CHAPTER 8

ELECTRICAL CONDUCTIVITY MEASUREMENT

8.1 INTRODUCTION

Electrical conductivity is an important experiment tool to probe the structural defects and internal purity of semi-insulating crystalline solids, because unlike metals and semiconductors where electrons are the charge carriers, in semi-insulators the prime factors contributing to their electrical conductivity are the crystal defects. Useful information regarding the mobility and generation as well as the movement of lattice defects in hydrogen bonded crystals can be obtained by studying the electrical conductivity of these crystals.

Protonic conductivity, referred to as hole conduction, plays a key role in important processes as diverse as the photosynthesis in green plant and the production of electricity in hydrogen fuel cell. The protonic conductivities of SrZr$_{0.95}$M$_{0.05}$O$_3$ doped with four acceptor ions have been studied in the single crystalline form by Higuchi et al. Hunt discussed the origin of sublinear frequency dependence of ac conductivity in dielectrics using percolation theory. In fact, proton tunneling which gives rise to delocalization of protons, observed through polarized Raman spectra taken on ADP is conjectured to be supporting the mechanism. The nearly universal tendencies of the frequency dependence of ac conductivity $\sigma(\omega) \propto \omega^n$ ($n < 1$ for weak temperature and frequency dependence) of materials have generated many theoretical investigations into the ‘universality’. Temperature dependence of transport property of n-ZrNiSn single crystals has been analyzed by Arushanov et al. and it is shown that the scattering due to acoustic phonons and ionized impurities is most important in the high and low temperature region, respectively. The d.c. conduction properties of TiSbSe$_2$ as a function of temperature at different d.c. electric fields reveal non-ohmic type of conduction and Poole-Frenkel conduction mechanism dominant in crystals.

Most of the investigations on tartrates, vanadates, phosphates, struvite, oxalates and other ferroelectric materials, ceramics described electrical conductivity in terms of electrons (or holes), polarons, impurities and thereby the mechanism of ionic conductivity was established, where some carriers are observed to be trapped at defect sites, and that accounts for the very low conductivity of some ionic materials at room temperature.
The cadmium oxalate trihydrate single crystals contain three water molecules bonded in the lattice. The heat supplied therefore, is likely to break, first, the weaker bonds of the water molecules with cadmium oxalate lattice, thus making the liberated water to escape away from the crystal. The purpose of the present chapter is to investigate, what role these escaped water molecules have on the conduction mechanism. The study of electrical conductivity and the related electrical parameters of the laboratory grown crystals in association with thermal behavior has been used in this chapter to understand the mechanism in the hydrated solids of cadmium oxalate.

8.2 EXPERIMENTAL

Cadmium oxalate trihydrate (CdC$_2$O$_4$·3H$_2$O) single crystals grown using controlled diffusion process in agar-agar gels (chapter 4) were used for the present purpose. Crystal as well as their pellets with silver paste applied for good contacts were employed. To obtain pelletized samples, the crystals grown in the laboratory were finely ground and the resulting powder was compressed in a die of diameter 1 cm under a pressure of $10 \times 10^5$ gm/cm$^2$ using a hand operated hydraulic press.

The electrical conductivity measurements were carried out in the temperature range 30 to 300 °C for seven different input frequencies in the range 500 Hz to 1 MHz. The specimen was mounted between two stainless steel electrodes and the assembly was then put into the resistance-heated furnace wherein the sample temperature was monitored using a chromel-alumel thermocouple, maintaining constant heating rate during the whole experiment. The D.C. resistance of the sample was measured by ‘MEGGER’ megohmmeter (MM29:U.K.). The frequency dependent resistance was determined using a precision type ‘Hewlett Packard’ 4284A LCR meter. The observed values of capacitance and dissipation factor as obtained (see chapter 7) at different temperatures were converted into electrical conductivity ($\sigma_{ac}$) by determining area and thickness of sample used.

8.3 RESULTS AND DISCUSSION

8.3.1 PRINCIPLE AND THEORY

The ac conductivity ($\sigma_{ac}$) is defined as

$$\sigma_{ac} = \frac{J}{E}$$  \hspace{1cm} (1)
where \( J \) is the current density and \( E \) the electric field strength which is \( E = D/\varepsilon \), \( D \) being the displacement vector, \( \varepsilon \) is the complex permittivity of the material. For a parallel plate capacitor the electric field intensity is the ratio of the potential difference between the plates of the capacitor to the interplate distance. i.e.

\[
E = \frac{V}{d}
\]

(2)

Since \( \frac{Q}{A} = \frac{V\varepsilon}{d} \), the current density \( J \) is given by

\[
J = \frac{dQ}{dt} = \frac{d}{dt} \left( \frac{V\varepsilon}{d} \right) = \frac{\varepsilon}{d} \frac{dV}{dt} \therefore J = \frac{\varepsilon}{d} Vj\omega
\]

(3)

Substituting for \( E \) and \( J \) in Eq. (1)

\[
\sigma_{ac} = \varepsilon j\omega
\]

\[
\sigma_{ac} = (\varepsilon' - j\varepsilon^*) j\omega = \varepsilon' j\omega + \omega\varepsilon^*
\]

(4)

In order that the ac conductivity may be a real quantity, the term containing \( j \) has to be neglected, hence

\[
\sigma_{ac} = \omega\varepsilon''
\]

(5)

The two components \( \varepsilon' \) and \( \varepsilon'' \) of the complex dielectric constant, \( \varepsilon \), are frequency dependent,

\[
\varepsilon'(\omega) = D_o \cos(\delta / E_o)
\]

(6)

\[
\varepsilon''(\omega) = D_o \sin(\delta / E_o)
\]

(7)

The displacement vector is a time varying field, it will not be in phase with \( E \), producing a phase difference \( \delta \) between them. From (6) and (7), we have

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}
\]

(8)

Substituting the value of \( \varepsilon''(\omega) \) from (8) into (5), we have

\[
\sigma_{ac} = \omega\varepsilon' (\omega) \tan \delta = 2\Pi f \tan \delta \varepsilon_o \varepsilon_r
\]

(9)

where \( \omega = 2\Pi f \) and \( \varepsilon' = \varepsilon_o \varepsilon_r \), where \( \varepsilon_r \) is the relative permittivity of the material and \( \varepsilon_o \), the permittivity of free space

\[
\sigma_{ac} = \frac{2\Pi f \tan \delta C t}{A}
\]

(10)
This Eq.(10) has been used to calculate the a.c. conductivity of the crystals.

### 8.3.2 AC CONDUCTIVITY

The plot of $\ln \sigma$ against 1000/T as obtained at different frequencies for (001) plane is shown in Fig.8.1. One can notice a lesser temperature dependence with increasing frequency, but it is relatively more at higher temperatures. Three noticeable peaks at 323 K, 353 K and 383 K are due to liberation of water molecules. Thereafter, relatively faster increase in the value of conductivity is observed. There occurs ion-dipole interaction between dipole moments of water molecules and the effective ionic charges. As temperature of the crystal increases, the thermal energy makes the water molecules free, dehydrating the crystal. When the thermal energy is of the order of ion-dipole interaction, the contacts between water molecules and the effective ionic charges will break, giving rise to the three noticeable peaks. This allows thermally generated charge carriers to develop space charge in some regions due to the accumulation of charges. At still higher temperatures the polarization increases because of ease of accumulation of excess charge carriers in the absence of ion-dipole contacts and results in increase in electrical conductivity. The dipole-ion interaction and the band type conduction balance each other. The conductivity further increases with temperature, and it is due to the condensation of the structural-OH group. This also suggests a mechanism different from charge transport where the conductivity depends on the ability of water located in the surface to rotate, similar to Grothus type transport$^{26}$). The shape of the curves in Fig.8.1 suggests two different regimes, one with weak temperature dependence and other with relatively stronger temperature dependence. Overall, the ac component of the frequency dependent conductivity $\sigma_{\omega}(\omega)$ can be expressed as the sum of the two different conduction mechanisms$^{27}$)

$$\sigma_{\omega}(\omega) = \sigma_f + \sigma_s$$

where $\sigma_f$ represents the relatively weak temperature dependent mechanism which is to be interpreted as being due to hopping between localized states at the Fermi level, and $\sigma_s$ represents the strong temperature dependence component and is numerically obtained by subtracting $\sigma_f$ from $\sigma_{\omega}(\omega)$ and this mechanism may be interpreted as being due to hopping between localized states near band edges (edges of the valence and/or the conduction band), in agreement with the concept of Rockstad$^{27}$).
The relationship between the ac conductivity and the applied frequency at different constant temperature values, shown in Fig. 8.2, can be fitted to a power law,

$$\sigma_{ac} = A\omega^n$$

(12)

where $A$ is a constant for a particular temperature and $n$ is a power exponent which represents the degree of interaction between mobile ions and the environment surrounding them. Many manifestations of the hopping models and experiments to determine the value of $n$ in the range of 0.6-1.0 have been given\(^{28,29}\). The frequency dependence of ac conductivity which rises almost linearly (Fig. 8.2), is most likely due to hopping of electrons between two pairs of localized states, the conduction being due to small polarons\(^{30,31}\). The values of frequency exponent $n$ in Eq. (13) are obtained from the slopes of $\ln\sigma_{ac}$ versus $\ln f$ curves. The dependence of the frequency exponent $n$ on temperature (Fig. 8.3) shows increase in ‘$n$’ upto the water liberating temperature, which matches with the data obtained from DTA – TGA (chapter 6), and then decreases with an increase of temperature through frequency and temperature ranges. The fact that the frequency exponent $n$ is temperature dependent indicates that the bipolaron conduction is a thermally activated process which takes place under the assistance of lattice phonons which are indeed active in the crystal under impressed electric field (see chapter 10). The frequency dispersion behavior is attributed to the coulomb interaction effects between the mobile ions as well as the ions with the environment within materials\(^{32}\). Since the numerical values of $n$ lie in the range $0.5<n<0.9$, band type or electron hopping conduction mechanism appears to be operative.

The conductivity as a function of temperature for different values of frequency is shown in Fig. 8.4 for (100) plane. The conductivity decreases gradually upto 409 K and then shows an increase. The dip at 409 K reveals the phase transition in crystal which may again indicate that the crystal becomes completely dehydrated with the liberation of water molecules from its structure. We suggest that the change in conductivity at 409 K along $a$ axis (and not along $c$-axis) for crystal can be related to the rotation of the $\mathrm{C}_2\mathrm{O}_4$ group. The dielectric behavior of the crystal (chapter 7) shows that the orientation along $\pm a$-axis must have a lower energy than that at along $c$-axis. Figure 8.5 shows the conductivity as a function of frequency for different temperatures for different values of frequency applied on (100) plane. The trend of the graph is similar to that obtained for (001) plane in Fig.8.2.
Further, as seen from Fig. 8.6, the measured value of conductivity of palletized sample is smaller than that of the single crystals. The conductivity in pellet is lower because of the charged carriers that get trapped at grain boundaries. The conductivity decreases, indicating metallic behavior, as the temperature decreases at lower value of frequency. This decrease is observed up to 343 K, a sharp anomaly at 353 K is due to the liberation of water molecules and then later the conductivity increases with temperature.

### 8.3.3 DC Conductivity

The reciprocal temperature dependence of the logarithmic d.c. electrical conductivity is shown in Fig. 8.7 for the as grown (001) surface. One may distinguish two types of conduction: one at lower temperature which is extrinsic type of conduction, and the other at higher temperature which is of intrinsic type. Although the graph as obtained for the crystal has a nature similar to a semiconductor\(^{33}\), \(\ln \sigma_{dc} \) versus \(1/T\) curve is not perfect linear through. Consequently, a hopping conduction in part, with a small polaron model\(^{34}\) may be applicable. The values of \(\ln \sigma_{dc}\) at lower temperatures (303-363K) are most probably due to the presence of lattice water in the as-grown single crystals. A similar plot is also observed (Fig. 8.8) for a different orientation i.e. (100). One can notice conduction anisotropy, as judged from the little yet noticeable change in the magnitude of \(\sigma_{dc}\) as well as the shape of curves in the two orientations. The conductivity activation enthalpy \(E_a\) has been calculated using Arhenius Equation:

\[
\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)
\]

where \(\sigma_0\) is pre-exponential factor, \(E_a\), the activation energy and \(k\) is the Boltzmann constant. The activation energies for (001) and (100) planes are found to be 0.52 eV and 1.8 eV, respectively, on the low temperature side of the curves. However, the activation energies are 1.72 eV for (001) and 1.7 eV for (100) on the high temperature side of the curves. The \(\ln \sigma \) vs 1000/T curve also indicates extrinsic to intrinsic semiconductor transition. The (303-373) K range is, in fact, the metal like behavior because carrier transport occurs via scattering by static imperfections, until the dehydration begins. Here the conduction is thought to be due to proton hopping\(^{35}\). On (100) plane, the liberation of a water molecule at 375 K is followed by two water molecules at 389 K and 401 K on the low temperature side of the curves.
The thermograms (chapter 6) are not able to reveal the sequential steps of dehydration at which the coordinated water is expelled out at what temperature. Interestingly, conductivity data are able to reveal this feature very distinctly. The peaks in Fig. 8.7 represent the distinct dehydration stages of crystal. The fact that the loosening of bonds and hence removal of the water molecules from the crystal lattice results in the availability of large –OH ions (seemingly protons)\(^{14}\) to migrate and this is manifested by dramatic increase in conductivity, seen a pulse at specified temperature. Thus, conductivity peaks can be regarded as a sure test of sample dehydration.

Above the temperature 402 K, indicated around the dip in the \(\sigma_{dc}\), the crystal of cadmium oxalate no longer remains in crystalline form due to liberation of the embedded water. Beyond 402 K, the material behaves, like a normal semiconductor, showing negative temperature coefficient of resistivity with activation energy equal to 1.58 eV for (001) plane. Beyond this temperature the crystal becomes disordered.

For a disordered system the conductivity (\(\sigma\)) is known\(^5,36\) to be expressed as

\[
\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^p\right]
\]

where \(\sigma_0\), the pre-exponential factor, is either independent or slowly varying function of temperature. Also \(T_0 = \frac{e^2}{\epsilon_r a}, a^{-1}\) and \(\epsilon_r\) being the electron localization range and the dielectric constant of the material, respectively. The exponent \(p\) depends on the grain size and the temperature range of measurements. Its value may be 0.25 for Mott's hopping\(^37\) and 0.5 to 1.0 for Efros hopping\(^38\), depending on the variation of density of states with energy within the coulomb type electron-electron correlation, which leads to a weak gap near the Fermi level due to the exciton effect. This idea of the coulomb gap was first introduced by Efros and Shklovskii\(^39\). If \(kT\) becomes greater than or equal to coulomb gap, where \(T\) is temperature of measurement, then coulomb gap effect does not become prominent. Outside the coulomb gap, hopping of the carriers in the localized state becomes prominent and the conductivity obeys the Mott’s relation\(^40\) and hence the corresponding conductivity could be expressed by Eq. (15),

\[
\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{1+x}}\right]
\]

where \(x\) is the dimensionality of the system. Here, for the three-dimensional system, \(x=3\). Also, \(T_0 = \beta a_m^{-1} g_o\), where \(a_{m}^{-1}\) is decay length of the wave function, \(g_o\) the Mott DOS at Fermi level and \(\beta\) a constant. In order to determine the exponent \(p\) in Eq. (14), we rewrite the temperature dependence of the conductivity using the relation\(^41\),

\[
\ln\sigma(T) = \ln\sigma_0 - \left(\frac{T_0}{T}\right)^p
\]

If we write\(^42\)
Ch.8. Electrical conductivity measurement

\[ W(T) = \frac{d \ln \sigma(T)}{d \ln T}, \] (17)

then \( p \) can be determined from the slope of the plot of \( \ln [W(T)] \) vs \( \ln(T) \), as shown in Fig 8.9, which is, on an average, a straight line. It may be noteworthy that the average value of \( p \) equal to 0.65 is an indication of the variable range hopping (VRH) conduction mechanism occurring within the coulomb gap (Efros-Shklovskii\(^{39}\)). In this process, the electrons jump from one localized state to the other in which there is an overlap of the wave function\(^{43}\). The difference in the eigen energies of the two localized states involved in the transition is compensated by the absorption or emission of phonons, indicating existence of indirect bandgap (chapter 10).

### 8.3.4 EVALUATION OF HOPPING PARAMETERS FROM ES MODEL\(^{38}\)

The plot of \( \ln(1/\sigma) \) vs \( 1/T^{0.65} \) (as shown in Fig 8.10) for cadmium oxalate is also drawn. From its slope, using least square fitting method, the value of parameter \( T_0 \) is obtained as 4776 K. Now, we can calculate several other pertinent parameters.

The tunneling exponent \( \alpha_m \) is given as

\[ \alpha_m = kT_0[(\pi g_2)^{1/3}]/10.5 \] (18)

where \( g_2 \) is given by

\[ g_2 = (3^{8/3} \pi^2 \varepsilon_r^3 \varepsilon_0^3)/(2^{5/3}e^6), \] (19)

The temperature dependent optimum hopping distance \( R_{opt} \) is given by

\[ R_{opt} = 0.25 \alpha_m^{-1}(T_0/T)^{1/2}, \] (20)

where \( \alpha_m^{-1} \) is the decay length. Thus, the average hopping energy, \( W_{opt} \) may be estimated from the relation,

\[ W_{opt} = 0.5k(T_0T)^{1/2}, \] (21)

and the width of the coulomb gap (\( \Delta \)) from the relation\(^{44}\)

\[ \Delta = k/2 \left(T_0T^*\right)^{1/2} \] (22)

where \( T^* \) is the temperature at which the Eq. (14) begins to be satisfied. In our case, we have \( T^* = 388 \text{ K} \). All the above obtained values are summarized in Table 8.1. In principle, one would expect both Mott and ES variable range hopping to be operative on the same sample in the different temperature ranges. The cross-over temperature between the Mott’s and Efros type of VRH is determined by the half width of the coulomb gap.
8.3.5 DC CONDUCTIVITY FOR THE SAMPLE IN PELLET FORM

Apart from studying crystals in different orientations, we have also studied the electrical conductivity of microcrystalline pellet also. The graphs of ln$\sigma$ vs 1000/T are shown plotted in Fig 8.11. The conductivity shows predominantly a clear, sharp maximum at a temperature of dehydration, because of shorting of two electrodes for a microcrystalline pellet having intercrystallite water. The transition peak is sensitive to frequency (Fig 8.11). The high frequency signal gives relatively a less peak height while the low frequency signal gives a large height peak. This is in consonance with the fact that the electrical conduction at lower range of frequencies is more prominent than the higher range, as observed.

8.4 CONCLUSIONS

1. The ac conductivity of cadmium oxalate follows $\sigma \propto \omega^{0.65}$, a power law. The obtained value of exponent $p$ (=0.65) shows the Effros hopping conduction mechanism for the crystal.

2. The frequency dependence of ac conductivity indicates the conduction to be due to small polarons.

3. The dc conductivity of the material has values between the normal conductivities of a semiconductor and an insulator.

4. The activation energy required to move permanent intrinsic defects in the crystal lattice is equal to 1.12 eV.

5. The deviation in the temperature dependence with respect to the two planes conspicuously implies conduction anisotropy.

REFERENCES

40) N. F. Mott, *J. Non-Crystall. Solids*, 1 (1968) 1
Table 8.1 Some parameters computed from dc electrical conductivity

<table>
<thead>
<tr>
<th>$p$</th>
<th>$\alpha_m^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>$2.745 \times 10^{-10}$ m</td>
</tr>
<tr>
<td>$T_0$</td>
<td>$R_{opt}$ = 0.288 nm</td>
</tr>
<tr>
<td>4776</td>
<td></td>
</tr>
<tr>
<td>$g_2$</td>
<td>$W_{opt}$ = 0.0886 eV</td>
</tr>
<tr>
<td>$7.46 \times 10^{88}$ mol$^{-3}$ J$^{-3}$m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_m$</td>
<td>$\Delta$ = 0.092 eV</td>
</tr>
<tr>
<td>$3.14 \times 10^9$ m$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8.1 Plot of a.c. conductivity versus reciprocal of temperature for (001) plane
Fig. 8.2  Plot of a.c. conductivity versus frequency for (001) plane

Fig. 8.3  Plot of power exponent n versus T representing transport mechanism
Fig. 8.4 Plot of a.c. conductivity versus reciprocal of temperature for (100) plane

Fig. 8.5 Plot of a.c. conductivity versus frequency for (100) plane
**Fig. 8.6** Plot of a.c. conductivity versus reciprocal of temperature for pellet sample

**Fig. 8.7** Plot of d.c. conductivity versus reciprocal of temperature for (001) plane
Ch. 8. Electrical conductivity measurement

\[ y = 9.4123x - 49.033 \]

\[ y = -8.6014x - 1.2902 \]

**Fig. 8.8** Plot of d.c. conductivity versus reciprocal of temperature for (100) plane

\[ y = 0.6568x - 0.6655 \]

\[ y = 5.891x - 0.6655 \]

**Fig. 8.9** Plot of ln W(T) versus ln T for (001) plane
Ch.8. Electrical conductivity measurement

\[ y = -4776x + 120.94 \]

![Graph](image)

**Fig. 8.10** Plot of \( \ln \left( \frac{1}{\sigma} \right) \) versus \( \ln 1/T^{0.65} \) for (001) plane

![Graph](image)

**Fig. 8.11** Plot of d.c. conductivity versus reciprocal of temperature for pellet sample