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# FURTHER INVESTIGATIONS ON THE SPECTROSCOPIC AND THERMOPHYSICAL PROPERTIES OF VANADIUM BRONZE POLYCRYSTALS *

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## ABSTRACT

Mixed sodium–vanadium oxide (vanadium bronze) polycrystals were prepared carefully. The crystalline phase formed was identified and investigated by X-ray diffraction analysis. The prepared bronze was extensively studied in comparison with pure $V_2O_5$ using infrared absorption spectra, IR measurements and the temperature dependence of electrical conductivity. Results obtained are interpreted, correlated and discussed in detail, for the first time, with regard to the electronic properties of the test samples.

## INTRODUCTION

Vanadium has been the subject of intensive study in recent years [1]. The temperature dependence of electrical conductivity, thermal EMF and EPR signals in addition to the nature of paramagnetism and electrical conductivity of various bronzes including $MV_6O_{15}$ (M = K, Na) have been studied, and it has been deduced that the alkali metal is ionized $V^{4+}$ formed [2]. Pletnov et al. [3] investigated some physical properties of bronzes. Their results indicated that the unpaired electrons are localized at the $V^{4+}$ centers. Kapustkin et al. [4] deduced that thermally-activated electron hopping

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* It gives me (M.M. Abou Sekkina) great pleasure to contribute to this commemorative special issue of Thermochimica Acta in honor of Prof. Dr. W.W. Wendlandt's 60th birthday. Professor Wendlandt was the driving force in the establishment of Thermochimica Acta, now a major journal with world-wide distribution, having been Editor from its inception. We are all aware of Prof. Wendlandt's numerous contributions to and great activity in the field of thermal analysis; I have known him personally for many years as an honest man with an excellent scientific attitude.

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between V atoms controls the electrical conductivity values. The electrical conductivity increased sharply at 700–800 K, and became metallic at higher temperature. Hagenmüller et al. [5] studied the crystal structure, phase composition an physical properties of five series of bronzes containing Li, Na, K and Cu.

The present article is aimed at further investigating the thermophysical properties of sodium–vanadium bronze.

## EXPERIMENTAL

### *Sample preparation*

In the present investigation, sodium hydroxide (purity = 99.97%) was used for the preparation of the bronze. The calculated amounts of NaOH and $V_2O_5$ (purity = 99.987%) were gently heated to dryness, and then fired at 800 °C for 6 h in an electric muffle furnace.

### *X-ray diffraction measurements*

The room temperature X-ray diffraction patterns of the test samples were undertaken using a Schimadzu (Japan) X-ray diffractometer. A Cu $K_\alpha$, Ni-filter and an adjustable slit at the focal point of the monochromator were used. The diffraction patterns were recorded automatically at room temperature in the range of $2\theta° = 10–80°$. A Geiger Müller tube was adjusted at a rate of one degree per minute, throughout the run.

### *Infrared absorption spectra measurements*

The room temperature infrared absorption spectra of the test materials were conducted using a Perkin-Elmer IR spectrophotometer. The solid potassium bromide disk technique was applied in the region 4000–200 $cm^{-1}$.

### *DC-electrical conductivity measurements*

The DC-electrical conductivity was measured by a method as previously described by Abou Sekkina et al. [6] with some modifications at room and elevated temperatures up to $\simeq 500$ °C.

### *Thermogravimetric analysis (T.G.A.) and differential scanning calorimetry (DSC) measurements*

These were carried out using the Du Pont instruments (U.S.A.) No. 990526 for T.G.A. and No. 990525 for DSC measurements. Nitrogen was

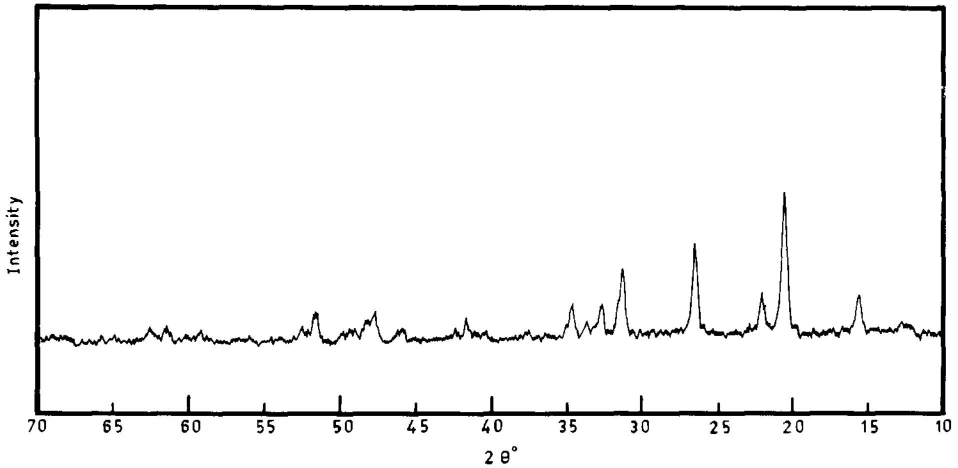

Fig. 1. The room temperature Cu $K_\alpha$ X-ray diffraction pattern of $V_2O_5$.

used as the atmosphere for differential scanning calorimetry (DSC) measurements. The amount of $V_2O_5$ used was 0.01239 g and the amount of bronze taken was 0.02069 g. Measurements were carried out at room and elevated temperature up to 500 °C.

## RESULTS AND DISCUSSION

The room-temperature X-ray diffractograms of both $V_2O_5$ and Na–V bronze are shown in Figs. 1 and 2. The pure oxide pattern agrees with the ASTM X-ray card and the previously published structural data [7–9]. It can

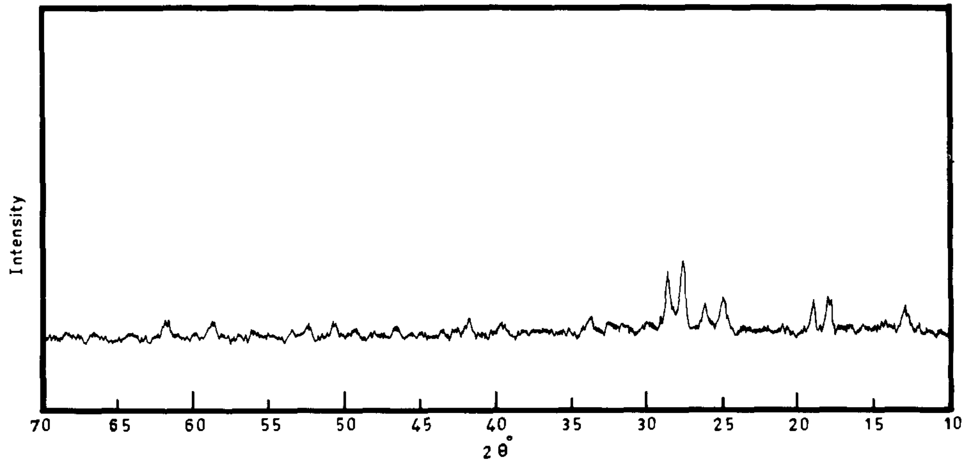

Fig. 2. The room temperature Cu $K_\alpha$ X-ray diffraction pattern of Na–V bronze.

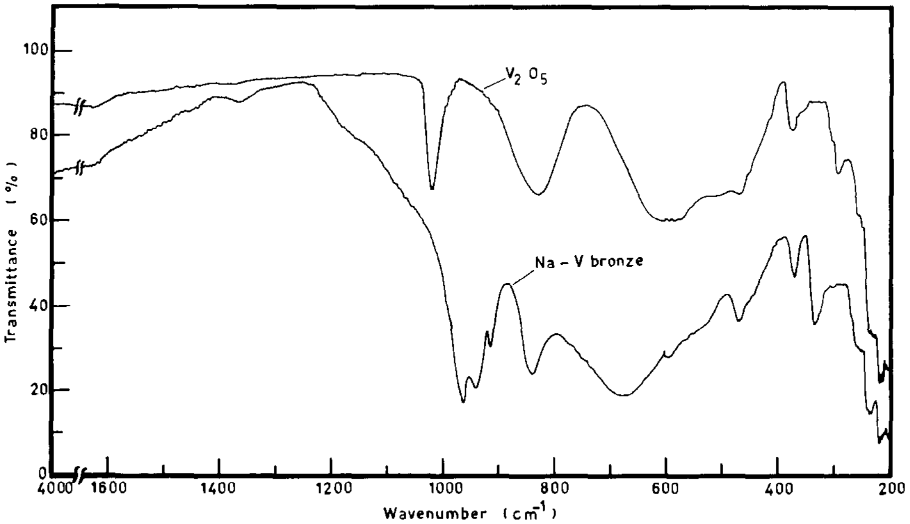

Fig. 3. The room temperature solid KBr infrared absorption spectra of $V_2O_5$ and Na–V bronze.

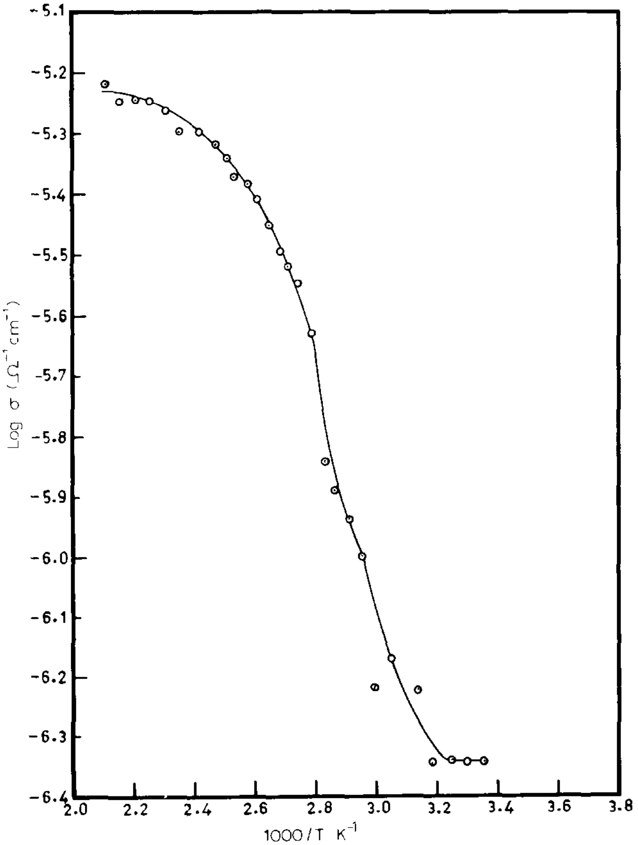

Fig. 4. An illustration showing the variation of logarithmic DC-electrical conductivity as a function of reciprocal of the absolute temperature of $V_2O_5$ semiconductor.

be easily seen that the oxide phase disappeared completely from the X-ray pattern of the bronze (Fig. 2). This suggests the formation of new bronze phases instead of the V-oxide phase. The bronze phases were reported to have the formulae $Na_{2.70}V_6O_{16}$ [10] and $Na_{1.9}V_{12}O_{29.2}$ [11]; other phases were reported by Wadsley [12]. The structure of $Na_{0.33}V_2O_5$ phase has been studied extensively.

The room temperature infrared absorption spectra of $V_2O_5$ and the bronze are clearly shown in Fig. 3. For $V_2O_5$, the IR absorption bands appear at 375, 380, 460, 610, 825 and 1025 $cm^{-1}$. On the other hand, the absorption bands for bronze appear at 340, 370, 475, 840, 910, 940 and 960 $cm^{-1}$. It can be easily seen from Fig. 3 that the general features of the IR spectra of $V_2O_5$ and the bronze are similar. The observed slight differences in the number and location of some absorption bands could be interpreted in the light of the incorporation of sodium into the lattice of the oxide bronze [13], i.e. throughout the formation of V-bronze. This may induce lattice defects by

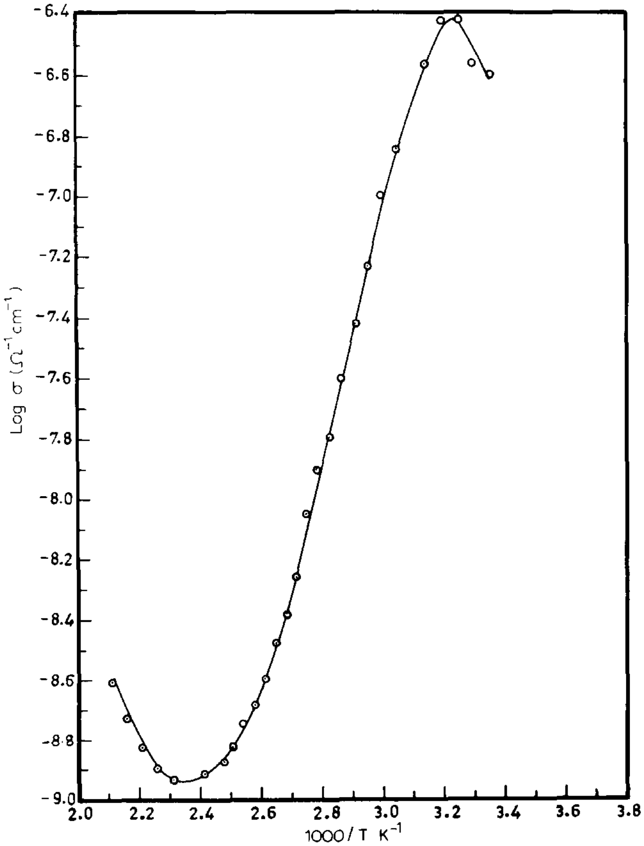

Fig. 5. A diagram showing the variation of logarithmic DC-electrical conductivity as a function of reciprocal of the absolute temperature for Na–V bronze semiconductor.

creating donor centers. The latter is associated with an increased number of free current carriers, thus causing further absorption in the IR region [14,15]. The observed IR absorption bands for both $V_2O_5$ and bronze could be assigned to metal–oxygen stretching vibration [16]. The appearance of new bands in the IR spectrum of bronze confirms that it is not a simple sodium vanadate lattice but may be correlated with other complex bronze structure.

Figures 4 and 5 show the variation of DC-electrical conductivity (log $\sigma$) as a function of the reciprocal of the absolute temperature ($1000/T$ $K^{-1}$) for $V_2O_5$ and bronze respectively. Since there are positive temperature coefficients of electrical conductivity in each case, i.e. all over the curve (Fig. 4) and in the middle region (Fig. 5), the two investigated materials are semiconductors. Furthermore, in certain regions of the curve (Figs. 4 and 5), sodium–vanadium bronze shows metallic conduction in addition to its semiconducting character in the other temperature zones. The decreased electrical conductivity of bronze over that of $V_2O_5$ can be correlated with the disturbance in the lattice brought about by the inclusion and/or incorporation of sodium atoms into the $V_2O_5$ lattice resulting in some rearrangement of the electronic structure of the prepared V-bronze. Thus an equilibrium between $V^{4+}$ and $V^{5+}$ is usually proposed in such cases. In our view, it is important to note that in the case of bronze, the induced metallic conduc-

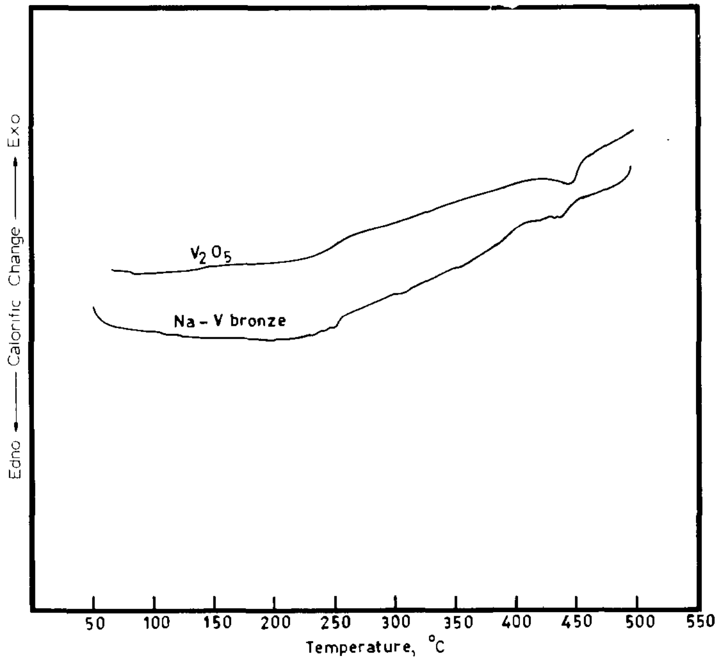

Fig. 6. A representation showing the differential scanning calorimetry (DSC) thermograms of both $V_2O_5$ and Na–V bronze semiconductors.

tion mechanism at relatively high temperature (Fig. 5) could plausibly be correlated with thermally activated jumps of electrons [4] betwen V atoms.

The differential scanning calorimetry (DSC) thermograms of both vanadium oxide and bronze are clearly shown in Fig. 6, for the temperature range 25–500 ° C. The test samples were also first subjected to thermogravimetric analysis (T.G.A.), showing no weight change up to 500 ° C. This confirms the high thermal stability of vanadium oxide and the prepared bronze in the investigated temperature range. This was in accordance with earlier data given by Ulicka and Zurkova [17]. From the DSC thermograms (Fig. 6), it can be easily seen that V-oxide and V-bronze show similar behavior. The samples have an endothermic peak at 450 ° C and 425 ° C respectively for V-oxide and V-bronze. The relatively high temperature peak for V-oxide indicates its higher thermal stability than that of the V-bronze sample. However, these two endothermic peaks are most probably due to the formation of non-stoichiometric materials and/or lattice rearrangements.

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