screened plasma resonance frequency[18]. In bronzes this frequency occurs in the visible region of the spectrum, its exact position being dependent on the free electron concentration and hence x, therefore the colour of the bronze is determined by x[19]. The optical absorption was interpreted as due to polaron absorption[20] or to interband transition of conduction band electrons and the absorbance changes in the visible region are closely related with reflectance changes in the same spectral region[21]. The spectral changes observed in the present study may be associated with change in electronic band structure of the bronzes with the formation of new energy levels with increasing Na content[7] which are attributed to an increase in free electron concentration[22].

The electrical conductivity (σ) as a function of temperature (T) for seven representative x is shown in Fig. 4. All samples exhibited the negative temperature coefficient of conductivity, i.e., the electrical

conductivity decreases with increasing temperature over the entire temperature range studied. The conductivity behaviour indicates the metallic nature of conduction in these samples[23]. The thermoelectric power of sodium tungsten bronzes being of the same sign as that observed for *n*-type semi-conductors and for metals in which conduction is predominantly electronic, indicates that the charge carriers in Na_XWO_3 are free electrons[1]. Each Na atom in Na_XWO_3 is completely ionized to give a cation located interstitially in a host WO_3 structure and an electron which is a free carrier in the host conduction band[5]. The decrease in carrier mobility at higher temperature may be due to lattice scattering through the thermal motion of the atoms of the host structure[24]. Thus, the decrease in carrier's mobility is the important factor for the observed decrease in conductivity with increasing temperature. As shown by the typical curves of Fig. 4, the electrical conductivity was observed to increase with increasing sodium concentration in sodium tungsten bronzes. This behaviour of the conductivity of Na_XWO_3 may be explained in the following manner. For x less than 0.75, there is only one conduction band and each sodium atom contributes one electron to the conduction band[10]. Therefore, it is reasonable to suppose that the area of the Fermi surface increases with increasing sodium concentration, which leads to increase in the conductivity. Mackintosh[25] observed that in the vicinity of x = 0.75 for Na_XWO_3 there is a quite small decrease in the conductivity and assumed that this anomaly is a consequence of partial ordering of the sodium atoms. For x larger than 0.75, there are two conduction bands which contribute to the conductivity. The electrons in the nearly filled band will have a larger effective mass than the electrons in the nearly empty band. Thus, the contribution to the conductivity from the nearly filled band will be less than contribution from the nearly empty band. The total conductivity will therefore, increase with increasing sodium concentration[10]. The plots of log σ versus $1/T$ (Fig. 3) is obviously non-linear, indicating non-Arrhenius activation of conductivity and the decrease in conductivity with increasing temperature is presumably due to decreasing of carriers mobility as consequence of lattice scattering[1,26].

Conclusion

Based on XRD results, two distinct phases are identified in the range $0.25 \leq \times \leq 0.85$. Tetragonal

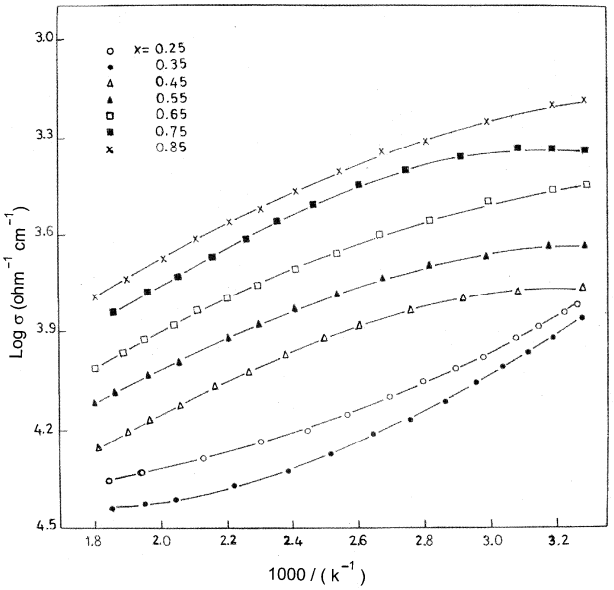

Fig. 4—Plot of electrical conductivity as a function of temperature for different compositions of sodium tungsten bronze, Na_XWO_3.

$Na_\chi WO_3$ for x = 0.25 and 0.35 and cubic Na_XWO_3 for x values from 0.45 to 0.85. With increasing sodium content a slight shift in IR absorption bands to higher frequencies and the bands absorption is observed to increase. The optical measurements indicated that, the reflection wavelength depends on the composition and higher reflectivities for Na_XWO_3, above 70%, was found for the bronze with high sodium concentration. The observed spectral changes are presumably associated with change in electronic band structure of the bronzes. The ac conductivity measurements indicated that the conductivity is metallic in nature and the conductivity decreases with increasing temperature. An increase in the conductivity with increasing sodium concentration in the bronzes is observed.

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