JOURNAL OF MATERIALS SCIENCE 15 (1980) 1293–1296

Electrical conductivity, thermoelectric power and dielectric constant of $NiWO_4$

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The a.c. electrical conductivity (σ_{ac}), thermoelectric power (θ) and dielectric constant (ϵ') of antiferromagnetic $NiWO_4$ are presented. σ_{ac} and ϵ' have been measured in the temperature range 300 to 1000 K and θ in the temperature range 600 to 1000 K. Conductivity data are interpreted in the light of band theory of solids. The compound obeys the exponential law of conductivity $\sigma = \sigma_0 \exp(-W/kT)$. Activation energy has been estimated as 0.75 eV. The conductivity result is summarized in the following equation

$$\sigma = 2.86 \exp(-0.75\,\text{eV}/kT)\,\Omega^{-1}\,\text{cm}^{-1}$$

in the intrinsic region. The material is *p*-type below 660 K and above 950 K, and is *n*-type between 660 and 950 K.

1. Introduction

$NiWO_4$ is a member of the isomorphous series $MeWO_4$ [where Me = Zn, Mn, Cr, Fe, Co, Ni, etc.] of transition metal tungstates containing small cations. It is an antiferromagnetic compound with a Neël temperature of 67 K [1]. The magnetic and optical properties of $NiWO_4$ have been widely investigated by various workers [1–5]. Thermophysical and dielectric measurements have also been reported [6, 7] but the electrical transport properties of not only $NiWO_4$ but of the whole family of transition metal tungstates are still unreported.

$NiWO_4$ crystals are brown, lustrous and transluscent rhombic prisms. $NiWO_4$ has a monoclinic structure with $a_0 = 4.60 \pm 0.015$, $b_0 = 5.66 \pm 0.02$, $c_0 = 4.91 \pm 0.015$ Å and $\beta = 90°5' \pm 5'$ [8]. It belongs to the space group *P*2/*c*. The magnetic unit cell (2*a*, *b*, *c*) determined by neutron diffraction has twice the volume of the chemical unit cell (*a*, *b*, *c*). The Subnikov group is *Pa*2/*c* [9]. The volume of the unit cell is 225.9 Å^3. The melting point has been reported as 1390 ± 10° C [8].

In the present paper, we report our results of the a.c. electrical conductivity, thermoelectric power and dielectric constant above 300 K. Related parameters are also estimated.

2. Experimental details

The crystals of $NiWO_4$ used in our work were grown by the flux method. Since the shape and size of the crystals were not suitable for our measurements, they were ground to powder which was made into a pellet under a pressure of $4.0 \times 10^6\,\text{g cm}^{-2}$, using a hydraulic press and a suitable die. Before measurement, both faces of the pellets were coated with silver paint to ensure good contact with the platinum foil electrodes. The pellet was annealed, cleaned and dried for several hours at 400° C before measurement. Electrical conductivity was measured using a conductivity meter "Systronics" type 302′ made in India. The conductivity meter works at a frequency of 50 Hz in the range of 0.1 to 10 μmhos and at 2 kHz in the higher ranges. Thermo e.m.f. was measured with a vernier potentiometer, and temperature with a Pt/Pt 13% Rh thermocouple. The static dielectric constant was measured using a Ruthonsaw Universal Bridge, made in India, which operates at 1 kHz.

3. Results and discussion

3.1. Electrical conductivity

Fig. 1 shows the variation of log σ versus $10^3/T$. Below 400 K, the curve has a positive slope, and

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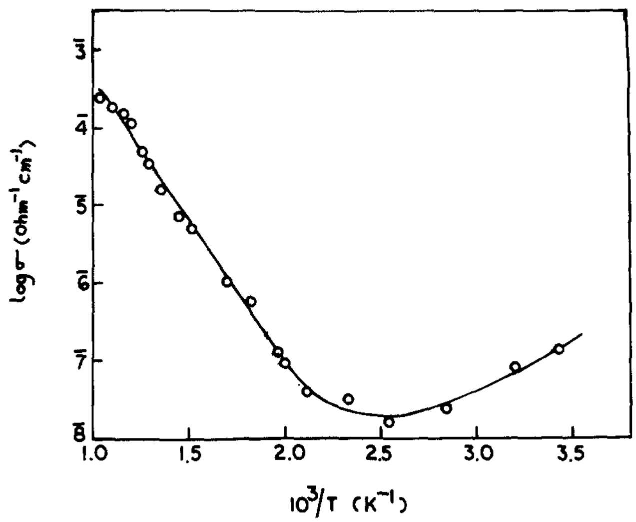

Figure 1 Variation of conductivity as a function of temperature in $NiWO_4$.

around 400 K a broad minimum. This behaviour of the curve may be attributed to absorbed water and perhaps to hydrate formation in the compound at lower temperatures, which may also apply to the variation in dielectric constant with respect to temperature (Fig. 3). The variation of log σ with respect to $1/T$ above 500 K is linear and can be expressed by the well-known exponential relation for intrinsic semiconductors,

$$\sigma_i = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_e, m_h)^{3/4}(\mu_e + \mu_h)\,e^{-E_g/2kT}$$

or

$$\sigma_i = \sigma_0(T)\,e^{-E_g/2kT} \tag{1}$$

where

$$\sigma_0(T) = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_e, m_h)^{3/4}(\mu_e + \mu_h).$$

$(\mu_e + \mu_h)$ varies with T roughly as $T^{-3/2}$, therefore σ_0 may be taken to be approximately independent of temperature. It is obvious from Equation 1 that a plot of log σ_i versus $1/T$ should yield a straight line having a slope $-E_g/2k$. where m_e, μ_e and m_h, μ_h are effective masses and mobilities of the electrons and holes, respectively, and E_g is the energy band gap of the compound. The linear portion of Fig. 1 above 500 K can be summarized in the following equation

$$\sigma_{a.c.} = 2.86\exp\left(-\frac{0.75\,\text{eV}}{kT}\right)\Omega^{-1}\,\text{cm}^{-1}.$$

The value of E_g estimated from the slope of the graph is 1.50 eV. The conductivity data above 500 K can be explained by the band theory of solids. The valence bands seem to be the filled O^{2-}: 2p and Ni^{2+}: $3d^8$ $[t_{2g}^6\,e_g^2]$ bands and the conduction bands seem to be the empty Ni^{2+}: $3d^2$ $[e_g^2]$ and W^{6+}: 5d bands. Ni^{2+} sub-bands arise due to the splittings by crystal and exchange fields [10]. These narrow bands lie within the $\sigma\sigma$ band gap, i.e. within the top of the 2p and the bottom of the 5d empty bands [11]. So there is a probability of two types of conduction: (i) by the transfer of d-electrons between neighbouring metal ions and (ii) by exciting an electron from the valence bands to the conduction bands. But according to Suchet [12], whenever a compound contains only empty or completely filled sub-levels, it cannot lend itself to transfer, so the first probability can be ruled out for this compound. The conduction can be explained as in conventional semiconductors using the band theory of solids. However, at higher temperatures the probability of polaron formation due to the narrow d-band cannot be ruled out; this seems probable and is in agreement with the dielectric constant and thermoelectric power results. Since at higher temperatures mobility increases exponentially with temperature, small polarons should also contribute to conduction by thermally activated hopping [13, 14]; this is evident from the increase of θ with T at high temperature.

3.2. Thermoelectric power

Thermo e.m.f. has been measured in the temperature range 600 to 1000 K. The thermoelectric power is calculated using the formula

$$\theta = \frac{\Delta V}{\Delta T}$$

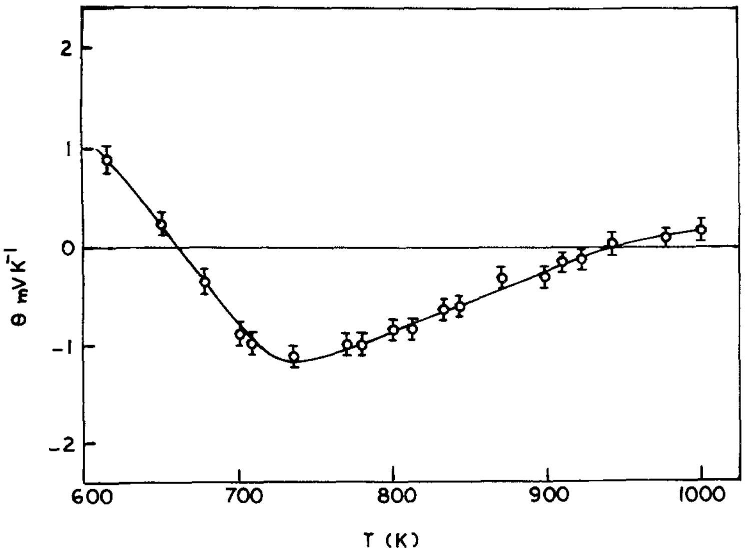

Figure 2 Variation of thermoelectric power as a function of temperature in $NiWO_4$.

where θ is thermoelectric power in mV K^{-1}, ΔV is thermo e.m.f. in mV and ΔT is the temperature difference across the pellet. The variation of θ versus T is shown in Fig. 2. Since θ is positive below 660 K, the compound is p-type below this temperature, apparently on account of cationic impurities, etc. In the temperature range 660 to 950 K, θ is negative, thus the compound is n-type in this temperature range, and it becomes again p-type above 950 K. At lower temperatures, short-range self-polarization of the lattice traps the holes (cationic impurities) at local ionic sites, and hole transport occurs by electron exchange between Ni^{2+} and adjacent Ni^{3+}; to some extent, it also occurs because of the hygroscopic nature of the compound and possible transition metal impurities. Therefore, the compound is p-type at low temperatures below 660 K. As the temperature is increased, the thermally generated charge carriers, i.e. the number of electrons, increases in the conduction band, and therefore the conduction is dominated by electrons between 660 and 950 K. θ shows a flat minimum around 750 K, corresponding to a minimum number of holes and a maximum number of conduction electrons [15]. Above 750 K, thermoelectric power increases with temperature. This increase in θ can be attributed to the following two reasons: (i) at higher temperatures, electrons are excited from the filled O^{2-}: 2p band to the filled narrow Ni^{2+}: $3d^8$ and empty narrow Ni^{2+}: $3d^2$ bands, but since these bands are very narrow, the electrons are trapped in the bands before reaching the comparatively wide W^{6+}: 5d and 4s 4p bands. Therefore, the number of conduction electrons available for conduction becomes less compared to the number of holes available in the O^{2-}: 2p band; (ii) the bands are narrow in comparison to the O^{2-}: 2p valence band, thus the electron mobility is less than the mobility of the holes. The contribution of the holes increases with temperature and becomes dominant above 950 K, therefore the compound becomes p-type again above 950 K.

3.3. Static dielectric constant

The static dielectric constant of the $NiWO_4$ pellet has been measured in the temperature range 300 to 1000 K. The result is shown in Fig. 3, where $\log \epsilon'$ is plotted against T. The nature of the variation of ϵ' with temperature is similar to the variation of σ with temperature. ϵ' decreases with T from room temperature to 350 K, for the reason already given in the case of σ. As the temperature is increased, the compound is dehydrated, and thus the available volume for ions per unit volume is increased and the density of the compound is decreased, with the result that ϵ' decreases. Above 350 K, ϵ' increases rather slowly with temperature in accordance with the nature of ionic compounds [16, 17] and also because of the increase in the number of charge carriers with temperature, owing to the semiconducting behaviour of the compound. Owing to the increase in the number of charge carriers, space charge polarization takes place and ϵ' increases. Above 700 K, the increase is very rapid, which is a general characteristic of semiconducting materials, because the number of charge carriers increases exponentially with tem-

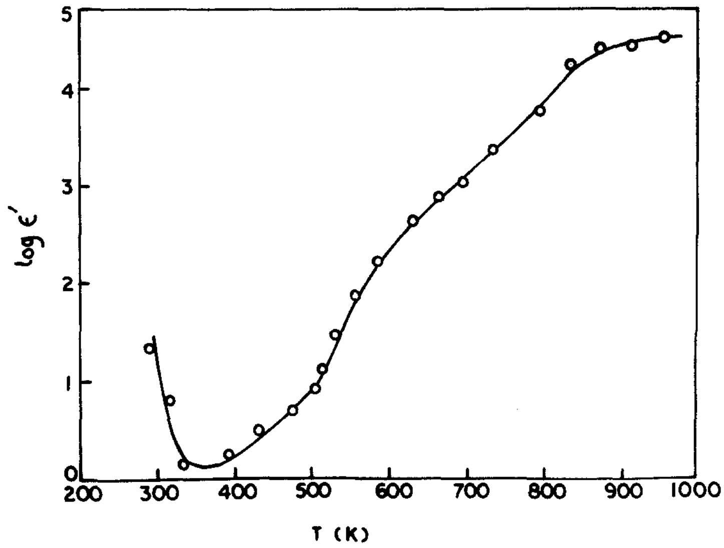

Figure 3 Variation of dielectric constant as a function of temperature in $NiWO_4$.

perature. If these charge carriers are impeded by trapping, etc., as is apparent from thermoelectric measurements, the space-charge polarization builds up because it is proportional to the number of charge carriers. Thus a straight line should be obtained, if we plot log ϵ' versus T, which seems to be true in our case. This rapid increase in ϵ' is also expected to be due to the formation of small polarons at such high temperatures, formed as a result of the interaction of thermally generated charge carriers with the optical mode frequency of the lattice, as has been pointed out by Swell [18].

Acknowledgements

One of the authors (R.B.) is grateful to the CSIR, India, for providing financial assistance. We also thank Professor Nitish K. Sanyal for his encouragement.

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Received 13 September and accepted 23 October 1979.