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On the electrical conductivity, thermoelectric power and dielectric constant of $ZnMoO_4$

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Abstract : Measurements of electrical conductivity, thermoelectric power and dielectric constant were performed on a polycrystalline sample of zinc molybdate over an extensive range of temperature (300–1250 K). It is found that the compound is *n*-type semiconductor with energy band gap 2.94 eV Combining electrical conductivity and thermoelectric power data, we have estimated activation energy and charge carrier mobility which show that the conduction is of the normal band type.

Keywords Electrical conductivity, thermoelectric power, dielectric constant, zinc molybdate

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1. Introduction

Zinc molybdate ($ZnMoO_4$) is a member of isostructural series of $3d$-transition metal molybdates. Diamagnetic $ZnMoO_4$ is triclinic with lattice constant [1] $a = 9.625 \pm 0.015$ Å, $b = 6.965 \pm 0.010$ Å, $c = 8.373 \pm 0.015$ Å, $\alpha = 103.28 \pm 0.15°$, $\beta = 96.30 \pm 0.15°$ and $\gamma = 106.72 \pm 0.15°$ at 298 K with six formula weight in the unit cell. It has formula weight (f_w) = 225.308 and melting point 1125°C [2]. This paper reports our study on the a.c. and d.c. electrical conductivities, thermoelectric power and dielectric constant of $ZnMoO_4$, which do not appear to have been studied earlier.

2. Experimental technique

The material, zinc molybdate (purity 99.99%), was obtained from M/S Rarco Research Lab., Bombay, India. The impurities (0.01%) expected were in the form of oxides or molybdates. The measurements were made using powdered specimens pelletized at a pressure of 7.0×10^6 gm cm^{-2}, as well as a hand-operated hydraulic press and a suitable die. The pellets were

annealed for 24 hrs at 1200 K, in a tightly closed platinum crucible. The pellets were cleaned, dried and gently silver painted on two faces before they were put into the sample holder. The sample holder for thermoelectric power measurements was specially designed for this purpose. A thermal gradient ($\Delta T \approx 20$ K) is produced across the sample with the help of a small heater placed just below one of the platinum electrodes. The thermoelectromotive force (ΔE) and electrical conductivity (σ_{dc}) was measured by a digital multimeter (PM 2522/90, Philips, India) with an accuracy better than ± 0.25% and ± 0.20% in the case of resistance and e.m.f. measurements respectively. For all the measurements, the two electrode-method was employed. A.c. conductivity and dielectric constant were measured using auto computing LCR-Q meter (4910, Applied Electronics Ltd., Thana, India) which operates at an internal frequency of 1 kHz. The procedural details are described elsewhere [3,4].

3. Results and discussion

The electrical conductivity (σ_p) and the density (d_p) of pellets annealed round 1200 K for 24 hours, increase almost linearly with pelletising pressure (P) upto $P \approx 3.0 \times 10^6$ gm cm^{-2}. This increase becomes slow for higher values of P and is almost constant for pellets made at 6.0×10^6 gm cm^{-2}. However, the density of the pellets made at high pressure ($P > 7.0 \times 10^6$ gm cm^{-2}), remains slightly less than the reported X-ray density (d_o) of the material. Thus to account for the pore fraction $f = (d_o - d_p)/d_o$, σ_p have been corrected. The crystalline value of σ_c has been obtained using the relation [5]

$$\sigma_c = \sigma_p \left(1 + \frac{f}{1 + f^{2/3}}\right). \qquad (1)$$

The thermoelectric power (S) value does not significantly depend upon P and therefore no correction for pore fraction has been applied to it.

The σ values initially depend on heating and cooling cycles but after few heating and cooling cycles, they repeat in successive cycles. These repeatable values have been taken as the bulk values of the parameter for the solid. Electrical conductivity does not depend upon the electrode materials (silver paint, platinum foil *etc.*) within the accuracy of our measurement.

The variation of $\log\sigma_{dc}$ and $\log\sigma_{ac}$ with $10^3/T$ is shown in Figure 1. It is seen that the curve is linear in the temperature range 300–1250 K. The a.c. and d.c. conductivities are almost the same for $T \approx 700$ K except that at lower temperature $\sigma_{dc} < \sigma_{ac}$. Figure 2 shows the variation of S *vs* $10^3/T$ plot in the temperature range 300-1250 K. Thermoelectric power (S) is negative in the entire temperature range studied, showing that majority charge carriers are electrons.

It is common to explain electrical transport in solids using band theory with appropriate scattering mechanism. In transition metal solids 3*d*-orbital split into a lower triplet of t_{2g} symmetry and a higher doublet of e_g symmetry. Intrinsic conduction in this compound will result from electron transfer from the filled valence (O^{2-} : $2p$) band to the empty

conduction (derived from octahedral Zn^{2+} : t_{2g} states) band. On a two band model, the electrical conductivity of intrinsic semiconductors can be expressed by the relations [6]

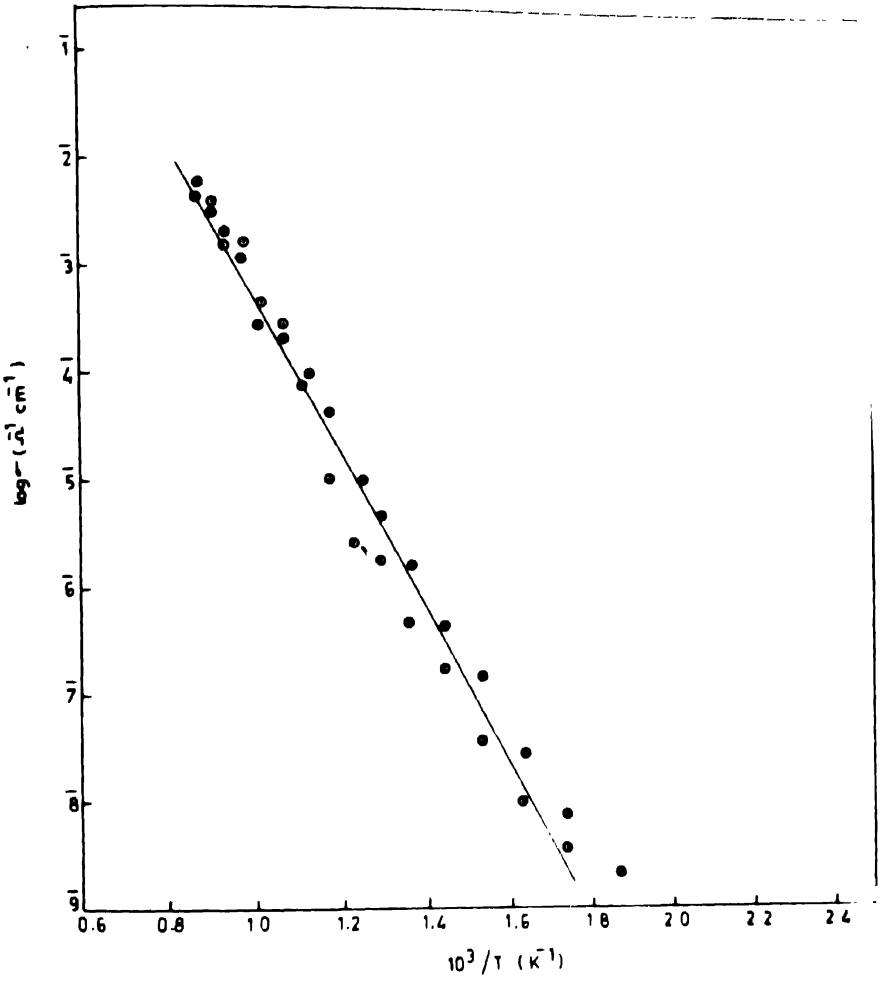

Figure 1. Variation of electrical conductivity (log σ_{ac} and log σ_{dc}) with inverse of temperature ($10^3/T$) in $ZnMoO_4$. (Θ) d.c conductivity, (●) a.c. conductivity

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

or

$$\sigma = \sigma_0(T) \exp\left(-E_g/2kT\right), \tag{3}$$

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

$$= K'T^{3/2} a^{3/4} (1 + c) m_h^{3/2} \mu_h, \tag{5}$$

$$K' = 2e\left(\frac{2\pi k}{h^2}\right)^{3/2}, \qquad a = \left(\frac{m_e}{m_h}\right), \qquad c = \left(\frac{\mu_e}{\mu_h}\right),$$

where m_e and m_h are effective masses of the electron and hole, μ_e and μ_h are the mobilities of electron and hole respectively and E_g is the energy band gap of the solid. The variation of $\sigma_0(T)$ with temperature is negligibly small in comparison to exponential term in eq. (2).

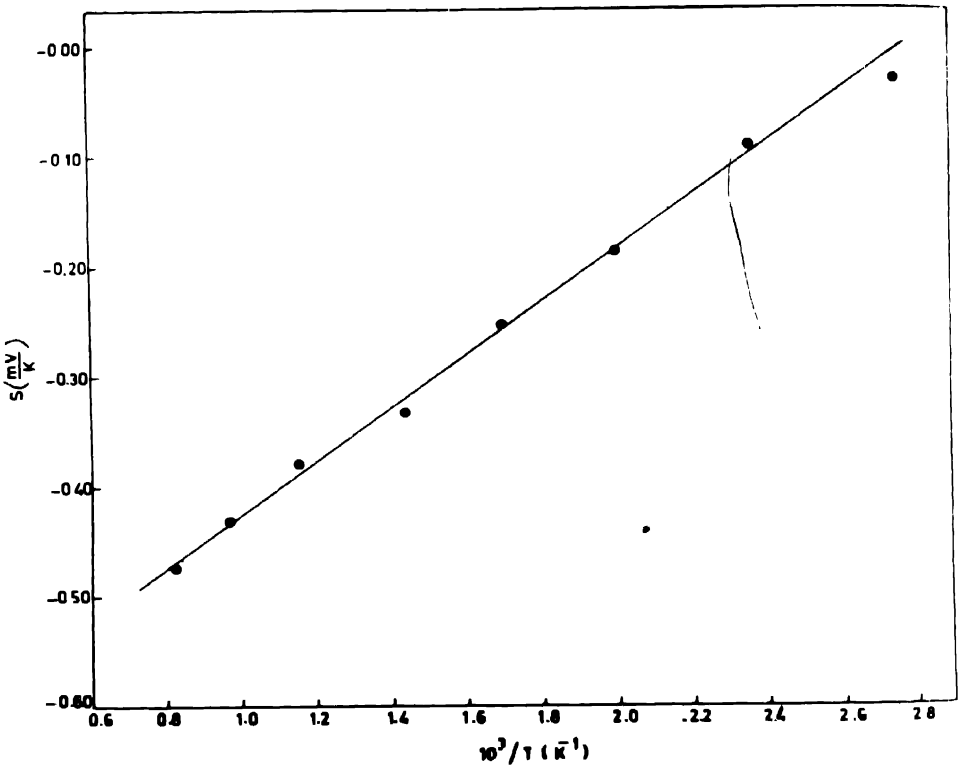

Figure 2. Variation of thermoelectric power (S) with inverse temperature ($10^3/T$) in $ZnMoO_4$

Hence, the plot of log σ *vs* $1/T$ curve should be a straight line for intrinsic semiconductors The plot of log σ *vs* $10^3/T$ curve are actually a straight line in the temperature range measured From this curve we have evaluated $\sigma_0(T)$ and E_g for this material, which comes out to be 1.20 $\times 10^4$ ohm^{-1} cm^{-1} and 2.94 eV respectively.

Two band model in the simplest approach yield following relation for the variation of thermoelectric power (S) with temperature [6]

$$S = \left[\frac{E_g}{2e}\left(\frac{c-1}{c+1}\right)\frac{1}{T} + \frac{2k}{e}\left(\frac{c-1}{c+1}\right) + \frac{3k}{4e}\log_e a\right] \tag{6}$$

or

$$S = \frac{\cdot\cdot 1}{T} + K \tag{7}$$

with
$$\frac{E_g}{2e}\frac{(c-1)}{(c+1)}, \tag{8}$$

$$K = \frac{2k}{e}\left(\frac{c-1}{c+1}\right) + \frac{3k}{4e}\log_e(a). \tag{9}$$

In band conduction it is reasonable to assume that both c and a will be fairly constant with temperature. Thus, a plot of S *vs* $10^3/T$ should yield a straight line. The experimental S *vs* $10^3/T$ curve is actually a straight line and give good support to the band conduction in this

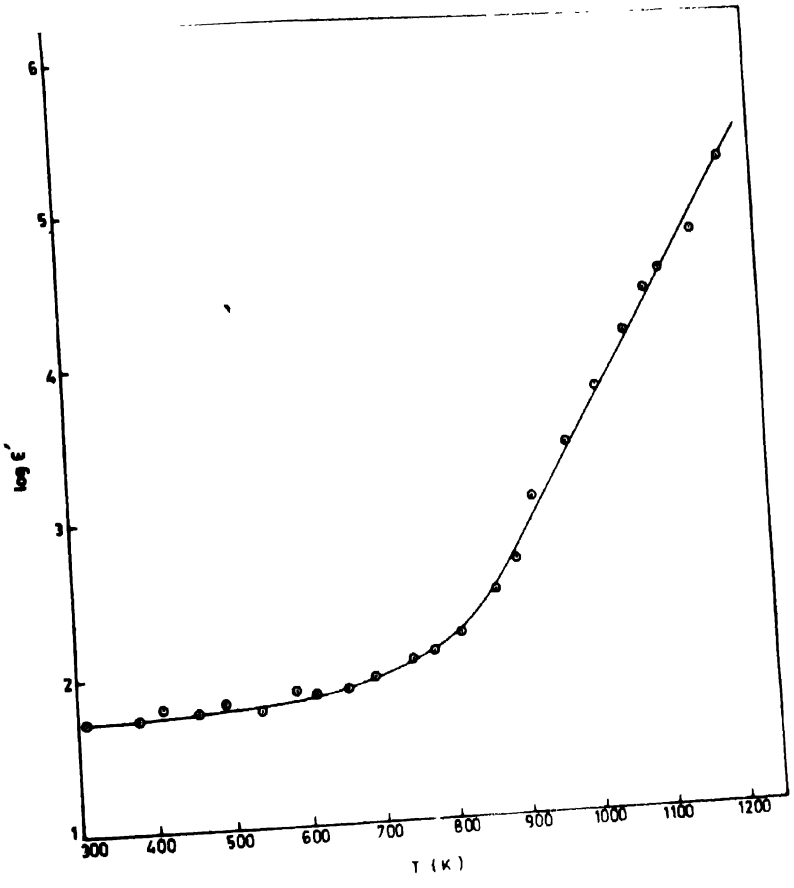

Figure 3. Variation of static dielectric constant (log ε') with temperature (T) in $ZnMoO_4$.

solid. It is easy to evaluate $c(=\mu_e/\mu_h)$ and $a(=m_e/m_h)$ from eqs. (7), (8) and (9) which are 0.7346 and 0.1559 respectively. From the evaluated value of (c), (a) and $\sigma_0(T)$ and taking $m_h = 10\,m$ (m is the free electron mass, we have taken $m_h = 10\,m$ bearing in mind narrow d-band), mobility of electron (μ_e) was estimated as 48 $cm^2\,V^{-1}\,sec^{-1}$.

The value of activation energy, 1.47 eV, $\sigma_0(T)$, 1.2×10^4 ohm^{-1} cm^{-1}, charge carrier mobility, 48 cm^2 V^{-1} sec^{-1} and the mean free path (L), which has been estimated using the expression [7]

$$L = \frac{3\mu}{4e}\sqrt{2\pi kT m_h}, \tag{10}$$

is 182.46 Å. Higher values of the charge carrier mobility and mean free path and a decrease in the mobility with temperature (as clear from the decrease in thermoelectric power with temperature) [8] confirm that in $ZnMoO_4$ the conduction is normal band type.

The static dielectric constant, ε', was measured in the temperature range 300-1250 K by measuring the capacitance of the capacitor formed with the pellet as the dielectric medium, using the relation [9]

$$\varepsilon' = C^{\,11.3\,t} \tag{11}$$

where C is the capacitance (pF), t is the thickness of the pellet (cm) and A is the surface area of the electrode (cm^2). The plot of log ε' *vs* T is shown in Figure 3. The dielectric constant ε' slowly increases with temperature up to 700 K and above 700 K, ε' increases rapidly. The slow variation of the dielectric constant with temperature is the usual trend in ionic solids [10] (ionicity of ZnO ≈ 0.6 to 0.7). The temperature has a complicated influence on the dielectric constant. Generally, increasing the temperature of a material, decreases the electronic polarization. The increase of ionic distance due to the temperature, influences the ionic and electronic polarizations. The decrease in electronic dielectric constant for many solids is found to be less than 3% for a temperature change of about 400°C [11]. Similarly, the changes in ionic polarization are not very large. Moreover, according to Debye's theory ε' is inversely proportional to temperature if the presence of a small number of dipoles and their contribution to dielectric constant is assumed. Therefore, it is expected that the dielectric constant of $ZnMoO_4$ should not change considerably with increasing temperature. However, in the present measurements of ε' *vs* temperature, we observe an increase of ε' with T. This increase in ε' may be due to space charge polarization, caused by impurities or interstitials.

Above 700 K, the rapid increase in ε' with temperature is due to the intrinsic nature of the compound. In the intrinsic semiconductors, the number of charge carriers increases exponentially with increasing temperature, which increases the dielectric constant to a large extent. Also in the narrow band semiconductors, the charge carriers are not able to move freely with the electric field. If these charges are trapped, a space charge polarization builds up and the macroscopic field distortion results. Due to this phenomena the dielectric constant of $ZnMoO_4$ increases rapidly above 700 K.

Acknowledgments

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