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Electrical transport properties of iron (II) molybdate

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Electrical conductivity, thermoelectric power and static dielectric constant of iron (II) molybdate have been measured in the temperature range 300 to 1000 K on pressed pellets of polycrystalline sample. It has been found that $FeMoO_4$ is a p-type semiconductor with energy gap 4.1 eV. Different conduction mechanisms have been found below and above 700 K. Below 700 K conduction is due to a small polaron hopping mechanism and above 700 K conduction is due to large polarons as well as normal band conduction mechanism. Activation energy W, $\sigma_0(T)$ and charge carrier mobility μ have been estimated in the two temperature ranges 300 to 700 K and 700 to 1000 K. Dielectric constant increases slowly with temperature up to 700 K and above 700 K, it increases exponentially with temperature.

1. Introduction

The role of iron (II) molybdate ($FeMoO_4$) in the catalytic oxidation processes [1] and its peculiar crystal structure [2] have drawn considerable attention of various scientists towards it. Normally 3d-transition metal molybdates crystallize in either Wolframite or Scheelite structure and the ideal Wolframite structure is monoclinic but $FeMoO_4$ is triclinic [3]. The crystal parameters of $FeMoO_4$ are $a = 0.49443$, $b = 0.57006$ and $c = 0.44078$ nm, $\alpha = 93.32$, $\beta = 90.27$ and $\gamma = 89.33$. The thermodynamic parameters of $FeMoO_4$ have been estimated by Weller [4] and these are $\Delta H_f^0 = -257\,\text{kcal mol}^{-1}$, $\delta G_f^0 = -233\,\text{kcal mol}^{-1}$, $\Delta S^0 = 30.9\,\text{cal K}^{-1}\text{mol}^{-1}$. Heat capacity measurements of $FeMoO_4$ has also been done [5]. The study of electrical conductivity, thermoelectric power and dielectric constant as a function of temperature represents a well established method for investigating defect structures and transport properties of oxide systems [6]. The electrical and magnetic properties of this compound are still unstudied. So in order to understand electrical conduction in iron (II) molybdate, we have measured, electrical conductivity, thermoelectric power and dielectric constant of it in the temperature range 300 to 1000 K and obtained data have been analysed in the light of various conduction mechanisms i.e. band model, localized model.

2. Experimental details

Iron (II) molybdate (purity 99.99%) has been procured from M/S Rare and Reaseach Chemicals, Bombay, India and has been used as such in our measurements. Due to lack of crystal growth facilities in our laboratory, we have used pressed pellets of the polycrystalline sample for various measurements. The pellet on which the final measurements were carried out was made at a pressure $8 \times 10^6\,\text{g cm}^{-2}$. The pellet was in the cylindrical form with diameter 1.15 cm and thickness 0.30 cm. Before mounting the pellet in the sample holder assembly, it was annealed at temperature 700 K for 24 h in a closed platinum crucible, in order to avoid oxidation at higher temperatures. The surfaces of the pellet, which were in contact of platinum electrodes were painted with the silver paint, obtained from the National Physical Laboratory, New Delhi, India, to ensure better electrical contact. In the case of electrical conductivity and thermoelectric power measurements annealing of the sample and painting of the surfaces in contact of the electrodes are very necessary to obtain good results [7].

The electrical conductivity and thermoelectric power have been measured with the help of a digital multimeter PM 2522/90, Philips (India), with an accuracy better than ±0.25% and ±0.20% in case of resistance and e.m.f. measurements respectively. Dielectric constant has been estimated by measuring the capacitance of a capacitor with the pellet as dielectric medium. A suitable sample holder has been used for this purpose. The capacitance has been recorded with the help of a Universal LCR Bridge model 901, Ruttonsha Simpson, India which works at an internal frequency of 1 kHz with the accuracy ±1.25% of the reading ±0.25% at full scale range. All the measurements for dielectric constant have been done at a fixed frequency of 1 kHz.

For thermoelectric power measurements, the temperature difference of $\Delta T = 20^\circ$C was produced across the pellet with the help of a microfurnace fitted with the sample holder assembly and the temperatures of both the surfaces have been recorded by chromel–alumel thermocouple wires attached with the platinum electrodes. Ambient temperature has been taken as the average of temperature of both the surfaces of the pellet. In all the measurements mica sheets have been used for thermal as well as electrical insulation purposes. The details regarding measuring procedure and other experimental details are given elsewhere [8].

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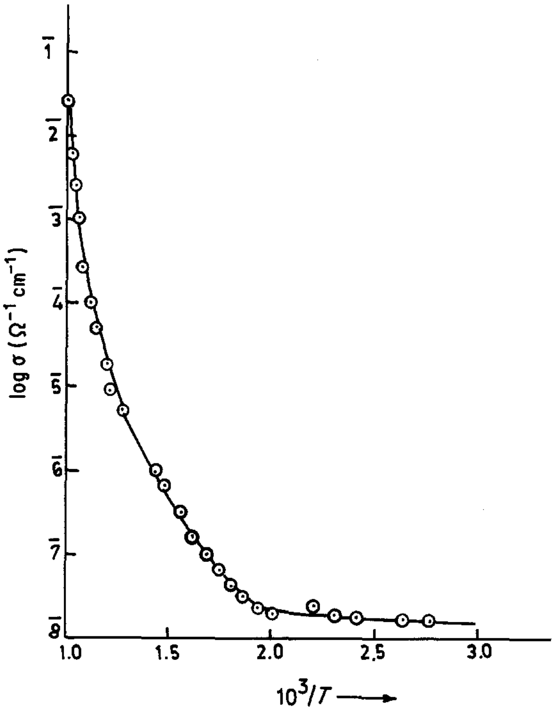

Figure 1 Variation of electrical conductivity (log σ) against reciprocal temperature ($10^3/T$) in iron (II) molybdate.

3. Results

Electrical conductivity σ, thermoelectric power S and static dielectric constant ε' of polycrystalline iron (II) molybdate have been measured in the temperature range 300 to 1000 K using two electrode method. Fig. 1 shows the logarithm of electrical conductivity against reciprocal temperature. Variations of thermoelectric power S with $10^3/T$ and log ε' with T are shown in Figs 2 and 3 respectively. The results indicate the semiconducting nature of the material and the positive value of thermoelectric power, investigated in the entire temperature range measured, shows that the majority charge carriers are holes. A marked change in slope at 700 K was observed in the three figures. This can be associated with the transition from extrinsic to intrinsic nature of the compound. Using the relations [9]

$$\sigma = \sigma_0 \exp(-(W/kT)) \tag{1}$$

with

$$\sigma_0(T) = K' a^{3/4}(1 + c) m_h^{3/2} \mu_h \tag{2}$$

where

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

(m_e, μ_e and m_h, μ_h are masses and mobilities of electrons and holes respectively)

$$\eta = \frac{E_g}{2e}\left(\frac{c - 1}{c + 1}\right) \tag{4}$$

where η is slope of S against $10^3/T$ curve and

$$K = \frac{2k}{e}\left(\frac{c - 1}{c + 1}\right) + \frac{3k}{4e}\log_e(a) \tag{5}$$

We have estimated activation energies, $\sigma_0(T)$ and charge carrier mobilities in the two temperature ranges 300 to 700 K and 700 to 1000 K and the data are given in Table I.

The static dielectric constant ε' of FeMoO$_4$ has been measured at a fixed frequency of 1 kHz and value of ε' at different temperatures has been calculated using the relation

$$\varepsilon' = C\frac{11.3t}{A} \tag{6}$$

where C is capacity in picofarads, t is thickness of the pellet in centimetres and A is surface area of the electrode in centimetres squared. It is evident from the Fig. 3 that the static dielectric constant increases slowly with temperature and the trend of increase in ε' is similar to the trend of increase in electrical conductivity with a change in slope at 700 K. The rate of increase of ε' is slow up to 700 K and after that it increases exponentially with temperature.

4. Discussion

The electrical transport data, given in the Table I, clearly indicate two different conduction mechanisms,

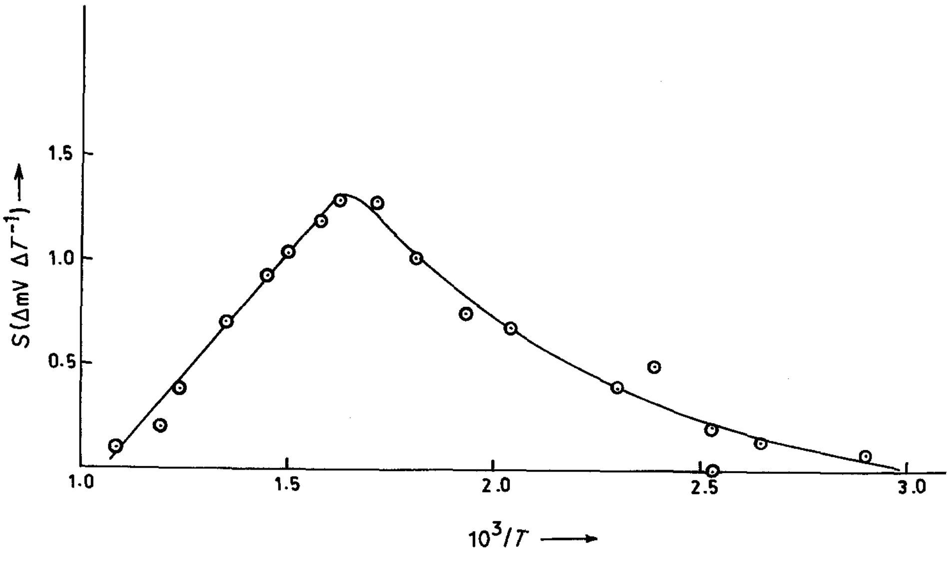

Figure 2 Variation of thermoelectric power (S) against reciprocal temperature ($10^3/T$) in iron (II) molybdate.

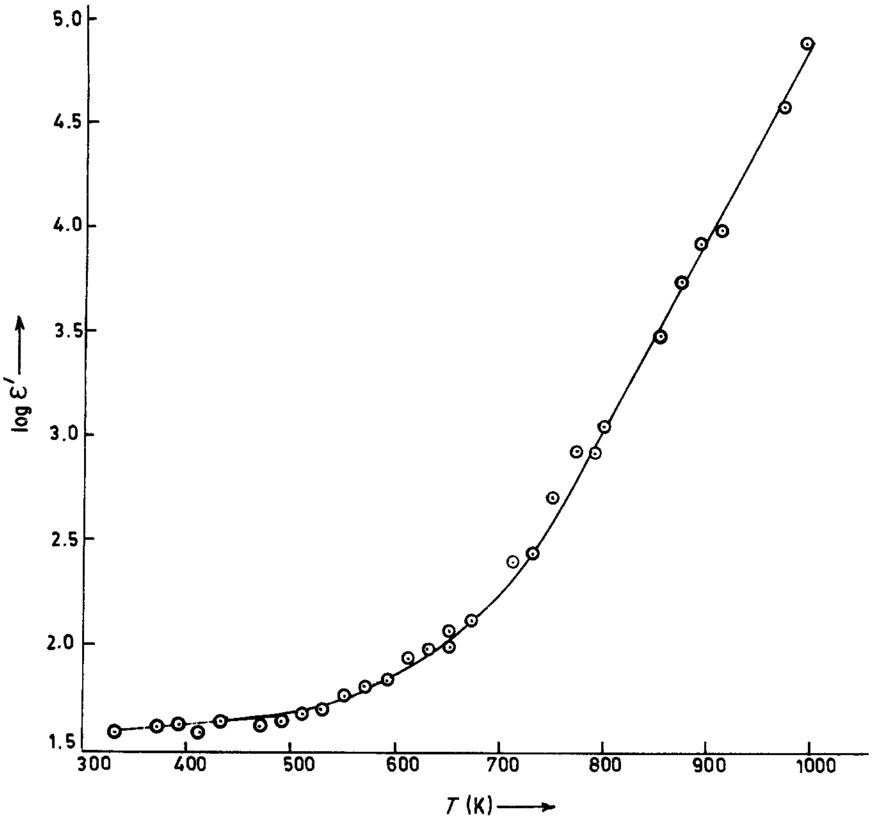

Figure 3 Variation of static dielectric constant (log ε′) against temperature (T) in iron (II) molybdate.

below and above 700 K, in iron (II) molybdate. The extremly low value of activation energy $W = 0.06\,\text{eV}$ and the hole mobility $9 \times 10^{-3}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$, calculated from the electrical conductivity and thermoelectric power measurements, suggests extrinsic conduction, governed by native defects or interstitials and impurities present in the forbidden energy gap of the material. Such impurities or defects may not be removed easily in transition metal oxides. Moreover $FeMoO_4$ is a highly ionic material (ionicity of FeO 0.9 to 0.8) [10] and FeO is an oxygen excess compound, so excess oxygen atoms as interstitials are always present in this material. In view of the low activation energy 0.06 eV and charge carrier mobility $9 \times 10^{-3}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$, the electrical conduction in iron (II) molybdate may take place either by band type conduction of ionized impurity centres or by some sort of polaronic motion. The band type conduction of ionized impurity centres contribute to conductivity, according to the relation [11]

$$\sigma_d = A \exp(-E_i/kT) \qquad (7)$$

where E_i is the ionization energy of donors or acceptors. Usually $E_i \sim 0.1\,\text{eV}$. The activation energy, calculated by us below 700 K is 0.06 eV which is much less than the ionization energy $E_i \sim 0.1\,\text{eV}$. Moreover this model should not be taken seriously for a material having narrow energy bands or a magnetic material, because the electrons or holes, though coming from impurity centres, will interact later on and will behave like polarons. So the band type conduction of ionized impurity centres is ruled out in this material. The only possibility left with us is to consider small polaron conduction below 700 K in $FeMoO_4$ due to low value of the charge carrier mobility $9 \times 10^{-3}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$. Small polaron formation is also probable in this material due to the fact that in narrow band, low mobility semiconductors, like transition metals or rare earth oxides, there is strong coupling between charge carriers and lattice vibrations [12]. At low temperature, the small polarons move by Bloch type band motion while at higher temperature, they move by a thermally activated hopping process. The small polaron band conduction is not possible for such a temperature range 300 to 700 K [13]. So it seems probable that small polaron hopping conduction is responsible for electrical transport in $FeMoO_4$ below 700 K. The contribution of a small polaron hopping mechanism towards electrical conductivity is given by the relation [14, 15]

$$\sigma T^{1/2} = A \exp(-W_H/kT) \qquad (8)$$

where W_H is small polaron hopping energy. We have plotted $\log(\sigma T^{1/2})$ against $10^3/T$ for temperatures below 700 K and the plot is shown in Fig. 4. The curve is a straight line and the hopping energy calculated from the slope of the curve is 0.08 eV. The small

TABLE I Activation energy $\sigma_0(T)$ and charge carrier mobility of $FeMoO_4$

Temperature range (K)	Activation energy (eV)	$\sigma_0(T)$ ($\Omega^{-1}\,\text{cm}^{-1}$)	Charge carrier mobility
300 to 700	0.06	1.05×10^{-7}	$9 \times 10^{-3}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$ ($m_h = 100\,m$, $T = 600\,\text{K}$)
700 to 1000	2.1	1.35×10^{8}	$0.06\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$ ($m_h = 10\,m$, $T = 800\,\text{K}$)

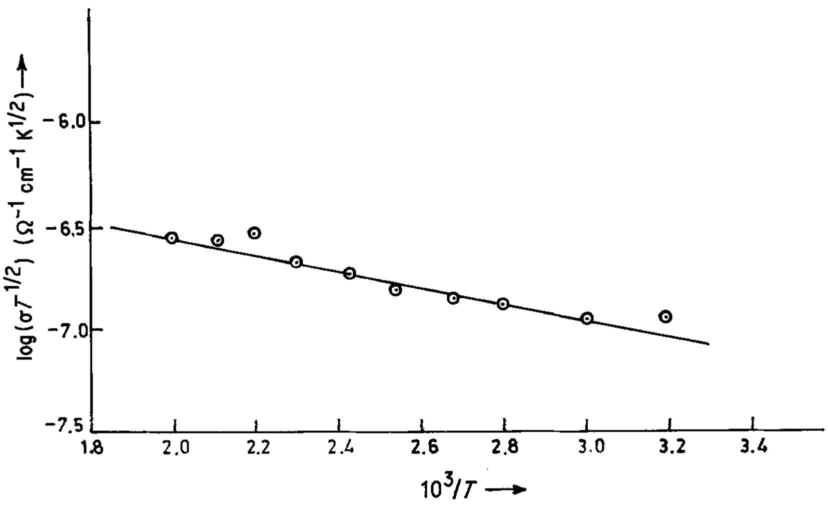

Figure 4 Variation of log $(\sigma T^{1/2})$ against reciprocal temperature $(10^3/T)$ in iron (II) molybdate.

polaron hopping energy 0.08 eV is in reasonable agreement with the activation energy 0.06 eV below 700 K for $FeMoO_4$, therefore we conclude that the electrical conduction in iron (II) molybdate below 700 K is due to small polaron hopping mechanism and the activation energy is entirely due to thermally increased mobility which increases according to the relation [12]

$$\mu^{sp} = \frac{\mu_0}{T^{3/2}} \exp\left(-\frac{E_m}{kT}\right) \qquad (9)$$

where E_m is the activation energy for mobility. The mobility is an exponentially increasing function of temperature. Since the conduction below 700 K in $FeMoO_4$ is due to small polaron hopping mechanism as a result of lattice defects, interstititals and impurities, the charge carrier concentration becomes constant after certain temperature and the increase in electrical conductivity and thermoelectric power is solely due to increasing mobility of charge carriers which increases exponentially with temperature.

The intrinsic nature of compound arises above 700 K with the activation energy 2.1 eV and the charge carrier mobility 0.06 $cm^2 V^{-1} sec^{-1}$ (m_h = 10 m, T = 800 K). The value of activation energy 2.1 eV suggests normal band conduction in iron (II) molybdate because for normal band conduction the activation energy should be of the order of 2.3 eV [16] but the charge carrier mobility 0.06 $cm^2 V^{-1} sec^{-1}$ indicates large polaron band conduction, which conducts via normal band conduction with enhanced mass of charge carriers. In iron (II) molybdate, the bands available for conduction are O^{2-} : 2p, Fe^{2+} : $3d^4$, Mo^{6+} : 4d along with 4s and 4p bands associated with Fe^{2+} ions. For normal band conduction involving O^{2+} : 2p and Fe: $3d^4$, 4s, 4p bands, the activation energy should be of the order of 2.3 eV, which is almost equal to our estimated value of activation energy. Moreover, iron (II) molybdate contains narrow 3d bands and these narrow 3d bands split into a lower six fold degenerate (t_{2g}) sub-band and an upper four-fold (e_g) sub-band due to octahedral crystal field splitting [17]. Hence the valence band will comprise of filled O^{2-} : 2p and Fe^{2+} : 3d ($t_{2g}\uparrow^3 e_g \uparrow^2 t_{2g}\downarrow^1$) bands and the conduction band will contain empty Fe^{2+}: 3d ($t_{2g}\downarrow^2 e_g \downarrow^2$) and Mo^{6+}: 4d along with 4s and 4p bands associated with Fe^{2+} ions.

The decrease of thermoelectric power with increasing temperature is associated with the large polaron conduction. The mobility of large polarons decreases with temperature [18] consequently a decrease in thermoelectric power. It is due to the fact that the exponential increase in the number of electrons and mobility of negative charge carriers compensate rapidly for some of the positive charge carriers which reduces the net thermoelectric power. Due to these factors, low mobility semiconductors are impracticable for thermoelectric applications [19].

The slow variation of ε' with temperature up to 700 K is due to ionic nature of the compound [20]. This is due to lattice expansion and polarizability of the ions is affected by the changes in the temperature and the available volume. The exponential increase in ε' above 700 K is due to large polaron formation. These large polarons increase the polarizability of the ions to a greater extent resulting thereby a large increase in ε'. The exponential increase of charge carriers above 700 K also contributes towards dielectric constant.

5. Conclusions

(a) The results of the electrical conductivity, thermoelectric power and static dielectric constant show the semiconducting nature of the compound with energy gap 4.1 eV. The majority charge carriers are holes.

(b) A marked change in conduction mechanism occurs at 700 K. Below 700 K there is an extrinsic conduction and above 700 K an intrinsic condution occurs.

(c) Two different conduction mechanism are responsible for electrical conduction. Below 700 K, electrical conduction is due to a small polaron hopping mechanism and above 700 K, large polaron as well as normal band conduction are responsible for electrical conduction.

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