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A.C. CONDUCTIVITY OF $MnWO_4$

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Abstract—The a.c. electrical conductivity of $MnWO_4$ from 10 Hz to 10 MHz has been measured in the 425–900 K temperature range using pressed pellets. The a.c. conductivity shows a frequency dependence at lower temperatures whereas at higher temperatures it is almost frequency independent up to about 1 MHz. At lower temperatures σ_{ac} varies as ω^s where $s \lesssim 1.2$. A plot of log σ vs $1/T$ using the a.c. conductivity values at 10 Hz, shows a discontinuity around 575 K. The activation energies below and above this temperature have been estimated to be 0.65 and 0.58 eV respectively. Differential thermal analysis (DTA) performed on powder samples shows the absence of any structural phase transitions at this temperature. These observations suggest that the electrical conduction below 575 K occurs essentially by thermally activated hopping of polarons whereas above this temperature, normal band-like conduction may dominate the conduction processes.

Keywords: A.C. Conductivity, manganese tungstate.

1. INTRODUCTION

Investigations of the physical properties of metal tungstates are of considerable importance both from a fundamental as well as a technological point of view. Magnetic properties of transition metal tungstates of Fe, Co, Ni, Cu and Mn have been studied by several workers [1–3]. Electrical transport properties of Fe, Co, Ni and Mn tungstates have been reported [4–7]. Valuable information on the electrical transport mechanisms in solids can be gained by studying the temperature dependence of a.c. conductivity. At low frequencies, a.c. conductivity measurements can be viewed largely as an extension of traditional d.c. conductivity measurements. However, at high frequencies, contact effects and internal barriers become capacitively short circuited and losses are expected to reflect bulk dissipative mechanisms. To our knowledge, the frequency dependence of the a.c. conductivity of the transition metal tungstates has not been reported. The measurements reported here are on the frequency dependence of the a.c. conductivity of $MnWO_4$ pellets from 10 Hz to 10 MHz in the 425–900 K temperature range. Our observations support the possibility of a hopping transport mechanism between localized states at temperatures below 575 K and a band type mechanism above this temperature as suggested by Bharati *et al.* [5].

2. EXPERIMENTAL

Manganese tungstate was prepared by allowing a warm solution of sodium tungstate to react slowly with a warm solution of manganese sulphate. The resultant dark brown precipitate was filtered, washed several times with hot water and dried at 200°C. The manganese and the tungsten contents were analysed colorimetrically [11] using the potassium iodate and the potassium thiocyanate methods respectively. These analyses confirm the composition of the precipitate to be $MnWO_4 \cdot 2H_2O$ and the material obtained after drying at 200°C to be $MnWO_4$. The identity of the material was further confirmed by X-ray powder diffraction measurements. Pellets of about 2 mm thickness and 13 mm diameter were pressed in a stainless steel die using a pressure of 300 MPa. The pressed pellets were annealed at 400°C for 24 h, following which gold electrodes were evaporated on to them. The a.c. conductivity of the pellets at various temperatures was determined by measuring the complex impedance from 10 Hz to 10 MHz using an HP 4192A LRC meter. The pellet was first heated slowly to 700°C in a Heraus tube furnace and the impedance measurements were taken during the cooling cycle at 25°C intervals. The furnace temperature was controlled by a Eutrotherm 810 controller and the sample temperature was measured using a chromel–alumel thermocouple, fixed close to the sample. Differential thermal analysis was performed using a Stanton Redcroft model DTA 637-4 thermal analyzer. A 10 mg reference sample of Al_2O_3, a heating rate of 2°C min^{-1}, a chart speed of 6 cm h^{-1} and a sensitivity of 10 mV were used for the DTA study.

3. RESULTS

The a.c. conductivity from 10 Hz to 10 MHz and in the 425–900 K temperature range is shown

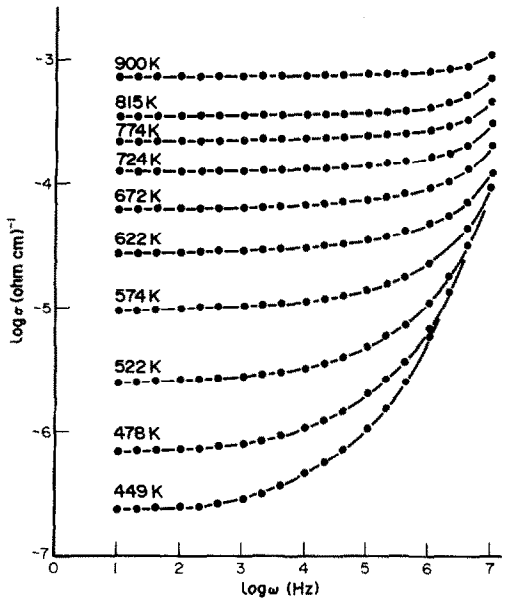

Fig. 1. Frequency dependance of a.c. conductivity of $MnWO_4$ at different temperatures.

in Fig. 1. At the lower temperatures around 500 K, the conductivity exhibits a significant frequency dependent behaviour. At higher frequencies the a.c. conductivity appears to follow a ω^s behaviour with $s \lesssim 1.2$. As the temperature is raised, the conductivity becomes less and less frequency dependent and at 900 K, it is nearly frequency independent up to 1 MHz. Figure 2 shows the log σ vs $1/T$ variation using the σ values taken at the lowest frequency of 10 Hz. The variation shows a discontinuity at around 575 K indicating a change in the conduction process. The two straight lines above and below this temperature follow the Arrhenius relationship given by

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

but with two different slopes. The activation energies estimated from these slopes are 0.65 and 0.58 eV respectively for temperatures below and above 575 K. The corresponding pre-exponential factors are 4.31×10^{-6} (ohm cm)$^{-1}$ and 3.46×10^{-4} (ohm cm)$^{-1}$ respectively. The differential thermal analysis performed on powder samples, however, does not show any transition peaks around 575 K, indicating the absence of any structural phase transitions at this temperature.

4. DISCUSSION

A.C. Conductivities of several amorphous and crystalline solids have been studied by various workers [8–10]. According to Mott and Davies [10] information about localized states can be gained by studying the a.c. conductivity. For a wide variety of low-mobility solids, the a.c. conductivity due to the hopping of carriers is expected to be proportional to ω^s where $0.5 < s < 2$, whereas normal band type a.c. conductivity is expected to be largely frequency independent.

To explain the conductivity data, one has to consider the probable conduction mechanisms in the material. In $3d$-transition metal compounds the conduction mechanisms are expected to be rather complex due to the complexity of their electronic structure. However, one can gain some idea of the conduction process by considering the frequency and temperature dependence of the electrical conductivity.

In $MnWO_4$, as in many other $3d$-transition metal oxides, the $2s$ and $2p$ oxygen orbitals strongly overlap the $4s$ and $4p$ orbitals of the $3d$-transition metal ions. This gives rise to a strong hybridization leading to a wide energy band gap between the top of the filled $2p$ band and the bottom of the $4s$ and $4p$ conduction bands. The narrow $3d$ bands of the transition metal cation lie within this energy gap and are split by the crystal and exchange fields. Therefore, two competing processes can be expected to contribute to the observed electrical conduction in these materials. In $MnWO_4$, conduction by the hopping of charge carriers in the narrow $3d$ bands appears to be the dominant mechanism at the lower temperatures, below 575 K, as inferred from the $\sigma \sim \omega^s$ dependence and the small activation energy of 0.65 eV. For $MnWO_4$ single crystals, Bharati *et al.* [5] have estimated the drift mobility of carriers, using electrical conductivity and thermoelectric data, to be $\sim 1 \times 10^{-3}$ cm^2 V^{-1} s^{-1}. This low value of the mobility, the ionic nature of the compound and the presence of the $3d$-narrow bands strongly suggest the possibility of polaron formation by the holes in this

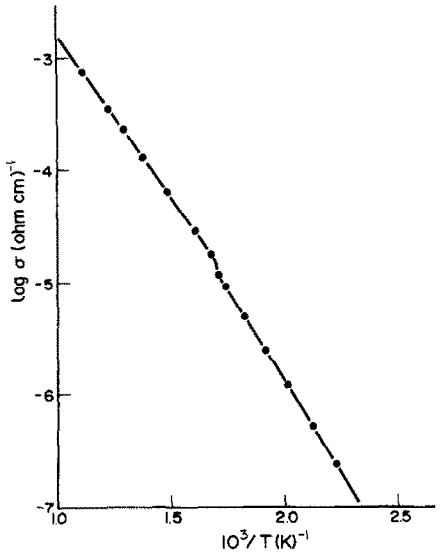

Fig. 2. Variation of a.c. conductivity at 10 Hz with temperature for $MnWO_4$.

material. Thermally activated hopping of polarons from a Mn^{2+} site to a Mn^{3+} site could give rise to the observed $\sigma \sim \omega^s$ type dependence characteristic of the hopping of carriers between localized states [8–10].

The discontinuity observed in the log σ vs $1/T$ plot at 575 K clearly shows that there is a change in the nature of the transport process at this temperature. The frequency independent behavior of conductivity over a wide temperature range at the higher temperatures suggests that the dominant conductivity mechanism at temperatures above 575 K could be a band-type conduction by polarons. The small value of 0.58 eV obtained for the activation energy above 575 K may be taken as evidence for the polaron motion within a narrow d band, making the dominant contribution to the conduction process at these temperatures. The possibility of multiple hops between localized states could also give rise to a frequency independent a.c. conductivity at higher temperatures as the hopping process is phonon assisted [8, 9]. However, in that case, one should expect to see a gradual change in the slope in the log σ vs $1/T$ plot shown in Fig. 2. The appearance of a discontinuity in the slope in Fig. 2 evidently rules out the possibility of phonon assisted multiple hops at the higher temperatures.

With the available data it is difficult to identify the exact nature of the polarons participating in the conduction process. We have noted, however, that fitting our data to the equation $\sigma T = \sigma_0 \exp(-Q/kT)$ in the log σT vs $1/T$ form does not result in a linear plot. This may be used to rule out the possibility of conduction by small polarons. On the other hand, the observed linearity of the log σ vs $1/T$ plots at both lower and higher temperatures suggests that the charge carriers involved in the conduction process are large polarons obeying the transport equation $\sigma = \sigma_0 \exp(-Q/kT)$.

5. CONCLUSION

An investigation of the frequency and temperature dependence of the a.c. conductivity in $MnWO_4$ suggests that electrical conduction at temperatures below 575 K occurs essentially by the hopping of polarons between two localized states. Above this temperature, normal band-type motion of polarons appears to be the dominant conduction process. The results obtained are generally in agreement with the mechanisms suggested by other workers [5].

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