CHAPTER VI

ELECTRICAL CONDUCTIVITY OF LIGHT RARE-EARTH ZIRCONATE COMPOUNDS AT HIGH TEMPERATURE

6.1 INTRODUCTION

The electrical conductivity and dielectric constant are interesting properties which provide important information regarding the conduction mechanism in the solids. The determination of electrical conduction mechanism in the solids having very little conductivity is a difficult task. In general, one has to find out first whether the conduction is electronic or ionic or mixed (both ionic and electronic) then to determine the source of ionic conduction (anion or cation vacancies or interstitial etc.) or the electronic conduction (intrinsic or extrinsic). After this has been decided one has to find out the mechanism of conduction and evaluate various parameters like number (n), activation energy ($E_a$) and mobility ($\mu$) of charge carriers using appropriate models. To have good quantitative idea of above mentioned parameters, one needs several types of experimental data, e.g. electrical conductivity ($\sigma$) as a function of time, electric field, ac signal frequency, temperature and doping, dielectric constant ($K'$) and loss ($K''$) as a function of frequency and temperature etc. It is not easy to obtain all these data in any single laboratory. A quantitative understanding and semi qualitative analysis of the conduction mechanism can be presented by studying the electrical conductivity as a function of various parameters (Dwivedi et al. 2001, Hirota et al. 2003, Aung et al. 2005). In general electrical conductivity gives mixed information about number and mobility of charge carriers. The study of electrical conductivity yields some important information about conduction process in any solid. Using this methodology we have investigate electrical transport mechanism of light rare-earth zirconate compounds and details are presented in this chapter.
6.2 MATERIAL PREPARATION AND EXPERIMENTAL PROCEDURE

The studied compounds of general formula \( R_2Zr_2O_7 \) (Where \( R = \text{La, Ce, Pr, Sm, Nd and Eu} \)) were prepared by using procedure described in chapter IV and characterised by X-ray diffraction techniques. The main measurement done is electrical conductivity for the electrical transport study. The details about the apparatus used and procedure adopted are given in chapter III. Measurement of electrical conductivity was performed on pressed pellets because of the difficulty in growing large single crystals of these compounds needed for such measurements due to their high melting point and our limited facilities. In pellets grain boundaries and air pores considerably reduce \( \sigma \) values and often measurements on them do not reflect the bulk value for the material. It is not possible to eliminate them completely, however pellets can be prepared in such a way that these effects are considerably reduced. In such a situation the bulk value for the material can be obtained employing suitable corrections. The first requirement in this direction is to make pellets of uniform density. This has been achieved by using a proper steel die and keeping \( t^2/A \) (Where t is the thickness and A the face area of the pellet) ratio less than 0.4 fixed by other workers (Kumar 1971, Tripathi 1981, Tripathi and Lal 1982 and Lal et al. 1982). The details are described in chapter IV.

6.3 STUDY OF PELLET DENSITY AND ELECTRICAL CONDUCTIVITY AS A FUNCTION OF PELLETIZING PRESSURE

The density of pellets of each studied compound well annealed at appropriate temperature have been obtained from the measurement of its volume and mass. The mass of each compound is obtained by weighing the pellets on a sensitive balance. The thickness and area of the pellets are taken out and thereby the density of the pellets is calculated. The density measurement has been done on each pellet of the compound made at a pressure ranging from \( 3.04 \times 10^8 \) to \( 8.24 \times 10^8 \) Nm\(^{-2} \). The variation of pellet
density \( (d_p) \) with pelletizing pressure \( (P) \) is shown in Fig. 6.1 for different compounds. It is seen from these figures that the pellet density \( (d_p) \) depends upon the pelletizing pressure. It increases almost linearly till \( P \) equals \( 6 \times 10^8 \) Nm\(^{-2} \) and after that the increase becomes slow and when \( p \) exceeds \( 7.19 \times 10^8 \) Nm\(^{-2} \), the density becomes almost constant. The maximum density of the pressed pellets, however, remains less than the reported X-ray density \( (d_0) \) of the materials. Thus pores exist in the pressed pellets. The pore fraction \( (f_p) \) for highest pressed pellet is determined using the relation

\[
f_p = \frac{d_0 - d_p}{d_0}
\]  

(6.1)

The values of \( d_0, d_p \) and \( f_p \) for all the studied compounds are given in Table 6.1. The pore fraction is so small that the bulk value of any parameter can be obtained using suitable corrections.

**TABLE-6.1**

**THE X-RAY DENSITY \( (d_0) \), PELLET DENSITY \( (d_p) \) OF HIGHEST PRESSED PELLET AND PORE FRACTION \( (f_p) \) FOR STUDIED COMPOUNDS**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( d_0 \times 10^{-3} ) (Kgm(^{-3} ))</th>
<th>( d_p \times 10^{-3} ) (Kgm(^{-3} ))</th>
<th>( f_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_2\text{Zr}_2\text{O}_7 )</td>
<td>3.68</td>
<td>3.67</td>
<td>0.003</td>
</tr>
<tr>
<td>( \text{Ce}_2\text{Zr}_2\text{O}_7 )</td>
<td>4.49</td>
<td>4.25</td>
<td>0.054</td>
</tr>
<tr>
<td>( \text{Pr}_2\text{Zr}_2\text{O}_7 )</td>
<td>3.04</td>
<td>3.03</td>
<td>0.003</td>
</tr>
<tr>
<td>( \text{Nd}_2\text{Zr}_2\text{O}_7 )</td>
<td>3.81</td>
<td>3.75</td>
<td>0.016</td>
</tr>
<tr>
<td>( \text{Sm}_2\text{Zr}_2\text{O}_7 )</td>
<td>5.05</td>
<td>5.00</td>
<td>0.009</td>
</tr>
<tr>
<td>( \text{Eu}_2\text{Zr}_2\text{O}_7 )</td>
<td>3.32</td>
<td>3.27</td>
<td>0.015</td>
</tr>
</tbody>
</table>

The electrical conductivity \( (\sigma_p) \) of several pellets of each compound made at different pelletizing pressures \( (P) \) were measured using silver foil electrodes at a fixed temperature. The plots of \( \log\sigma_p \) vs \( P \) for different
FIG 6.1 PLOTS OF PELLET DENSITY ($d_p$) AGAINST PELLETIZING PRESSURE ($P$)
compounds are given in Fig. 6.2. It is seen from this figure that \( \log \sigma_p \) depends upon pressures. It increases with \( P \) and tends to become constant when \( P \) exceeds \( 7.19 \times 10^8 \) Nm\(^{-2}\). The relatively low conductivity observed at lower pressure is obviously due to presence of less conducting grain boundary regions. These and likewise effects decrease to some extent when pelletizing pressure is increased. This fact is strengthened further by the observed constancy in the density of the pellets at higher pelletizing pressures \( \sigma_p \) of pellets made at same \( P \) having different dimensions are practically same. No effect of pellet shape and size has been observed on \( \sigma_p \). It has been generally observed that both conductivity and density of the pellets attain their maximum value at the same pelletizing pressure. Though the constancy observed in \( d_p \) and \( \sigma_p \) ensures significant reduction of grain boundary effect yet the density of the pellet lesser than the X-ray density of the material indicates that \( \sigma_p \) may be significantly smaller than the crystalline value of electrical conductivity (\( \sigma \)). The estimation of \( \sigma \) from \( \sigma_p \) has been done by a standard relation (Russel 1935).

\[
\sigma = \sigma_p \left(1 + \frac{f}{1+f^3}\right)
\]

(6.2)

6.4 STUDY OF CURRENT DENSITY AS A FUNCTION OF APPLIED ELECTRIC FIELD

In the measurement of electrical conductivity (\( \sigma \)) the role of the electrode is very important. For such measurement it is essential that the contact between the pellet and electrode interface is ohmic (Roberts 1968). Even in the case of the ohmic contact, the contact resistance play an important role in the measurement of \( \sigma \) for high conducting solids. However, they are relatively less important in the case of low conducting solids. To ensure the ohmic contact between the pellet and electrode interface, the
FIG 5.2 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY OF PELLETS (Log $\sigma_p$) AGAINST PELLETIZING PRESSURE (P) AT CONSTANT TEMPERATURE (T = 666K)
current through the pellet has been measured at different applied voltages at constant temperature. Both current through and voltage across the pellet have been measured using Keithley digital multimeter type 171. Using dimension of the pellet, the current density (J) and electric field (E) have been evaluated. The results for different compounds are shown in Fig. 6.3. It is seen from this figure that except at very low fields, J vs E plots are linear. This ensures ohmic contact between pellet and electrode interface. In all further measurements we have used well sintered pellets made at higher pelletizing pressures and electric field (E) in the range where contact between electrode and pellet interface was ohmic.

6.5 STUDY OF ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FREQUENCY AND TIME

Various superfluous effects, not at all connected with the bulk properties of the crystals can arise purely due to grain boundaries. The grain boundary effects in pellet are reduced if fine and uniform powders are taken for making pellets and sintered at higher temperature for significantly long time. In any case, if sintered pellets are used for conductivity measurements then it is necessary to ensure that grain boundaries effects are negligible. This can be demonstrated by measuring \( \sigma \) at various frequencies and showing that it does not depend appreciably on it. To show that grain boundary effects are minimized, the electrical conductivity of some highly pressed pellets of each compounds have been measured at different ac signal frequencies at a constant temperature. The overall error in conductivity measurement were less than two percent. The frequencies of measurement are 100Hz, 1KHz and 10KHz. The plot of \( \log \sigma \) as a function of logarithm of ac signal frequency for all compounds are shown in Fig.6.4. It is seen from these figures that conductivity is nearly independent of frequency. This indicates that grain boundary effects are sufficiently minimized for highly pressed pellets. The dc values of electrical conductivity are also given in these figures. They are almost same as ac conductivity at that temperature.
FIG. 6.3 PLOTS OF CURRENT DENSITY (J) AGAINST ELECTRIC FIELD (E) AT CONSTANT TEMPERATURE
FIG. 6.4 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST LOGARITHM OF AC SIGNAL FREQUENCY (Log $f$) AT CONSTANT TEMPERATURE
Current density through the light rare-earth zirconate compounds have been measured with time at constant temperature. The applied field was in the range corresponding to ohmic contact. The results obtained are shown in Fig.6.5. It is observed from these figures that the current is independent of time. From these observations we conclude that there is no ionic conductivity in studied compounds.

6.6 STUDY OF ac ELECTRICAL CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

The ac electrical conductivity measurement of few pellets of each light rare-earth zirconate compounds have been carried out in air in temperature range 300K to 1125K. The measurements have been done on pellets made at $P > 7.19 \times 10^8 \text{Nm}^{-2}$ and sintered at 1500K for 50 hrs. The conductivity values for a particular compound do not differ from sample to sample. It is also independent of pellet thickness. Further for each pellet no significant difference has been observed in conductivity values during heating and cooling cycles. It also remains almost same irrespective of thermal history or self life of the pellet. The mean value of conductivity for few pellets of each compound has been taken as bulk conductivity of pressed pellets. The crystalline value of electrical conductivity ($\sigma$) has been calculated using relation 6.2. The variation of $\log \sigma$ with inverse of absolute temperature ($T^{-1}$) for different compounds are shown in Figs. 6.6 to 6.11. It is seen from these figures that $\sigma$ values for these compounds are between $10^{-7}$–$10^{-1} \text{\Omega}^{-1}\text{m}^{-1}$ in the temperature range 300-1125K. It is seen from the figures that each plot can be divided into two linear ranges, namely range I below $T<T_1$, and range II above $T>T_1$. The temperature $T_1$ is termed as transition or break temperature and are listed in table 6.2 for studied compounds. The linear region of $\log \sigma$ vs $T^{-1}$ plot can be represented by the usual relation

$$\sigma = \sigma_0 \exp \left( \frac{-E_\sigma}{kT} \right)$$

(6.3)
FIG: 6.5 PLOTS OF CURRENT DENSITY (J) AGAINST TIME (t) AT CONSTANT TEMPERATURE AND FIELD

\[ J(Am^{-2}) \times 10^2 \]

- \( \text{La}_2\text{Zr}_2\text{O}_7 \), \( T = 1025K \), \( E = 2.1 \times 10^3 \text{ (vm}^{-1}) \)

- \( \text{Ce}_2\text{Zr}_2\text{O}_7 \), \( T = 850K \), \( E = 7.8 \times 10^3 \text{ (vm}^{-1}) \)

- \( \text{Pr}_2\text{Zr}_2\text{O}_7 \), \( T = 530K \), \( E = 1.3 \times 10^3 \text{ (vm}^{-1}) \)

- \( \text{Nd}_2\text{Zr}_2\text{O}_7 \), \( T = 910K \), \( E = 1.5 \times 10^3 \text{ (vm}^{-1}) \)

- \( \text{Sm}_2\text{Zr}_2\text{O}_7 \), \( T = 800K \), \( E = 5.1 \times 10^3 \text{ (vm}^{-1}) \)

- \( \text{Eu}_2\text{Zr}_2\text{O}_7 \), \( T = 750K \), \( E = 6.5 \times 10^3 \text{ (vm}^{-1}) \)
FIG. 6.6 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log\(\sigma\)) AGAINST INVERSE OF ABSOLUTE TEMPERATURE (T\(^{-1}\))
FIG. 6.7 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY ($\log(\sigma)$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 6.8 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log\(\sigma\)) AGAINST INVERSE OF ABSOLUTE TEMPERATURE (T\(^{-1}\))
FIG 6.9 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY ($\log\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 6.10 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY ($\log(\sigma)$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 6.11 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY ($\log(\sigma)$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$).
The values of pre-exponential constant ($\sigma_0$) and activation energy ($E_a$) have been evaluated from the experimental plot and are also given in Table 6.2 to 6.3.

**TABLE-6.2**

**CONSTANTS OF THE LINEAR RANGE T<T₁ IN Log$\sigma$ vs T$^{-1}$ PLOTS AND BREAK TEMPERATURE T₁ FOR ZIRCONATE COMPOUNDS**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_1$ (K)</th>
<th>$\sigma_0$ ($\Omega^{-1}m^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$Zr$_2$O$_7$</td>
<td>632</td>
<td>3.33×10$^{-6}$</td>
<td>0.13</td>
</tr>
<tr>
<td>Ce$_2$Zr$_2$O$_7$</td>
<td>676</td>
<td>1.78×10$^{-6}$</td>
<td>0.10</td>
</tr>
<tr>
<td>Pr$_2$Zr$_2$O$_7$</td>
<td>550</td>
<td>7.29×10$^{-4}$</td>
<td>0.12</td>
</tr>
<tr>
<td>Nd$_2$Zr$_2$O$_7$</td>
<td>641</td>
<td>3.50×10$^{-5}$</td>
<td>0.13</td>
</tr>
<tr>
<td>Sm$_2$Zr$_2$O$_7$</td>
<td>613</td>
<td>2.60×10$^{-6}$</td>
<td>0.10</td>
</tr>
<tr>
<td>Eu$_2$Zr$_2$O$_7$</td>
<td>694</td>
<td>4.68×10$^{-5}$</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**TABLE-6.3**

**CONSTANTS OF THE LINEAR RANGE T>T₁ IN Log$\sigma$ vs T$^{-1}$ PLOTS AND BREAK TEMPERATURE T₁ FOR ZIRCONATE COMPOUNDS**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_1$ (K)</th>
<th>$\sigma_0$ ($\Omega^{-1}m^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$Zr$_2$O$_7$</td>
<td>632</td>
<td>1.25×10$^{7}$</td>
<td>2.1</td>
</tr>
<tr>
<td>Ce$_2$Zr$_2$O$_7$</td>
<td>676</td>
<td>8.54×10$^{10}$</td>
<td>2.7</td>
</tr>
<tr>
<td>Pr$_2$Zr$_2$O$_7$</td>
<td>550</td>
<td>2.18×10$^{16}$</td>
<td>2.6</td>
</tr>
<tr>
<td>Nd$_2$Zr$_2$O$_7$</td>
<td>641</td>
<td>7.88×10$^{7}$</td>
<td>2.1</td>
</tr>
</tbody>
</table>
6.7 DISCUSSION

The variation of electrical conductivity as a function of various parameters have been presented in preceding sections. One of these results is the variation of dc electrical conductivity with time. It has been found independent of time even at relatively higher current and sufficiently long time. Also no significant difference has been observed between dc and ac values of electrical conductivity at any temperature. Further, ac conductivity has been found independent of signal frequencies. All these observations indicate that light rare-earth zirconate compounds are essentially electronic conductors and ionic conductivity if any, is significantly small. Thus majority charge carriers in these solids are either electrons or holes. Around 300K electrical conductivity of studied compounds lies in the range $10^{-7} - 10^{-4} \Omega^{-1}m^{-1}$ and increases with the increase of temperature. Hence at normal temperature the studied compounds are typical semiconducting solids. The conductivity is highest for $\text{Pr}_2\text{Zr}_2\text{O}_7$ and lowest for $\text{La}_2\text{Zr}_2\text{O}_7$. The log$\sigma$ vs T$^{-1}$ plots for the studied compounds have two linear regions. One lying below $T_1$ and other above $T_1$. The slope of log$\sigma$ vs T$^{-1}$ plots for the first region is small (~0.1 eV) for all the studied compounds. The pre-exponential constant ($\sigma_0$) for all the studied compounds in this region is also small (~$10^{-4}$–$10^{-6}\Omega^{-1}m^{-1}$). Both these values are not appropriate for intrinsic conduction. Thus at temperature $T$<$T_1$, the electrical conductivity in these compounds seems to be extrinsic. Above $T_1$ the values of activation energy as well as the pre-exponential constant of the studied compounds are large. Hence above $T_1$ the electrical conduction seems to be intrinsic.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
<th>Conductivity</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sm}_2\text{Zr}_2\text{O}_7$</td>
<td>613</td>
<td>$5.04 \times 10^{14}$</td>
<td>2.9</td>
</tr>
<tr>
<td>$\text{Eu}_2\text{Zr}_2\text{O}_7$</td>
<td>694</td>
<td>$3.51 \times 10^{10}$</td>
<td>2.5</td>
</tr>
</tbody>
</table>
It has been discussed that electrical conduction below $T_1$ in all studied compounds are due to impurities or defects. Thus in order to explain the electrical conduction one has to look possible defects and impurities in these materials. Chemical impurities in these compounds are also expected. Thus formation of defect centres either due to non-stoichiometry or chemical defect are quite probable. The charge carriers from these centres may be thermally excited to respective bands and conduct via band mechanism or they may be localised and may conduct via hopping mechanism. Thus extrinsic conduction in these solids is due to impurities and $E_a$ refers to the ionization energy of charge carriers.

The activation energy estimated above $T_1$ is given in Table 6.3 seems to be an intrinsic activation energy because $\sigma_0$ is in the correct range for intrinsic electrical conductivity. Thus the change in the nature of the log$\sigma$ vs $T^{-1}$ plot at $T= T_1$ (break temperature) is due to the change in the conduction mechanism i.e. transition from extrinsic to intrinsic conduction

6.8 CONCLUSION

On the basis of above studies following conclusions can be drawn about electrical conduction of studied compounds.

1. These are semi-conducting materials with electrical conductivity value lying in the range $10^{-7} \Omega^{-1}m^{-1}$ to $10^{-4} \Omega^{-1}m^{-1}$ which becomes of the order of $10^{-3} \Omega^{-1}m^{-1}$ to $10^0 \Omega^{-1}m^{-1}$. The maximum electrical conductivity is observed for $\text{Pr}_2\text{Zr}_2\text{O}_7$ and lowest for $\text{La}_2\text{Zr}_2\text{O}_7$.

2. The log$\sigma$ vs $T^{-1}$ plots can be divided into two ranges. First below $T<T_1$ and second above $T>T_1$.

3. The electrical conduction below $T_1$ is essentially extrinsic always associated with impurities, defect and interstitials. Above $T_1$ conduction is essentially intrinsic.

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