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THERMOPHYSICAL PROPERTIES OF VANADIUM BRONZE POLYCRYSTALS

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Mixed sodium-vanadium oxide (vanadium bronze) polycrystals were carefully prepared. 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 via infrared absorption spectra, IR measurements and the temperature-dependence of the electrical conductivity. The results obtained are interpreted, correlated and discussed in detail, for the first time, with regard to the electronic properties of the test samples.

Vanadium bronze has been the subject of intensive study [1]. The temperature-dependence of the electrical conductivity, the thermal EMF and EPR signals, and the natures of the 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 and V^{4+} is 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+} centres. Kapuskin et al. [4] deduced that thermally-activated electron hopping between V atoms controls the electrical conductivity values. The electrical conductivity increased sharply at 700–800 K, and became metallic at higher uemperature. Hagenmüller et al. [5] studied the crystal structure, phase composition and physical properties of five series of bronzes containing Li, Na, K and Cu.

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

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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° for 6 h in an electric muffle furnace.

X-ray diffraction measurements

The room-temperature X-ray diffraction patterns of the test samples were taken with a Schimadzu (Japan) X-ray diffractometer. A CuK_α, 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 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 recorded with 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 the method previously described by Abou Sekkina et al. [6], with some modifications, at room and elevated temperature up to $\simeq 500°$.

Thermogravimetric analysis and differential scanning calorimetry measurements

These were carried out with DuPont instruments (USA) 990526 for TG and 990525 for DSC measurements. Nitrogen was used as the atmosphere for 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°.

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 that on the ASTM X-ray card and the previously published structural data [7–9]. It can readily be 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 have been 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 the $Na_{0.33}V_2O_5$ 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, 910, 940 and 960 cm^{-1}. It can clearly be seen from Fig. 3 that the general features of the IR spectra of V_2O_5 and the bronze are similar. The slight difference observed in the number and location of some absorption bands could be interpreted in light of the incorporation of sodium into the lattice of the oxide bronze [13], i.e. throughout the formation of the V-bronze. This may induce lattice defects by creating donor centres. The latter phenomenon is associated with an increased number of free current carriers, thereby causing further absorption in the IR region [14, 15]. The observed IR absorption bands for both V_2O_5 and the

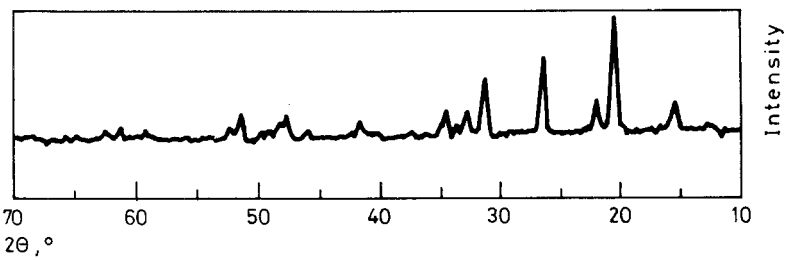

Fig. 1 The room temperature CuK_α X-ray diffraction pattern of V_2O_5

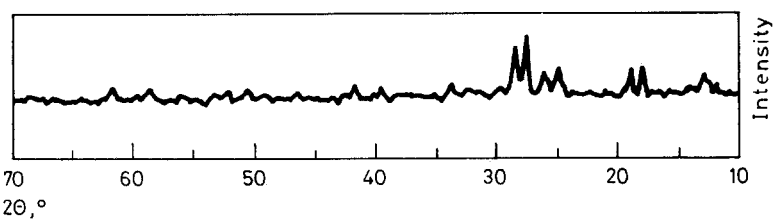

Fig. 2 The room temperature CuK_α X-ray diffraction pattern of Na–V bronze

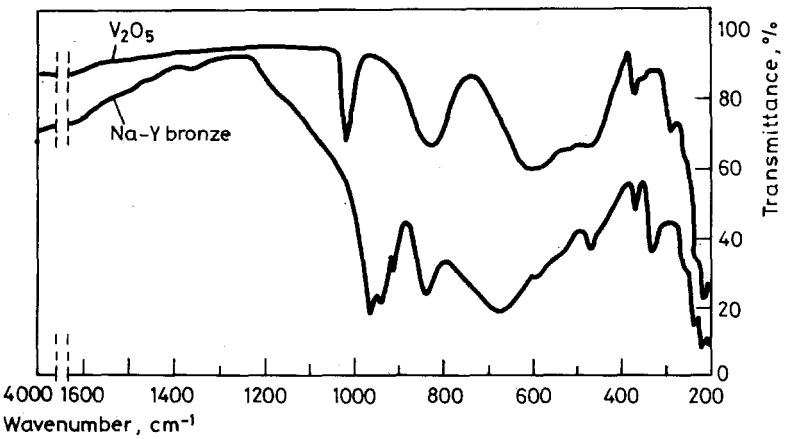

Fig. 3 The room temperature solid KBr infrared absorption spectra of V_2O_5 and Na–V bronze

bronze could be assigned to metal-oxygen stretching vibrations [16]. The appearance of new bands in the IR spectrum of the bronze confirms that it is not a simple sodium vanadate lattice, but may be correlated with other complex bronze structures.

Figures 4 and 5 show the variation of the DC-electrical conductivity ($\log \sigma$) as a function of the reciprocal of the absolute temperature ($1000/T\ K^{-1}$) for V_2O_5 and the bronze, respectively. Since there are positive temperature coefficients of the electrical conductivity in each case, i.e. throughout the curve (Fig. 4) and in the middle region (Fig. 5), the two investigated materials are semiconductors. Furthermore, in certain regions of the curves (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 the bronze over that of V_2O_5 can be correlated with the disturbance brought about in the lattice 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 the bronze the induced metallic conduction mechanism at relatively high temperature (Fig. 5) could plausibly be correlated with thermally activated jumps of electrons [4] between V atoms.

The DSC curves of both vanadium oxide and the bronze are shown in Fig. 6, for the temperature range 25–500°. The test samples were subjected to TG which showed no weight change up to 500°. 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

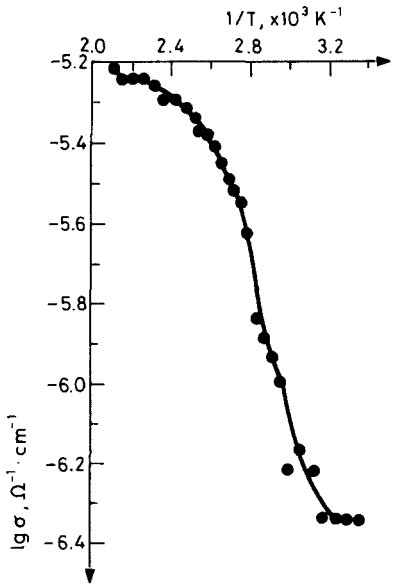

Fig. 4 An illustration showing the variation of logarithmic DC-electrical conductivity as a function of reciprocal of the absolute temperature of V_2O_5 semiconductor

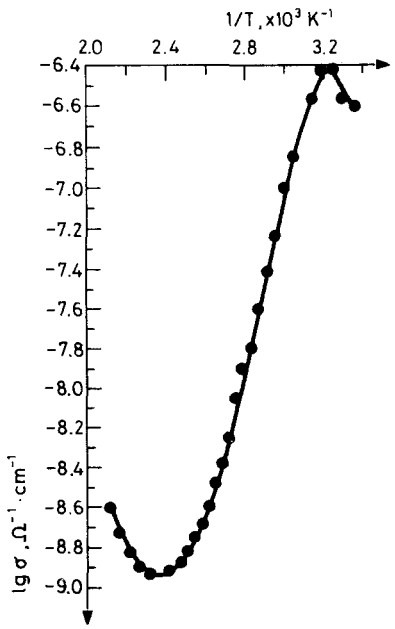

Fig. 5 A diagram showing the variation of logarithmic DC-electrical conductivity as a function of reciprocal of the absolute temperature for Na–V bronze semiconductor

the DSC curves (Fig. 6), it can be seen that V-oxide and the V-bronze exhibit similar behaviour. The samples of V-oxide and V-bronze give an endothermic peak at 450° and 425°, respectively. The relatively high-temperature peak for V-oxide indicates its higher thermal stability than that of V-bronze sample. However, these two endothermic peaks are most probably due to the formation of non-stoichiometric materials and/or lattice rearrangements.

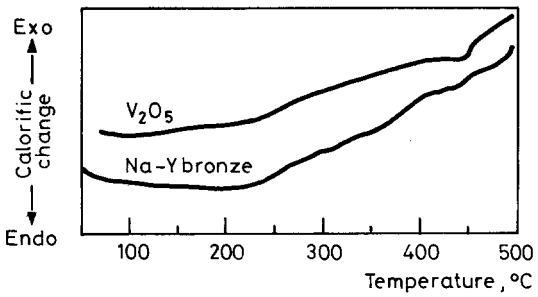

Fig. 6 A representation showing the differential scanning calorimetry (DSC) curves of both V_2O_5 and Na–V bronze semiconductors

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Zusammenfassung — Polykristalle von Natrium-Vanadium-oxiden (Vanadiumbronze) wurden sorgfältig dargestellt. Die erhaltene kristalline Phase wurde mittels Röntgendiffraktionsanalyse identifiziert und untersucht. Die hergestellte Bronze wurde im Vergleich zu reinem V_2O_5 eingehend mit Hilfe von Infrarotabsorptionsspektren, von Temperaturabhängigkeit der elektrischen Leitfähigkeit und durch IR-Messungen untersucht. Die erhaltenen Ergebnisse wurden in erster Näherung in Bezug auf die elektronischen Eigenschaften der Proben interpretiert, miteinander korreliert und ausführlich erläutert.

Резюме — Полученные поликристаллы смешанной натрий-ванадиевой окиси (ванадиевой бронзы) изучены и идентифицированы рентгеноструктурным анализом. Полученная бронза, наряду с чистой пятиокисью ванадия, была изучена с помощью ИК спектроскопии и измерением температурной зависимости электропроводности. Впервые проведена детальная интерпретация, обсуждение и корреляция полученных результатов с электронными свойствами исследованных образцов.