JOURNAL OF MATERIALS SCIENCE **32** (1997) 353–356

Environment sensitive impedance spectroscopy and dc conductivity measurements on $NiWO_4$

A. K. BHATTACHARYA, R. G. BISWAS, A. HARTRIDGE
Centre for Catalytic Systems and Materials Engineering, Dept. of Engineering, University of Warwick, Coventry, CV4 7AL UK

Measurements of impedance spectroscopy and dc conductivity over the temperature range 300–1000K in atmospheres of dry and wet argon on antiferromagnetic $NiWO_4$ are presented. The measured polycrystalline material was produced by a co-precipitation route. The conductivity was found to be sensitive to moisture over the temperature range 300–450 K. Impedance spectroscopy measurements separated the contributions of the bulk lattice and grain boundaries to the conductivity. These were separated over the temperature range 615–833K by equivalent circuit modelling and an activation energy for the bulk lattice conductivity obtained. Conductivity measurements indicated that the compound is an intrinsic semiconductor and obeys the Arrhenius conductivity equation; $\sigma = 492.7 \exp(-1.15\ \text{eV}/kT)\Omega^{-1}\,\text{m}^{-1}$, above 625 K where *K* and *T* have their usual meaning.

1. Introduction

The electrical, magnetic and optical properties of transition metal tungstates are of interest due to their complex electronic structure. These materials have found use as catalysts [1] and humidity sensors [2, 3]. Nickel tungstate is antiferromagnetic with a Neél temperature of 67 K [4]. The compound has a monoclinic structure with space group $[\mathbf{C}_{2H}^{4} - \mathbf{P2/c}]$ [5], in which the oxygen ions are hexagonally close packed and the metal ions occupy a quarter of all the octahedral interstices. High temperature dc conductivity measurements have been reported for several single crystal $M^{2+}WO_4(M^{2+} = \text{Mn, Co, Ni, Cu})$ transition metal tungstates [6–9]. These measurements on flux grown single crystals may be in error due to the incorporation of alkali ions in the lattice from the flux [10]. It is also well known that conductivity measurements are influenced by grain boundary effects in a polycrystalline material. Sample preparation and thermal history also contribute to variations in the measured properties. Previously published work on single crystal [8] and polycrystalline [11] $NiWO_4$ have shown very different activation energies, even though the polycrystalline material was prepared from crushed single crystals. Impedance spectroscopy measurements over a suitable frequency range can allow the elucidation of the contributing effects of the bulk lattice and grain boundaries to the total conductivity of the sample.

In this work we discuss the preparation of $NiWO_4$ by a co-precipitation route. Temperature dependent conductivity measurements were performed using dc and impedance spectroscopy techniques in both wet and dry argon atmospheres.

2. Experimental

2.1. Sample Preparation

Polycrystalline samples of $NiWO_4$ were made by a co-precipitation route. Sodium tungstate di-hydrate (Aldrich 99%) was dissolved in distilled water that had been heated to 60 °C to produce a 0.24 M solution. Separately, nickel chloride hexahydrate (Aldrich 99%) was dissolved in distilled water to give a 0.72 M solution and then heated to 60 °C. The chloride solution was then poured steadily in to the vigorously stirred tungstate solution to give a fine lime-green precipitate. This was left stirring at 60 °C for 15 min. and then centrifuged at 3000 rpm for 5 min. The precipitate was then repeatedly washed with 150 ml distilled water and centrifuged, a total of 6 times, to wash out any remaining Na^+ ions. The dried cake was then calcined to 900 °C for 2 h to form the crystalline tungstate. Samples for the conductivity measurements were made by pressing the finely ground tungstate powder in a 16 mm vacuum die with a pressure of 348 MPa and firing the pellet to 900 °C for 2 h.

2.2. Sample characterization

X-ray powder diffraction patterns of $NiWO_4$ were recorded in the region of $2\theta = 10$–$80\,^{\circ}$C with a scanning speed of 0.25 ° per min on a Philips diffractometer (Model PW1710) using CuK_{α} radiation with a nickel filter.

The electrical characterization was performed using both dc and ac conductivity techniques. Platinum paste contacts (Gwent Electronic materials) were applied to the faces of the prepared pellets which were then fired at 1023 K for 10 min. Samples were

0022–2461

mounted between spring loaded platinum discs in an alumina sample holder and placed in a temperature controlled furnace. Measurements were made in dry and wet flowing argon atmospheres. Dc conductivity measurements were performed using a Keithley 220 constant current source and a Keithley 617 electrometer for the potential measurements. A four wire measurement configuration was used to contact to the Pt contacts. An average of two resistance measurements were made using two different applied currents at each measurement temperature. Measurements were taken on both heating and cooling of the sample. Impedance characteristics were measured using a Solartron 1260 Impedance/Gain-Phase analyser with a 100 mV excitation signal. The data were auto-integrated over 100 s to obtain better characteristics at low frequencies. The conductivity measurement equipment and temperature control of the furnace were computer controlled.

3. Results and discussion

A powder X-ray diffraction pattern of $NiWO_4$ used in this work is shown in Fig. 1. The sample appears to be single phase with no detectable amounts of residual oxides present.

The ac conductivity was measured over the temperature range of 614–957 K using complex impedance spectroscopy techniques. Data were collected in the frequency range 0.5 Hz to 1 MHz which usually allows the contributions of bulk lattice, grain boundary and electrode contributions to the impedance to be extracted. Initial measurements indicated that Na^+ contamination from insufficient washing of the lime green precipitate lead to vastly different impedance spectra for temperature run up and run down data. The refined washing procedure described in section 2.1 gave reproducible conductivity results and this data is presented here. An impedance spectrum obtained at 438 K is shown in Fig. 2. Each contribution has an associated relaxation frequency which can be simply modelled using a parallel combination of resistor and capacitor. Each process appears as a semicircle element using the impedance/admittance representation. The highest frequency arc, passes through the origin and is associated with the bulk conductivity of the sample. The contribution of bulk and grain boundary contributions were separated using an equivalent circuit of a series combination of two parallel capacitance and resistance values. Values were obtained using the Equivcrt [13] program by Boukamp for data obtained in the temperature range 342–560 K. An example of the level of the fit is shown in Fig. 3. The importance of the grain boundary contribution can be seen as it contributes 50% of the total resistance at 342 K. The conductivity of the bulk contribution can easily be calculated from the sample geometric parameters.

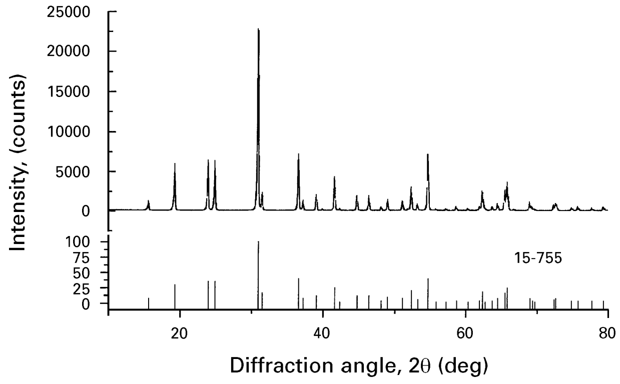

Figure 1 X-ray powder diffraction pattern for $NiWO_4$. For comparison purposes the JCPDS card no 15–755 [12] is also displayed.

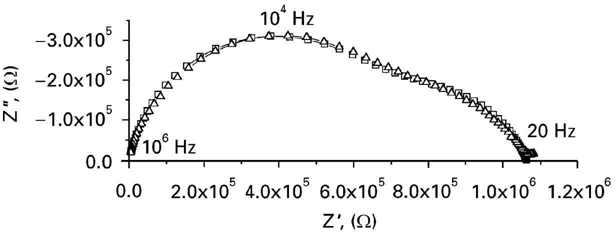

Figure 2 Nyquist plot for $NiWO_4$ at 438 K. (□) experimental, (△) equivalent circuit model.

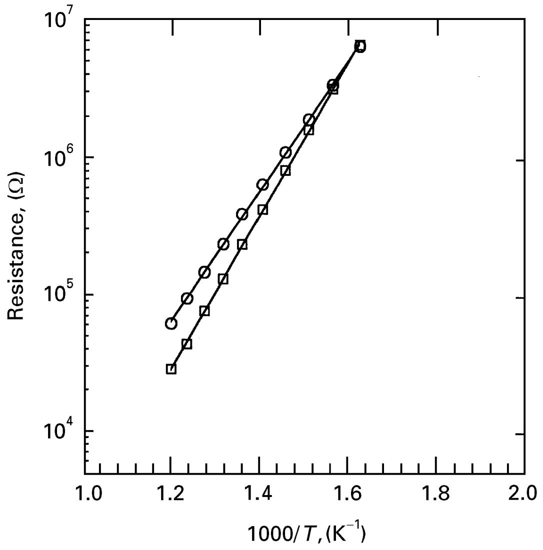

Figure 3 Plot of resistance contributions versus $10^3/T$. (□) bulk, (○) grain-boundary of $NiWO_4$ determined by impedance spectroscopy.

The variation of conductivity with temperature can be interpreted using the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_\sigma/kT). \quad (1)$$

where k and T have their usual meaning. The activation energy (E_σ) and pre-exponential factor (σ_0) for the bulk lattice contribution are calculated as $E_{\sigma(\text{bulk})} = 0.94$ eV and $\sigma_{0(\text{bulk})} = 77.2\ \Omega^{-1}\text{m}^{-1}$. Repeat measurements performed by recycling the temperature regime decreased the grain boundary contribution.

A comparison of the conductivity characteristics obtained from the impedance spectroscopy and dc conductivity in dry argon is presented in Fig. 4. The ac

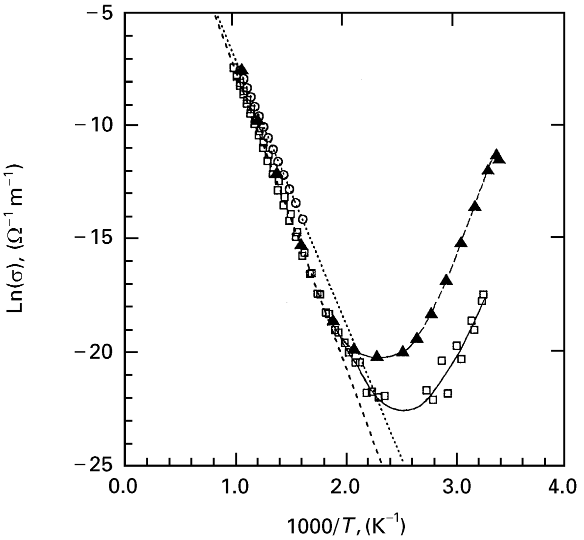

Figure 4 Variation of conductivity of $NiWO_4$ as a function of temperature; (○) ac σ dry argon, (□) dc σ in dry argon, (▲) dc σ in wet argon

value of the conductivity was obtained from the intercept of the low frequency arc of the grain boundary contribution. Above 370 K, σ_{dc} has a positive slope with a minimum at 500 K. Above 625 K the slope is negative and linear and can be described by the equation;

$$\sigma = 492.7 \exp\left(\frac{1.15\ \mathrm{eV}}{kT}\right)\Omega^{-1}\,\mathrm{m}^{-1} \qquad (2)$$

In order to understand the transport mechanism in this material the energy band structure of the material is required. It is well known that in the 3d transition metal oxides the 4s and 4p orbitals overlap the 2s and 2p oxygen orbitals. Due to the strong hybridization of the overlapping orbitals a large energy gap exists between the filled 2p band associated with the oxygen ions and the bottom of the 4s and 4p bands of the transition metal. The 3d levels are then located within the energy gap [14]. Each transition metal ion is surrounded by six oxygen ions with octahedral coordination. Exchange splitting and the resulting octahedral crystal field splits the 3d-orbital into a lower triplet of t_{2g} symmetry and a higher doublet of e_g symmetry. Therefore, the valence band will consist of a filled $O^{2-}:2p$ and $Ni^{2+}:3d^8$ $[t_{2g}{\uparrow\downarrow}^6\ e_g{\uparrow}^2]$ bands. The conduction bands are $Ni^{2+}:3d^2$ $[e_g{\downarrow}^2]$ and $W^{6+}:5d$ bands [15]. This type of band structure leads to three possible types of electronic conduction mechanism.

(i) excitation of electrons from filled $O^{2-}:2p$ band to a conduction band.

(ii) hopping conduction of electrons between neighbouring metal ions.

(iii) excitation of d electrons from filled valence band to empty conduction bands.

The temperature dependent equation for an intrinsic semiconductor is $\sigma = \sigma_0 \exp(-E_\sigma/2kT)$ suggesting that our material has a band gap of 2.30 eV. This energy appears to be too small for a conduction mechanism (i), as optical absorption measurements report this energy to be 3.5 eV [16]. Thus, the suggested conductivity mechanism involves the excitation of electrons from a valence 3d band to an empty 3d conduction band.

In $NiWO_4$, surface defects may lead to the existence of Ni^{3+} ions. As $NiWO_4$ contains narrow 3d bands, small polarons may be formed when the local polarization produced by the carriers hopping between Ni^{2+} and Ni^{3+}, is sufficient to trap them at one lattice site. Therefore the activation energy for conduction E_σ is the sum of E_μ the activation energy for carrier hopping and E_a the energy associated with carrier generation [15]. Measurement of the carrier mobility can be determined by Hall or thermopower measurements for a magnetic material. Thermopower measurements by Bharati *et al.* [11] have suggested that the observed low mobility p type conduction is a result of hole transport due to electron exchange between Ni^{2+} and adjacent Ni^{3+} ions. The increasing thermopower voltage with temperature is indicative of thermally activated hopping of small polarons.

The conductivity variation of $NiWO_4$ in wet argon is shown in Fig. 4. The change in conductivity due to moisture is most apparent between 300–450 K. There appears to be little effect at higher temperatures. Thermal cycling of the sample in a dry atmosphere restores the dry value of conductivity. This higher conductivity may be due to molecular water bonding with the $W^{6+}:5d$ band through lone pair donation thereby increasing the surface conductivity.

4. Summary

$NiWO_4$ has been found to be sensitive to moisture in the temperature range 300–400 K. Impedance spectroscopy has allowed the activation energy of the bulk lattice conduction to be calculated as 0.94 eV. The grain boundary contribution resistance is 50% of the total resistance at 342 K. The dc conductivity follows an Arrhenius conductivity relationship above 625 K and has an activation energy of 1.15 eV. This has been assigned to electron transitions between 3d bands.

Future work will include the measurement of the thermopower as well as measurements from other first row transition metal tungstates.

References

1. I. YASUO, U. KENJI, S. KOICHI, Y. KIYOSKI and O. TETSUTSUGU, *Jpn. Kokai Tokkyo Koho*, Jp 60 222 146.
2. HITACHI Ltd, *ibid*, Jp 60 22 301.
3. HITACHI Ltd, *ibid*, Jp 81 104 771.
4. L. G. VAN UITERT, I. R. C. SHERWOOD, H. J. WILLIAMS, J. J. RUBIN and W. A. BONNER, *J. Phys. Chem. Solids* **25** (1964) 1447.
5. V. V. EREMENKO, Y. G. LITVINKO and T. I. KAZAKOVA, *Sov. Phys. Solid State* **16** (1975) 2132.
6. R. BHARATI, R. A. SINGH and B. M. WANKLYN, *J. Phys. Chem. Solids* **43** (1982) 641.
7. *Idem, J. Mater. Sci.* **16** (1981) 775.
8. *Idem, ibid*, **18** (1983) 1540.

9. R. BHARATI, R. A. SINGH and Y. P. YADAVA, *J. Mater. Sci. Lett.* **2** (1983) 623.
10. B. M. WANKLYN, *J. Mater. Sci.* **7** (1972) 813.
11. R. BHARATI, R. A. SINGH and B. M. WANKLYN, *ibid.* **15** (1980) 1293.
12. JCPDS, Powder diffraction file 1991 (Joint Committe on Powder diffraction Swathmore PA).
13. B. A. BOUKAMP, University of Twente, 1989.
14. D. ADLER, *Rev. Mod. Phys.*, **40** (1968) 714.
15. P. A. COX, "Transition Metal Oxides", (Clarendon Press, Oxford, 1992).
16. M. YA. KSENDZOV and I. A. DRABKIN, *Sov. Phys. Solid State*, **7** (1965) 1519.

Received 19 April
and accepted 21 May 1996