Electrical transport properties of $Pr_2(MoO_4)_3$ single crystal

U S P Yadava, T H Ansari* and R A Singh

Department of Physics, DDU Gorakhpur University,
Gorakhpur-273 009, India
*Department of Physics, M J K College, (P G Centre),
Bettiah-845 438, India

Abstract : The ac and dc electrical conductivities, thermoelectric power and dielectric constant of $Pr_2(MoO_4)_3$ single crystal were measured in the temperature range 300–1000 K. A break in the $\log \sigma - \frac{1}{T}$ curve occurs at 600 K. The activation energies below and above this break temperature, have been estimated as 0.15 eV and 0.90 eV respectively. The mobility μ and mean free path (L) of the charge carriers were calculated by combining the electrical conductivity and thermoelectric power which shows that the compound is p-type semiconductor, having energy band gap 1.80 eV. The dielectric constant of the material increases slowly up to 600 K and after that it increase rapidly with increasing temperature and finally becomes almost constant at higher temperature.

1. Introduction

Rare-earth compounds are technologically important materials, especially the rare-earth molybdate have proven industrial importance in various ways. The electronic and thermal properties of these compounds provide wide applications in various industries, specially in energy conversion devices.

In the present paper, we discuss the electrical conduction mechanism of $Pr_2(MoO_4)_3$ using various electrical transport parameters *i.e.*, activation energy, $\sigma_0(T)$, charge carrier mobility *etc*. These parameters have been estimated by measuring the ac and dc electrical conductivities, thermoelectric power and dielectric constant in the temperature range 300–1000 K.

2. Experimental details

The single crystal of $Pr_2(MoO_4)_3$ were grown by the flux method at the Clarendon Laboratory, Oxford, UK, in solid form (purity 99.99%) and was used as such, in our investigation. Measurements of electrical conductivity, thermoelectric power and dielectric constant were done on single crystal. Details about the crystals growth and identification techniques are given elsewhere [1]. The crystal on which the measurements were carried out, has dimension $0.70 \times 0.30 \times 0.26$ cm^3. The crystal placed between the platinum electrodes, was mounted on a stainless steel sample holder assembly. The platinum foils were electrically insulated from the sample holder by mica sheets.

The dc electrical conductivity and thermoelectric power were measured with the help of a digital multimeter PM 2522/90 (Philips, India) with an accuracy of better than ±0.25% and 0.20% in the case of resistance and emf measurements respectively. The ac electrical conductivity and dielectric constant were measured by an autocomputing digital LCR-Q meter (model 4910, Applied Electronics Ltd., Thane, India) at an internal frequency of 1 KHz. The dielectric constant of the sample was determined at various temperature by measuring the capacity of the parallel-plate capacitor formed with the crystal as dielectric medium.

For the measurement of thermoelectric power, a temperature difference of 20°C was produced across the crystal with the help of a microfurnace placed just below one of the platinum electrodes. Temperature of both faces of the crystal were recorded using Chromel/Alumel thermocouples attached to the platinum electrodes. Each reading of thermo emf was taken after thermal equilibrium was attained (about $2\frac{1}{2}$ h) and the ambient temperature has been taken as the average temperatures of the two surfaces. The details regarding measuring procedures and experimental set up are given elsewhere [2,3].

3. Results

We have measured the ac and dc electrical conductivities of $Pr_2(MoO_4)_3$ in the 300–1000 K temperature range. Figure 1 shows the variation of log σ *versus* $10^3/T$. The curve follows the well known exponential relation for semiconductors $\sigma = \sigma_0 \exp(-\frac{W}{kT})$, but with two different slopes. A marked kink occurs at T ~600 K. In the 300–600 K temperature range, the ac conductivity is—larger than the dc conductivity, but at $T > 600$ K the two conductivities becomes almost equal. The data can be expressed by two straight lines, one below 600 K and other above 600 K as follows

$$\sigma_1 = 6.56 \times 10^{-6} \exp\left(-\frac{0.15 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad 300 \le T \le 600 \text{ K}, \qquad (1)$$

$$\sigma_2 = 2.45 \times 10^2 \exp\left(-\frac{0.90 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad 600 \le T \le 1000 \text{ K}. \qquad (2)$$

The activation energies and $\sigma_0(T)$ have been calculated from the slopes. The electrical transport parameters, activation energy W and $\sigma_0(T)$ in the two temperature regions have been tabulated in Table 1.

Table 1. Electrical transport parameters of Pr$_2$(MoO$_4$)$_3$ single crystal.

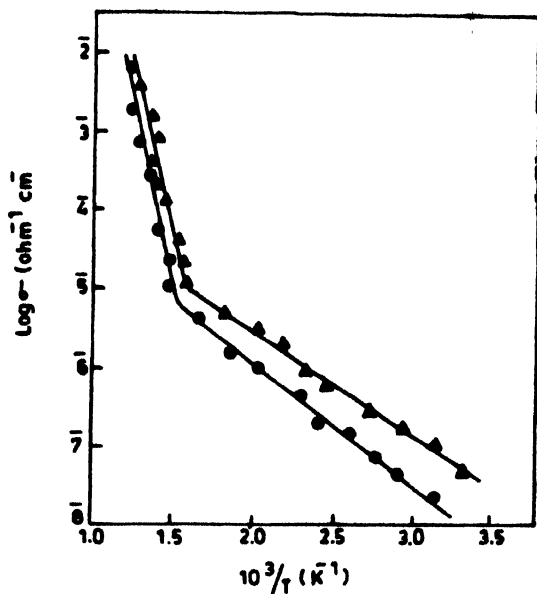| Temperature range (K)	Activation energy (eV)	$\sigma_0(T)$ Ω^{-1}cm^{-1}	Mobility (μ) cm^2/V–s
300–600 K	0.15	6.56×10^{-6}	4.78×10^{-10}
600–1000 K	0.90	2.45×10^2	0.75×10^{-5}

Figure 1. Variation of electrical conductivity with temperature ⊖ – dc conductivity, ▲ – ac conductivity.

The activation energies below and above 600 K are 0.15 eV and 0.90 eV, respectively. In semiconducting material, the electrical conduction at low temperature is always associated with impurities, defects and interstitials which generally provide states in the forbidden energy gap of the material and lower the value of activation energy. The contribution of defects or impurities towards conduction in solid can be explained in terms of donors or acceptors and is represented by the expression [4]

$$\sigma_d = A \exp\left(-\frac{E_i}{kT}\right),$$ (3)

where E_i is the ionization energy of donors or acceptors, and usually E_i ~0.1 eV for semiconducting material. The activation energy found below 600 K is approximately comparable to the ionization energy E_i and therefore the conclusion that electrical conduction is certainly due to impurities, point defects, or interstitials, seems to be reasonable.

73A(4)–13

The activation energy 0.90 eV estimated in the higher temperature range 600–1000 K seems to be an intrinsic activation energy because σ_0 is in the correct range for intrinsic conductivity. Thus, the change in the nature of the log σ *versus* $\frac{10^3}{T}$ curve at $T \approx 600$ K is due to the change in the conduction mechanism *i.e.* transition from extrinsic to intrinsic conduction.

The thermoelectric power (S) have been measured in the temperature region 300–1000 K using the formula

$$S = \frac{\Delta E}{\Delta T},\tag{4}$$

where ΔE is the thermoelectric emf generated across the crystal due to temperature difference ΔT. A plot of S *versus* $\frac{10^3}{T}$ is shown in Figure 2. S is found to be positive over
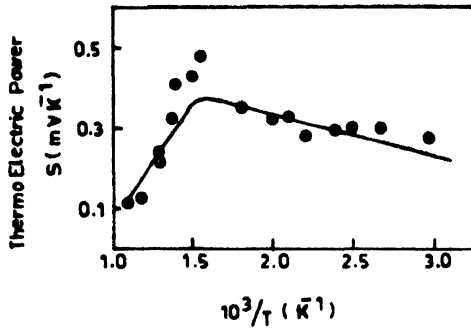
Figure 2. Variation of thermoelectric power with temperature.

the entire temperature range studied, showing that holes are the majority charge carriers and hence the compound is a p-type semiconductor. The variation of S, with temperature (T) is given by [5,6]

$$S = \frac{\eta}{T} + K,\tag{5}$$

where $$\eta = -\frac{W}{e}\left(\frac{c-1}{c+1}\right),\tag{6}$$

$$K = -\left[\frac{2k}{e}\left(\frac{c-1}{c+1}\right)\right] + \frac{3k}{4e}\log_e a.\tag{7}$$

$$C = \frac{\mu_e}{\mu_h} \quad \text{and} \quad a = \frac{m_e}{m_h}$$

Here, m_e, μ_e and m_h, μ_h are effective masses and mobilities of electrons and holes respectively. W is the activation energy. The charge carrier mobility was calculated from eqs. (1), (2) and (5) together with the value of σ_0 given by

$$\sigma_0 = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_e m_h)^{3/4}(\mu_e + \mu_h),\tag{8}$$

where T is the mean temperature of the respective range. k and h are Boltzmann and Planck constants respectively. Combining electrical conductivity and thermoelectric power data, the estimated values of the charge carrier mobility of holes is in the temperature range 300–600 K and 600–1000 K turn out to be 4.78×10^{-10} cm^2 V^{-1} sec^{-1} and 0.75×10^{-5} cm^2 V^{-1} sec^{-1} respectively. We have also calculated the value of mean free path (L) of the charge carriers using the relation [6]

$$L = \frac{3\mu}{4e} (2\pi m kT)^{1/2}$$ (9)

The value of L has been calculated at 468 K in the lower temperature range 300–600 K and at 813 K in the higher temperature range 600–1000 K. These are 0.43×10^{-9} Å and 0.86×10^{-4} Å respectively.

The static dielectric constant ε', has been measured at a fixed frequency (1 KHz) and the value of ε' at different temperature have been calculated using the following relation [7–9]

$$\varepsilon' = 11.3 \frac{Ct}{A},$$ (10)

where C is the capacitance in Picofarads, t is the thickness of the crystal in cm and A is the surface area of the electrodes in cm^2. It is obvious from Figure 3 that the static dielectric
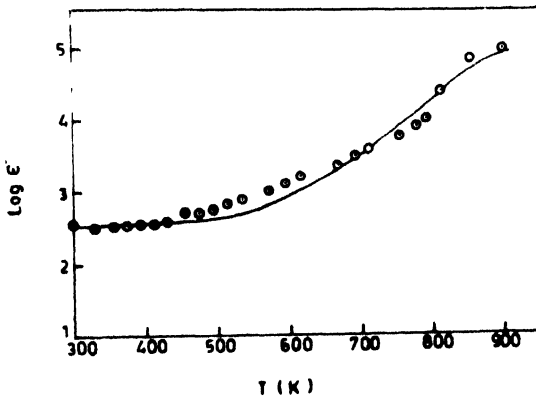

Figure 3. Variation of dielectric constant with temperature.

constant increases slowly with temperature, and the trend of the increase in ε' is similar to that of the electrical conductivity, with change in slope at 600 K. The rate of increase ε' is slow up to 600 K, and after that it increases exponentially with temperature.

4. Discussion

The electrical conduction in semiconductors at low temperature is always associated with impurities, defects and interstitials, which are generally present in these materials and lower the activation energy to large extent. Since the materials used are single crystal, there is less possibilities of impurities; however, some defects as interstitials may be present which cause the activation energy of Pr₂(MoO₄)₃ low (≈ 0.15 eV) below 600 K. In the

300–600 K temperature range, the charge carrier mobility 4.78×10^{-10} cm^2 V^{-1} sec^{-1} and mean free path 0.43×10^{-9} Å predict that small polaron conduction dominates in the lower temperature region. Moreover, the presence of narrow $4f$ band also facilitates small polaron. This is due to the interaction between the excess charge carriers (electrons or holes) present in the narrow band and the lattice ions which results in the distortion of the lattice thus producing a potential well deep enough to trap the charge carriers. In an ionic solid, the small polarons conduct by two distinct mechanism *viz.* small polaron band mechanism and small polaron hopping mechanism. In the case of small polaron band conduction, the mobility of charge carriers decreases with increasing temperature but in the case of small polaron hopping conduction, the mobility increases exponentially with temperature. In this compound, it is observed that the mobility of the charge carriers increases with temperature as shown by increase in the thermoelectric power with temperature below $T \sim 600$ K. Therefore, small polaron band conduction cannot take place in this compound in the 300–600 K temperature range. Hence the only possibility left is conduction *via* small polaron hopping mechanism. In hopping type conduction, small polarons move from one impurity site to another by a thermally activated hopping process and the mobility of the charge carriers increases exponentially with temperature. The variation of σ with temperature due to this mechanism is given by the expression [8,9]

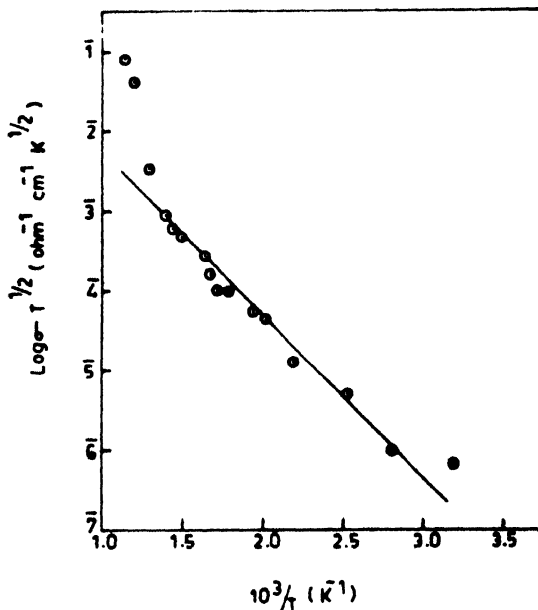$$\sigma T^{1/2} = A(T) \exp\left(-\frac{Wh}{kT}\right),$$ (11)

Figure 4. Variation of log $(\sigma T^{1/2})$ with temperature.

where W_h is the small polaron hopping energy and A is constant. Figure 4 shows the variation of log $(\sigma T^{1/2})$ with $\frac{10^3}{T}$. The plot is straight line, in the 300–1000 K

temperature range and the hopping energy can be calculated to be 0.40 eV. Hence the conduction is consistent with thermally activated small polaron hopping and the conductivity in this temperature range is entirely due to the mobility of the charge carriers which increases with temperature.

In the high temperature region 600–1000 K, the values of activation energy, charge carrier mobility and mean free path have been estimated as 0.90 eV, 0.75×10^{-5} cm^2 V^{-1} sec^{-1} and 0.86×10^{-4} Å respectively. These value strongly indicate that in this temperature range, conduction is of the normal band type. In $Pr_2(MoO_4)_3$, each Pr^{3+} ion carry two $4f$-electron and the ground state is Pr^{3+} ($4f^2$: $^3H_4$) [10]. To understand the electrical conduction mechanism in a material, it is necessary to have an idea of the electronic energy bands available for the electrical transport. The relevant bands for conduction in this solid are O^{2-} : $2p$ filled, Pr^{3+} : $4f$ partially filled and Mo^{6+} : $4d$ and Pr^{3+} : $5d$ empty bands. The only partially filled band expected in this solid is the $4f$ band, but it has been shown that $4f$ electrons have almost atomic character, even in rare earth solids, and form only narrow and high correlated bands [11]. The $5d$ band in rare-earth solids is regarded as the conduction band. Thus, it seems likely that electrons in $5d$ band, caused by the thermal excitation of electrons from $4f$ or $5p$ bands and holes left there by are responsible for electrical conduction above T ~600 K. So only appropriate bands for high mobility electrical conduction are Pr^{3+} : $5d$ empty band and O^{2-} : $2p$ filled band. The $2p$ band is expected to be a ordinary band and large polaron theory of conduction should be applied in this band. The $5d$ band is in comparison a narrow band, the mobility of charge carrier in $5d$ band is thus expected to be below in comparison to mobility of charge carrier in O^{2-} : $2p$ band. Thus intrinsic conductivity should be dominated by large polarons. The electron or hole current domination will depend upon the effective mass of the charge carriers in the empty band Pr^{3+} : $5d$ and filled band O^{2-} : $2p$ [12,13]. However, both these holes and electrons are expected to interact with the lattice and this may lead to the formation of large polarons as discussed by several authors [14–16].

Ac conductivity is found to be higher than dc conductivity below 600 K. Therefore, one can expect that electronic as well as ionic contributions are present in σ_{ac}. Above 600 K, σ_{ac} and σ_{dc} coincides nearly indicating that electronic charge carrier mobility and concentration become much larger than the mobility and concentration of the free ions.

At 600 K, the variation of S with $\dfrac{10^3}{T}$, further confirms that the electrical conduction in this compound is due to the small polaron hopping mechanism. Since the charge carrier concentration will become nearly constant after a certain temperature, the increase in thermoelectric power will mainly be due to an increase in the mobility of the charge carriers. The decrease in thermoelectric power S with increasing temperature in the

high temperature region ($T > 600$ K), is associated with normal band conduction. In band type conduction, the mobility decreases with temperature [17] and consequently yields a decrease in the absolute value of the thermoelectric power. In the present case, the decrease in thermoelectric power is due to the exponential increase in the number of charge carriers and the decrease in the mobility of the charge carriers. The dielectric constant of praseodymium molybdate increases slowly up to 600 K and after that it increases rapidly with increasing temperature. The slow increase in ε' in the temperature region 300–600 K is due to the ionic nature of the compound [18]. The trend of the variation of ε' with temperature is in accordance with the variation of electrical conductivity with temperature as shown in the Figure 1. The polarizability of the ions is greatly influenced by the available volume and temperature as a results of lattice expansion [19]. The increase in the polarizability of the individual ions is due to the large available volume, compensate for the decrease in the dielectric constant due to the decrease in the number of ions per cm^3. At the same time, however, the greater separation of the ions produced by the increasing volume weakens the forces between them and increases the atomic polarizability, leading to an increase in the dielectric constant.

The rapid increase in dielectric constant above 600 K is attributed to the exponential increase in the number of charge carriers in the intrinsic region. 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 a macroscopic field distortion results. Due to these phenomenon the dielectric constant ε' increases very rapidly above 600 K and finally becomes almost constant.

References

[1]   B M Wanklyn *J. Mater. Sci.* **7** 813 (1972)

[2]   Y P Yadava *PhD Thesis* (Gorakhpur University, Uttar Pradesh, India) (1985)

[3]   R Bharati, R A Singh and B M Wanklyn *J. Phys. Chem. Solids* **43** 641 (1982)

[4]   A J Dekker *Solid State Physics* (London : MacMillan) p 305 (1964)

[5]   T C Herman and J M Honing *Thermoelectric Power and Thermomagnetic Effects and Applications* (New York : McGraw Hill) p 142 (1976)

[6]   H W Russel *J. Am. Ceram. Soc.* **18** 1 (1935)

[7]   M Cusack *The Electrical and Magnetic Properties of Solids* (London : Longmans) p 215 (1967)

[8]   J P Suchet *Electrical Conduction in Solids Materials* (London : Pergamon) (1975)

[9]   T H Ansari and R A Singh *J. Phys. Chem. Solids* **52** 865 (1991)

[10] V M Gredescul, S A Gredescul, V V Eremendo and V M Naukemoko *J. Phys. Chem. Solids* **33** 859 (1972)

[11] C E T Goncalves Da Silva and L M Falicov *J. Phys.* **C5** 63 (1972)

[12] J M Ziman *Principles of the Theory of Solids* (London : Cambridge University Press) p 179 (1964)

[13] C Kittel *Introduction to Solid State Physics* (New York : Wiley) p 361 (1971)

[14]   H Frohlich *Adv. Phys.* **3** 325 (1954)

[15]   G R Allcock *Adv. Phys.* **5** 412 (1956)

[16]   J Appel *Solid State Physics* (New York : Academic) p 193 (1968)

[17]   H Sumi *J. Phys. Soc. Jpn.* **33** 327 (1972)

[18]   K Hubner *Phys. Stat. Sol.* **B69** K1 (1975)

[19]   C P Smyth *Dielectric Behaviour and Structure* (New York : McGraw Hill) (1955)