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Electrical properties of iron (III) molybdate

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Electrical transport properties, i.e. a.c. and d.c. electrical conductivities, thermoelectric power and dielectric constant, of $Fe_2(MoO_4)_3$ have been measured in the temperature range 300 to 1000 K on pressed pellets of a polycrystalline sample, using the two electrode method. Iron (III) molybdate has been found to be a p-type semiconductor with an energy gap of 3.1 eV. Intrinsic conduction occurs at ~ 750 K and the activation energies below and above 750 K are 0.51 and 1.55 eV, respectively. The thermoelectric power increases up to ~ 750 K and after that it decreases with increasing temperature. The dielectric constant increases with temperature over the entire temperature range measured except 650 to 750 K, where it has a constant value.

1. Introduction

Because of the extensive use of transition metal molybdates as catalysts and pigments and their use in the electronic industry, these compounds form a very important series of mixed oxides of 3d transition metals. The crystallographic properties of iron (III) molybdate have been extensively studied by various workers [1–3]. The crystal structure of $Fe_2(MoO_4)_3$ is monoclinic with space group $P^2 1/a$ and subcell Pnca. The structure consists of 16 FeO_6 octahedra and 24 MoO_4 tetrahedra; all the octahedra and tetrahedra are isolated from each other and share only corners. Different crystal parameters of $Fe_2(MoO_4)_3$ have been reported; according to Kafeli [1], they are $a = 1.55\,nm$, $b = 0.92\,nm$, $c = 1.81\,nm$ and $\beta = 125°$, and according to Chen [3] they are $a = 1.5707\,nm$, $b = 0.9231\,nm$, $c = 1.8204\,nm$ and $\beta = 125.25°$.

Mössbauer studies [4, 5] and polymorphism [6] in iron (III) molybdate have also been reported and the electrical conductivity of $Fe_2(MoO_4)$ has been measured [5, 7], but thermoelectric power and dielectric constant of this compound are still unreported. In order to understand electrical conduction in iron (III) molybdate, we have measured its a.c. and d.c. electrical conductivities, thermoelectric power and dielectric constant in the temperature range 300 to 1000 K and the data obtained have been analysed in the light of various conduction mechanisms involving band models and polaronic models.

2. Experimental details

Polycrystalline ferric molybdate [$Fe_2(MoO_4)_3$] powder, purity 99.99%, supplied by M/S Rare and Research Chemicals, Bombay, was used in these studies, in the form of pressed pellets. The material was crushed to very fine powdered form using an agate mortar and a pestle. It was found that electrical conductivity and thermoelectric power varied with pressure and became independent of pressure above $6 \times 10^6\,g\,cm^{-2}$ and therefore the pellet on which final measurements were carried out was made at a pressure of $6.5 \times 10^6\,g\,cm^{-2}$. Its diameter was 1.10 cm, its thickness 0.10 cm and its density was $3.24\,g\,cm^{-3}$, which is 72% of the crystal density of $Fe_2(MoO_4)_3$ ($4.49\,g\,cm^3$). Before mounting the pellet in the sample holder assembly, it was annealed at a temperature of 800 K for 18 h in a tightly closed platinum crucible in order to avoid oxidation at higher temperature.

The crucible was tightly closed by a pressed-on lid, initially with air inside. Annealing of the material leads to diffusion of grain boundaries and there is linking up of grains to form a connected structure. The gradual removal of pores leads to densification of the pellet [8, 9]. After annealing, the pellet reduced to about three-quarters of its initial volume and its density became $4.18\,g\,cm^{-3}$, which is 93% of the theoretical crystal density of the ferric molybdate ($4.49\,g\,cm^{-3}$). Annealing was done at 800 K because $Fe_2(MoO_4)_3$ partly decomposes above 820 K [10]. Both the surfaces which were in contact with platinum electrodes were painted with silver paint obtained from the National Physical Laboratory, New Delhi. Annealing and painting the surfaces of the pellet were very necessary in order to obtain good results from electrical conductivity and thermoelectric power measurements.

The d.c. electrical conductivity and thermoelectric power were measured using a digital multimeter (PM 2522/90 Philips, India) with accuracies better than ±0.25% and ±0.20% for resistance and e.m.f. measurements, respectively. The a.c. electrical conductivity was measured using a Universal LCR Bridge (901-I, Ruttonsha Simpson, India), which operates at an internal frequency of 1 kHz with an accuracy ±1.25% of the reading. The dielectric constant of the sample was determined at various temperatures by measuring the capacity of the parallel plate capacitor formed with the pellet as the dielectric medium. The capacity was recorded at a fixed frequency of 1 kHz, using the Universal LCR Bridge, the accuracy being the same as above.

For thermoelectric power measurement, a temperature difference of $\Delta T \sim 20°\,C$ was produced across the pellet using a microfurnace fitted with the sample

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holder assembly. The temperatures of both the surfaces were measured using chromel/alumel thermocouples firmly attached to the platinum electrodes. Each reading was taken after attaining thermal equilibrium (taking about 2.5 h) and the ambient temperature was taken as the average of the temperatures of the two surfaces of the pellet. In all the measurements, chromel/alumel thermocouples were used for temperature recording and mica sheets were used for thermal and electrical insulation purposes. The details of sample holder assembly, experimental arrangement and measuring procedure are given in our previous publications [11, 12].

3. Results and discussion

A.c. and d.c. electrical conductivities of $Fe_2(MoO_4)_3$ were measured in the temperature range 300 to 1000 K on the pressed pellet using the two-probe method. The variation of log $\sigma_{a.c.}$ and log $\sigma_{d.c.}$ with inverse temperature ($10^3/T$) are shown in Fig. 1. It is clear from Fig. 1 that the electrical conductivities follow the well-known exponential relation:

$$\sigma = \sigma_0(T) \exp(-W/kT) \qquad (1)$$

with two different slopes below and above about 750 K. In the $\sigma_{a.c.}$ curve there is an additional change in the slope at about 400 K. The activation energies and $\sigma_0(T)$, in the temperature ranges 300 to 750 and 750 to 1000 K were, respectively, determined from Fig. 1 and Equation 1 and calculated from the relation [13]:

$$\sigma_0(T) = K'T^{3/2}a^{3/4}(1 + c)m_e^{3/2}\mu_e \qquad (2)$$

where $K' = 2e(2\pi k/h^2)^{3/2}$

$$a = m_e/m_h, \; c = \mu_e/\mu_h$$

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

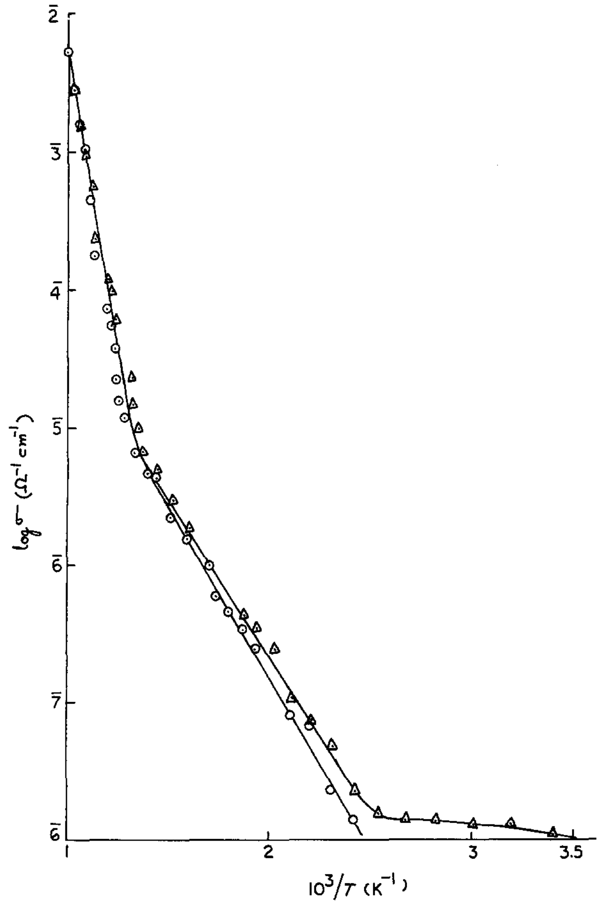

Figure 1 Variation of electrical conductivity (log $\sigma_{a.c.}$ and log $\sigma_{d.c.}$) with inverse of temperature ($10^3/T$) in iron (III) molybdate. (○) D.c. conductivity, (△) a.c. conductivity.

TABLE I Activation energy and $\sigma_0(T)$ for electrical conduction in $Fe_2(MoO_4)_3$

Temperature range (K)	Activation energy (eV)	$\sigma_0(T)(\Omega^{-1}cm^{-1})$
300–750	0.51	0.18×10^{-1}
750–1000	1.55	2.98×10^5

The values of $\sigma_0(T)$ and activation energies in different temperature ranges for the d.c. electrical conductivity are presented in Table I. At the lower temperatures ($T < 750$ K), the low value (0.51 eV) of the activation energy, and the observed values of σ, which are much larger than expected from the band theory of solids, show the influence of impurities, point defects or interstitials in this material. Defects and impurities cannot be eliminated easily or otherwise in any compound. The electrical conduction in iron (III) molybdate below ~750 K may be due to band-type conduction of ionized impurity centres or due to small polaron conduction. Band-type conduction of ionized impurity centres may be explained in terms of donors or acceptors [14] and its contribution to electrical conduction is given by the relation:

$$\sigma_d = A \exp(-E_i/kT) \qquad (3)$$

where E_i is the ionization energy of the donors or acceptors and E_i is usually ~0.1 eV. The activation energy calculated by us below 750 K is 0.51 eV, which is much larger than the ionization energy E_i (~0.1 eV), and hence the possibility of band-type conduction of ionized impurity centres is ruled out in this compound.

Because of the presence of narrow 3d bands Fe^{3+}: $3d^5$ in this compound, it seems that the impurity charge carriers become localized at lattice sites and thus form polarons. The increase in mobility of charge carriers, evidenced by increase in thermoelectric power up to ~750 K and its temperature dependence, suggest a small polaron hopping conduction in this compound below ~750 K, because small polaron band conduction is not possible at such high temperatures [15]. This conduction mechanism is also consistent with the localized electron model of Goodenough [16] for 3d-transition metal compounds having very narrow bands. The variation of electrical conduction is given by the relation [17]:

$$\sigma T^{1/2} = A(T) \exp(-W_H/kT) \qquad (4)$$

where W_H is the small polaron hopping energy and A is almost constant.

The activation energy above ~750 K is 1.55 eV, which seems to be the activation energy of intrinsic conduction in iron (III) molybdate. This value is

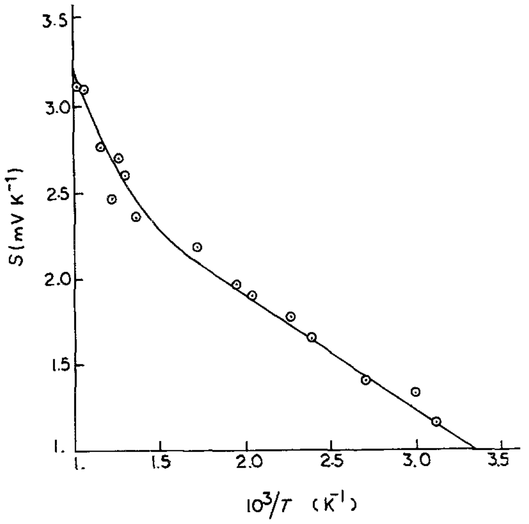

Figure 2 Variation of thermoelectric power (S) with inverse temperature ($10^3/T$) in iron (III) molybdate.

in reasonable agreement with the value of 1.3 eV reported by Orlandi *et al.* [5]; the difference between the two values may be due to impurities or the presence of grain boundaries in our sample, which considerably affect the activation energy.

The activation energy 1.55 eV is less than the activation energy 2.3 eV required for normal band conduction between 2p and 4s, 4p bands; so the activation energy of 1.55 eV calculated in the temperature range 750 to 1000 K certainly involves narrow 3d band conduction so the charge carriers will become localized at lattice sites, thus leading to the formation of polarons [18]. The decrease in mobility with increasing temperature indicates the formation of large polarons. Therefore electrical transport in iron (III) molybdate is not due to normal band conduction but due to large polarons which conduct via the band model with an enhanced mass of charge carriers. The relevant bands available for conduction in this material are filled Fe^{3+}: $3d^5$, O^{2-}: 2p and empty Fe^{3+}: 3d, Mo^{6+}: 4d along with 4s and 4p empty bands which are associated with Fe^{3+} ions. Moreover, the 3d band again splits into two groups, the triplet t_{2g} (dxy, dxz and dyz) and the doublet e_g ($d_{x^2-y^2}$ and d_{z^2}) due to the influence of crystal field splitting [19]. The difference in energy between upper doublet e_g and lower triplet t_{2g} is usually given by the crystal field splitting parameter Δ. Hence the valence band of $Fe_2(MoO_4)_3$ comprises $Fe^{3+}: 3d^5\,[t_{2g}^3 \uparrow e_g \uparrow]O^{2-}$: 2p and the conduction bands are Fe_e^{3+}: $3d^5[t_{2g}^3 \downarrow e_g^2 \downarrow]$, Mo^{6+}: 4d along with 4s, 4p bands associated with Fe^{3+} ions. The estimated value of the energy gap of iron (III) molybdate is 3.1 eV.

A.c. conductivity and d.c. conductivity are equal above ~750 K which shows that there is only an electronic contribution above this temperature. Below ~750 K, a.c. conductivity is slightly higher than d.c. conductivity because the latter has an ionic contribution. The change of slope of a.c. conductivity curve at ~400 K may be due to the presence of water molecules because the compound is hygroscopic. However, it cannot be understood clearly in the absence of other relevant data.

The thermoelectric power of iron (III) molybdate was measured in the temperature range 300 to 1000 K using the formula:

$$S = \Delta E/\Delta T \qquad (5)$$

where ΔE is the e.m.f. produced across the pellet due to temperature differences ΔT. The plot of S against $10^3/T$ is shown in Fig. 2. The increase in thermoelectric power with temperature and its positive value found over the entire temperature range shows that iron (III) molybdate is a p-type semiconductor, i.e. the majority of charge carriers are holes. The thermoelectric power increases linearly up to 750 K. The decrease in thermoelectric power with increasing temperature shows that electrical conduction is due to small polaron hopping. Because the charge carriers are lattice defects, i.e. vacancies or interstitials, the number of charge carriers will remain constant and the increase in thermoelectric power and electrical conductivity with temperature must be due to the increase in mobility of the charge carriers. The small polarons migrate from one lattice site to another adjacent lattice site with a thermally activated mobility which increases exponentially with temperature.

Above 750 K the thermoelectric power increases more rapidly. The value of the activation energy and the electrical conductivity results suggest large polaron formation. The large polaron mobility

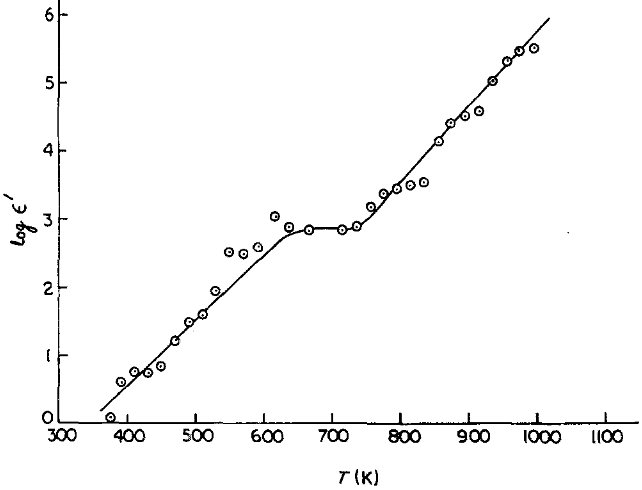

Figure 3 Variation of static dielectric constant (log ε') with temperature (T) in iron (III) molybdate.

decreases with temperature, so thermoelectric power should decrease with temperature; however, contrary to this the thermoelectric power increases with temperature. This unusual behaviour of thermoelectric power with temperature above 750 K is most probably due to the onset of ionic conduction at the higher temperatures.

The static dielectric constant, ε', was measured in the temperature range 300 to 1000 K by measuring the capacitance of the capacitor formed with the pellet as the dielectric material, using the formula [20]

$$\varepsilon' = c\frac{11.3t}{A} \qquad (6)$$

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 static dielectric constant ε' slowly increases with temperature up to 650 K, then becomes practically constant and finally above 750 K it increases.

The dielectric constant of a material consists of four contributions: electronic, ionic, dipolar and space charge polarization. At lower temperature and frequency, all these factors contribute to the dielectric constant [21]. We have measured the dielectric constant at a fixed frequency of 1 kHz. Temperature has a complex effect on the dielectric constant. Generally, increasing the temperature of the material decreases the electronic polarization, and the accompanying increase in ionic spacings influences the ionic and electronic polarization. Because the dielectric constant of $Fe_2(MoO_4)_3$ increases more rapidly than expected for ionic solids, this behaviour of ε' below 650 K may be attributed to space charge polarization due to crystal defects as well as to ionic polarization because of the ionic nature of the compound (ionicity of $Fe_2O_3 \sim 0.6$ to 0.7 [22] and $Fe_2(MoO_4)_3$ is a mixed oxide system of Fe_2O_3 and MoO_3). The low value of the activation energy (0.51 eV) suggests that the charge carrier concentration is high due to the presence of impurities and defects and that it produces space charge polarization which leads to an increase in ε'.

Above $\sim$750 K, the formation of large polarons takes place. These large polarons increase the polarizability of the ions to a greater extent, and in the intrinsic region the number of charge carriers increases exponentially with temperature. These two factors considerably enhance the dielectric constant resulting in a rapid increase in ε' with temperature.

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