CHAPTER 5

ELECTRICAL CONDUCTIVITY AND THERMOELECTRIC MEASUREMENTS

5.1 Introduction

It is well known that the existence of magnetic ordering in the family of transition metal tungstates (TMT), having the general formula MWO₄, where M = Cu, Fe, Cd, Zn, etc., gives rise to an important modification of the energy spectrum of conduction electrons [13,120]. Such a modification is likely to influence the electrical
properties, such as the electrical resistivity, which in TMT is likely to be of greater value than in ordinary metals.

The prime factors, many authors [22,106,121,122] have discussed, contributing to the electrical conductivity are the crystal defects such as isolated cations or anions (Schottky defects), cation substitutional impurities, cation vacancy-cation impurity complexes, Frenkel defects, etc. The available literature supplies some information about the electrical conductivity of rare-earth tungstates and other compounds [123-129] where the conduction mechanism has been explained in terms of electrons or holes, polarons and impurities. There is however, a brief report by Bharati et al. [130,131] and Doumerc [8] on the electrical conductivity of copper tungstate.

Now, one of the important themes to further characterize the grown crystals is to investigate them with regard to their transport properties, since a study of the mechanism of electrical transport in a crystal will lead to a proper understanding of the material. It is in this fitness that (in this chapter) a study of the dc electrical conductivity of unannealed, annealed single
crystalline as well as polycrystalline samples in the temperature range of 300 to 700 K, as available in laboratory, has been undertaken. The obtained data have been analysed in the light of various conduction mechanisms. The study in this chapter also includes the measurements made on thermoelectric power of the samples.

5.2 Experimental

5.2.1 Specimen preparation

The single crystals of CuWO₄, grown by the flux method, the details of which have been described in chapter 2, were selected in the form of regular platelets of dimensions 4.0 x 2.0 x 0.6 mm³. On the other hand, some of the grown crystals were ground to fine powder using a ball-mill and then pressed in the form of circular pellets of 10 mm diameter and 2 mm thickness, using a stainless steel die and hand-operated hydraulic press giving a pressure of 1124.91 kg cm⁻². The geometrical dimensions of the samples were measured using a travelling microscope (least count 0.001 cm).

5.2.2 Experimental arrangement

The electrical conductivity measurements were
carried out using the standard two electrode method. After applying silver paste on both the experimental surfaces, the specimen was mounted in between two flat stainless steel circular parallel electrodes of a specially designed ceramic conductivity cell which is shown schematically in figure 5.1. Both the upper and the lower cylindrical tubes of the cell are capable of being screwed in for proper contact of the sample with the electrodes. The data of observations (in this chapter) are the averages of the readings on five samples.

The dc electrical conductivity was measured with the help of a megohmmeter EBM 115 and a digital multimeter MECO-7, and the results are accurate to within 0.05 %.

5.2.3 Sample type and furnace

The investigations were made on four kinds of samples:

(i) the as-grown crystals,
(ii) the crystals annealed in air at 700°C for 80 hrs,
(iii) the crystals annealed in the presence of argon atmosphere at 700°C for 80 hrs, and
(iv) the pelletised samples.
For the study of the influence of temperature variation on the electrical conductivity, the ceramic cell was enclosed in a specially built resistance heating furnace, capable of giving steady temperatures up to 700°C. The temperature was raised slowly by regulating the power from 230 V, 50 Hz mains through a dimmerstat, and Pt-Pt 10% Rh thermocouple was employed to monitor the specimen temperature. The gross assemblage of the experimental set up is illustrated in figure 1.7 (chapter 1).

5.2.4 Set up for thermoelectric power

For thermoelectric measurements a sample holder assembly, schematically shown in figure 5.2 was employed. A thermal gradient was imposed across the sample by placing it between two nichrome wound heaters. A Chromel-Alumel thermocouple was placed just behind the copper strips, and an aluminium foil was used for contact with the samples. Copper wires were used as voltage probes. The entire system was kept in an evacuated glass chamber at a pressure of $10^{-5}$ torr, obtained by oil rotary pump backed with diffusion pump.
5.3 Results and discussion

5.3.1 Electrical conductivity of crystalline and pelletised samples

The electrical conduction in solids is normally explained using the band theory, according to which the variation of electrical conductivity, $\sigma$, and thermoelectric power, $\Theta$, in intrinsic semiconducting solids are given [132] by the following expressions:

$$\sigma(T) = \sigma_0 \exp \left[ - \frac{E_g}{2kT} \right] \quad (5.1)$$

where

$$\sigma_0(T) = 2e \left( \frac{2\pi kT}{\hbar^2} \right)^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h) \quad (5.2)$$

and,

$$\Theta(T) = \left( \frac{n}{T} \right) + A, \quad (5.3)$$

where

$$n = - \frac{E_A}{2e} \left( \frac{C-1}{C+1} \right) \quad (5.4)$$
\[ A = - \left[ \frac{2k}{e} \left( \frac{C-1}{C+1} \right) + \frac{3k}{4e} \log_e a \right] \quad (5.5) \]

\[ C = \frac{\mu_e}{\mu_h}, \quad a = \frac{m_e}{m_h}, \quad (5.6) \]

with \( k \) and \( h \) are Boltzmann constant and Planck's constant, respectively, \( m_e \), \( \mu_e \) and \( m_h \), \( \mu_h \) are the effective mass and mobility of electrons and holes respectively, \( E_g \) is the energy band gap of the solids. Then, knowing the values of \( E_g \) from the slope of the curve (figure 5.3) representing equation (5.1) and the value of \( \eta \) from figure 5.5 representing equation (5.3), \( C \) can be calculated from equation (5.4). Again, using the value of \( A \) obtained as the intercept from equation (5.3), the value of \( a \) is obtained from equation (5.5). Further, using equation (5.6), the equation (5.2) is rewritten as

\[ \sigma_o(T) = 2e \left( \frac{2\pi kT}{h^2} \right)^{3/2} (a \ m_h)^{3/4} \mu_e(1+\frac{1}{C}) \quad (5.7) \]

from this \( \mu_e \) can be calculated by substituting the evaluated values of \( \sigma_o(T) \), \( C \), \( a \) and \( m_h \); we may take \( m_h = 100 \ m \ [130] \) and \( m_e = 70 \ m \ [8] \), where \( m \) is the free electron mass; the basis of this approximation choice is that the material has a narrow d-band and the holes are localised in \( \text{Cu}^{2+} : 3d^9 \) filled band. Consequently, the carrier concentration, \( n \) and the life time, \( \tau_e \) are
calculated using the relations

\[ \sigma = n_e \mu_e \quad (5.8) \]

and

\[ \tau_e = \left( \frac{1}{e} \right) m_e \mu_e \quad (5.9) \]

The values of \( \mu_e \), \( n \) and \( \tau_e \) so obtained have been summarized in Table 5.1.

The measured Arrhenius data of dc conductivity versus temperature for different samples is shown graphically in figure 5.3. The case of the pellet and that of the as-grown crystal distinctly shows two regions viz., the intrinsic region (above 455 K) and the extrinsic region (below 455 K). These results can be fitted by the representative equations given in Table 5.2.

The conductivity data for semiconducting materials are generally explained using either or both of band model or localized model, large polaron model, etc. [133,134]. But, before applying a model, one has to know the electrical energy bands of the compound involved. The electronic properties of transition metal compounds are mostly characterized by d-band near the Fermi surface. It is also known that the 2s and 2p orbitals of oxygen
The values of $\mu$, $\tau_e$, and $n$ determined at 350 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu$ (m$^2$/V·s)</th>
<th>$\tau_e$ (sec)</th>
<th>$n$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown crystal</td>
<td>$1.791 \times 10^{-21}$</td>
<td>$7.137 \times 10^{-31}$</td>
<td>$1.078 \times 10^{32}$</td>
</tr>
<tr>
<td>Pellet</td>
<td>$3.962 \times 10^{-23}$</td>
<td>$1.579 \times 10^{-32}$</td>
<td>$2.676 \times 10^{32}$</td>
</tr>
</tbody>
</table>
Table 5.2

Representative equations for the two regions of figure 5.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extrinsic region (below 455 K)</th>
<th>Intrinsic region (above 455 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown crystal</td>
<td>$o_{ex} = 2.79 \times 10^{-11} \exp\left(\frac{-0.06}{kT}\right)$</td>
<td>$o_{in} = 1.2 \times 10^{-5} \exp\left(\frac{-1.18}{kT}\right)$</td>
</tr>
<tr>
<td>Pellet</td>
<td>$o_{ex} = 3.41 \times 10^{-10} \exp\left(\frac{-0.26}{kT}\right)$</td>
<td>$o_{in} = 1.12 \times 10^{-6} \exp\left(\frac{-1.06}{kT}\right)$</td>
</tr>
</tbody>
</table>
strongly overlap with the 4s and 4p orbitals of 3d-transition metal ions. This overlapping entails a strong hybridization, leading to a large energy gap between the top of the 2s band and the bottom of the 4s and 4p bands. In the transition metal compounds, the mobility of charge carriers is very low (Table 5.1) even at lower temperature (upto 455 K) due to the narrowness of d-band, and therefore a polaron is likely to be formed by the interaction of slow moving electrons with the lattice. But, since the data related to polaron coupling constant for this compound are not known, it is not possible to predict the type of polaron taking part in conduction [135-140]. At lower temperature (upto 455 K), the conduction is, therefore, believed to be due to impurities and thus the possibility of hopping conduction cannot be ruled out.

The extrinsic region (below 455 K, figure 5.3), slopes corresponding to the activation energy of the as-grown crystal and the pellet, which work out to be 0.062 eV and 0.259 eV, respectively. The lower value of activation energy in the case of the as-grown crystal suggests that :

(i) the charge carrier for conduction are not
thermally generated but are constants,

(ii) the extrinsic conduction is governed by native defects or interstitials and by impurities,

(iii) the electrical conduction might occur by ionized impurities centres or may be through polaronic motion.

The band-type conduction of ionized impurity centres is known to contribute to conductivity according to the relation [141].

\[ \sigma_{dc} = \sigma_0 \exp \left( - \frac{E_i}{2kT} \right) \quad (5.10) \]

where \( E_i \) is identified as the ionization energy of donors or acceptors (usually, \( E_i \approx 0.1 \text{ eV} \)). Now, compared to the crystal, conduction mechanism in the pellet appears to be different, because the latter has a relatively higher value of activation energy (0.259 eV). Thus the band-type conduction is possible for the case of the pellet, but not the crystal.

An alternative is to consider small polaron conduction below 455 K in the case of the as-grown crystal. The fact that the narrow band, low mobility semiconductors like the transition metal or rare earth
oxides exhibit a strong coupling between charge carriers and lattice vibrations [136], small polaron hopping conduction is supported here. The contribution of a small polaron hopping mechanism towards electrical conductivity is given by the relation [136,137].

\[ \sigma T^{1/2} = \sigma_0 \exp \left( - \frac{W_H}{kT} \right) \]  

(5.11)

where \( W_H \) is the small polaron hopping energy. Consequently, the plot of \( \ln \sigma T^{1/2} \) against \( 10^3/T \) at temperature below 455 K for the as-grown crystal shows straight line (figure 5.4), the hopping energy calculated from the slope of the curve is 0.082 eV. This polaron hopping energy is in very reasonable agreement with the activation energy (0.062 eV) calculated for the as-grown crystal below 455 K from figure 5.3. Therefore, one is inclined to conclude that the electrical conduction in CuWO\(_4\) single crystals below 455 K may be due to small polaron hopping (sph) mechanism, the activation being entirely due to thermally increased mobility, given by the relation [138,140].

\[ J_{sph} = \frac{\mu_0}{T^{3/2}} \exp \left[ - \frac{E_m}{kT} \right] \]  

(5.12)

where \( E_m \) is the activation for the mobility change. As a result of small polaron hopping via lattice defects,
interstitials and impurities, the charge carrier concentration remains constant up to a certain temperature and hence the increase in electrical conductivity is essentially due to increase in the mobility of charge carriers with temperature.

The intrinsic nature of the compound is observed to arise above 455 K, the activation energy measured from figure 5.3 being 1.18 eV for the as-grown crystal and 1.06 eV for the pellet. Owing to these relatively higher values of the activation energy and the electrical resistivity (10^10 ohm cm) it seems probable that the electrical conduction is brought about by an electron transferred from one Cu^{2+} to the adjacent Cu^{2+} ion. Such a transfer would lead to the formation of Cu^{3+} ions,

\[ \text{Cu}^{2+} + \text{Cu}^{2+} \rightarrow \text{Cu}^{3+} + \text{Cu}^+. \]

This process needs quite high energy, because both Cu^{3+} and Cu^{+} ions are less stable than Cu^{2+}. Evidently, in this region (above 455 K) the conduction by excitation of electrons from the valence band to the nearer conduction band seems more probable.

But, according to Suchet [142], compound containing either empty or completely filled 3d - sub
levels cannot tend itself to transfer. Now, the activation energy in the temperature range (455 - 700 K) for the as-grown crystal is 1.17 eV and hence the energy gap is expected to be 2.34 eV. But according to Bharti et al. [130], the energy gap between the O$^{2-}$ : 2p filled band and the empty Cu$^{2+}$ : 3d band in CuWO$_4$ is 2.96 eV (≈ 3 eV) in the same temperature range. Therefore, the estimated values of activation energy cannot be assigned as the activation energy for O$^{2+}$ : 2p $\rightarrow$ Cu$^{2+}$ : 3d (E$_g$) type conduction. This is, however, more likely to be the energy required to excite an electron from the 3d-band. Further, the lower value of the mobility (Table 5.1) indicates the formation of some kind of polarons. This, of course, seems quite reasonable because the presence of narrow 3d-bands may lessen the activation energy to some extent. The activation energy is reduced to an amount which is equal to the polaron binding energy, such polarons conduct according to the relation:

$$\sigma = \sigma_0 \exp \left[ \frac{-E_0 + \hbar\omega_0}{kT} \right]$$

(5.13)

where $\hbar\omega_0$ is the polaron binding energy. Obviously, the actual activation energy is less than the estimated value. The drop in activation energy around 455 K appears to be due to a change in the conduction mechanism. One might, therefore, argue that large or intermediate
mobility polarons change into small polarons. The low mobility polarons do not contribute considerably to the electrical conduction which result in decrease in the activation energy.

5.3.2 Conductivity of annealed crystals

On the other hand, the annealed samples show (figure 5.3) only one region as against two for the unannealed and the pelletised samples. The activation energy is found to be 0.495 eV and 0.545 eV for argon and air annealed samples, respectively. Due to the greater value of activation energy as compared to ionization energy (0.01 eV), small polaron hopping conduction does not seem probable, while large or small polaron as well as normal band conduction may be responsible for the observed electrical conduction.

The activation energy computed from the $\ln \sigma T^\frac{1}{2}$ versus $10^3/T$ (figure 5.4) is found to be 0.492 and 0.544 eV for argon and air annealed samples, respectively. The values worked out from figures 5.3 and 5.4 are nearly the same for the same kind of the sample. Therefore, it seems that small or large polaron band type conduction is probable and not the sph conduction.

The observation on the annealed samples is
interesting. In fact, the annealing is characterized [143] by small changes in particle size and dislocation density along with large changes in twin probability and electrical resistivity. The surface texture changes from coarse to smooth, the defects being annealed out, and hence it might be thought that a lowering of the resistivity would result, as observed (figure 5.3), signifying a greater degree of reflection of electrons from the surface after annealing. Further, the influence of argon gas compared to air, favoured the formation of dipoles by the interstitial and substitutional ion pairs, thereby leading to dipole concentration and the vacancy states. This gives rise to oxygen vacancies which are compensated by cationic reduction. Obviously, therefore, the argon annealed crystal shows lesser resistivity, as observed, compared to the air annealed crystal.

5.3.3 Thermoelectric power

The variation of thermoelectric power, $\theta(T)$, measured as a function of $10^3/T$ is shown in figure 5.5. $\theta$ is observed to be negative over the entire range of temperatures which reveals n-type nature of CuWO$_4$. The general behaviour of the three kinds of samples is fairly similar, as seen from figure 5.5. At lower temperatures
the mobility of electrons is very low, entailing low thermoelectric power, the sharp deflection of thermoelectric power at 396 K being due either to the presence of the narrow 3-d sub bands (there is a possibility of large polaron formation in the wide O\(^2\) \(2p\) band that conduct via band mechanism) or to the movement of oxygen ion vacancies owing to the ionic nature of the compound.

5.4 Conclusions

1. The observations on the electrical conductivity and the thermoelectric power reveal n-type character of CuWO\(_4\).

2. A deflection in the conduction mechanism is noticed to occur at 455 K in the case of the as-grown crystals and the pellets. There is an extrinsic conduction below 455 K and an intrinsic conduction above 455 K.

3. Below 455 K in the case of the single crystals, conduction is thought to be due to small polaron hopping mechanism. In the case of the pellets, the normal band type conduction is appropriate. Above 455 K, in both the samples, large polaron
as well as normal band conduction seems responsible for the electrical conduction.

4. The annealed samples exhibit one region of conduction, for which large polaron as well as normal band conduction seem more relevant.
Fig. 5.1

Schematic diagram of the conductivity cell

E - electrode,
S - sample
L - connecting leads
T - thermocouple
Fig. 5.2

Schematic diagram of the sample holder assembly for thermoelectric power measurements.

M - mica sheet,
H - heater,
S - sample,
Th - thermocouple, and
E - electrode.
The variation of electrical conductivity ($\ln \sigma$) against reciprocal temperature ($10^3 / T$).

- $\bullet$ as-grown crystal,
- $\Delta$ air-annealed crystal,
- $O$ pellet,
- $\triangle$ argon annealed crystal.

Fig. 5.3
The variation of $\ln \sigma T^{1/2}$ against reciprocal temperature ($10^{-3}/T$)

- $\bullet$ - as grown crystal,
- $\Delta$ - air annealed crystal and
- $\triangle$ - argon annealed crystal.
Fig. 5.5

The variation of thermoelectric power ($\theta$) against reciprocal temperature ($10^3/T$)

- $\bullet$ as grown crystal
- $\circ$ pellet and
- $\triangle$ argon annealed crystal