CHAPTER - 7

IMPEDEANCE SPECTROMETRICAL CHARACTERIZATION

The impedance spectroscopical analysis of all the grown crystals are discussed in this chapter. Nyquist plots were drawn and the relaxation frequencies were calculated were provided along with the results and discussion.

7.1. Introduction

Impedance spectroscopy or the method of Complex Impedance Analysis (CIA) has emerged out as a very powerful and useful tool [314-318] for characterizing many of the electrical properties of materials and their inter interface with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconductor, mixed electronic–ionic, and even insulators (dielectrics). The Complex Impedance Spectroscopy (CIS) gives the direct correlation between the response of a real system and an idealized model circuit composed of discrete electrical components. An equivalent Impedance spectroscopy has become extremely popular in the last few years because of the availability of very high quality impedance analyzers that work over extended frequency regions. This finds a wide range of application in various areas.
7.2. Impedance Measurements

The experimentally measured value of complex impedance are plotted as a function of frequency in a complex plane (ie, $Z'$ vs $Z''$) [319]. Actually it is $-Z''$ but for the shake of convenient, only modulus of the quantity $Z''$ has been used in all of the plots drawn in the present study. The plots also called as Nyquist plots (Cole–Cole plots) is an important non–destructive method of studying the electrical properties of the solids. These plots reveal special features that depend on the relative contributions from the grain, grain boundaries and electronic polarization process [320]. The electrical properties are determined by a series combination of such grain and grain boundary capacitances ($C_1$ and $C_2$) and resistances ($R_1$ and $R_2$). Each of these components are represented by a parallel RC elements. Each of the parallel RC elements are separated to measure their individual R and C values. This is best achieved using a combination of the impedance and modulus formalisms since each parallel RC elements gives rise to a semicircle in the complex plane. The plot of $Z''$ versus $Z'$ with $Z' = Z \cos \theta$ and $Z'' = Z \sin \theta$ are distinct semicircular arcs for processes having widely separated time constants and depressed looking semicircular arcs when the time constants are close to each other.

All the grown crystals cut into rectangular shape and polished were subjected to impedance measurements using Agilant 4284A LCR meter at two different temperatures viz. 30°C and 49°C (curie point temperature) and frequency ranging from 1Hz to 1MHz. The samples were coated with a good quality graphite to have good conducting surface layers. In the present study, the complex impedance plots of $Z''$ versus $Z'$ for all the eleven samples were plotted. From the measured values cole–cole plots were drawn. The bulk resistance and capacitance values could
obtained by the intercepts made by the semicircular arc on the real part of the impedance $Z'$. 

The relaxation frequencies ($f_s$) were determined from the complex impedance data ($Z'$ and $Z''$) using the relation, reduced from the complex dielectric constant ($\varepsilon'$ and $\varepsilon''$) data [326]

$$\tau = \frac{f_s}{Z''(f)} = \frac{Z''(f)}{(Z'(f) - Z_\infty)f}$$

$$f_s = \frac{(Z'(f) - Z_\infty)f}{Z''(f)}$$

### 7.3. Results and discussion

An important and non-destructive way of studying the electrical properties of the prepared sample is by the use of complex impedance spectroscopy. Nyquist plots (Cole–Cole plot) drawn for all the eleven grown crystals are shown in the figures 153-174, the measurements were made in the frequency range 1Hz to 1MHz at two different temperature, viz 30 and 49°C (curie point temperature), here complex impedance and phase angle were measured at a known frequency, the values of $Z' = Z \cos \theta$ and $Z'' = Z \sin \theta$ were found out. $Z'$ and $Z''$ values were plotted in a graph which shows a semicircular arcs that converged at the origin of the imaginary plane at very high frequency [321]. Each sample has three relaxation frequencies, Alexandru and AnnNY [75] has studied the effect of D-alanine in TGS crystal in the dielectric parameters. They found that the relaxation time is not a real constant on such large time interval. In a semi long scale, permittivity shows three stages, probably related to several mechanism of relaxation.
The three relaxation frequencies are provided in table 81. It is found that when the relaxation time decreased the radius of the semicircles got increased. It is shown that the relaxation frequencies for 49°C is $10^5$ times greater than that for 30°C, the radius of the semicircle at curie point temperature ($T_c = 49°C$) is very much less than that for 30°C, (for convenience, at 30°C $Z'$ and $Z''$ are taken in the order of $10^5 \Omega$ whereas, at 49°C it was taken in the order $10^4 \Omega$ in comparison curve ie, in figures 175-185) which shows that at curie point temperature ($T_c = 49°C$) the resistance of the sample is very low, it is also found that the radius of the semicircle increases with increase in the dopant concentration. This shows that at higher concentration, there is a increase of bulk resistance.
Figure 153: Nyquist plot for pure TGS crystal at 30°C

Figure 154: Nyquist plot for 1:0.002 CaTGS crystal at 30°C
Figure 155: Nyquist plot for 1:0.004 CaTGS crystal at 30°C

Figure 156: Nyquist plot for 1:0.006 CaTGS crystal at 30°C
Figure 157: Nyquist plot for 1:0.008 CaTGS crystal at 30°C

Figure 158: Nyquist plot for 1:0.010 CaTGS crystal at 30°C
Figure 159: Nyquist plot for 1:0.002 LaTGS crystal at 30°C

Figure 160: Nyquist plot for 1:0.004 LaTGS crystal at 30°C
Figure 161: Nyquist plot for 1:0.006 LaTGS crystal at 30°C

Figure 162: Nyquist plot for 1:0.008 LaTGS crystal at 30°C
Figure 163: Nyquist plot for 1:0.010 LaTGS crystal at 30°C

Figure 164: Nyquist plot for pure TGS crystal at 49°C
Figure 165: Nyquist plot for 1:0.002 CaTGS crystal at 49°C

Figure 166: Nyquist plot for 1:0.004 CaTGS crystal at 49°C
Figure 167: Nyquist plot for 1:0.006 CaTGS crystal at 49°C

Figure 168: Nyquist plot for 1:0.008 CaTGS crystal at 49°C
Figure 169: Nyquist plot for 1:0.010 CaTGS crystal at 49°C

Figure 170: Nyquist plot for 1:0.002 LaTGS crystal at 49°C
Figure 171: Nyquist plot for 1:0.004 LaTGS crystal at 49°C

Figure 172: Nyquist plot for 1:0.006 LaTGS crystal at 49°C
Figure 173: Nyquist plot for 1:0.008 LaTGS crystal at 49°C

Figure 174: Nyquist plot for 1:0.010 LaTGS crystal at 49°C
Figure 175: Comparison of Nyquist plots for pure TGS crystal at 30°C and 49°C

Figure 176: Comparison of Nyquist plots for 1:0.002 CaTGS crystal at 30°C and 49°C
Figure 177: Comparison of Nyquist plots for 1:0.004 CaTGS crystal at 30°C and 49°C

Figure 178: Comparison of Nyquist plots for 1:0.006 CaTGS crystal at 30°C and 49°C
Figure 179: Comparison of Nyquist plots for 1:0.008 CaTGS crystal at 30°C and 49°C

Figure 180: Comparison of Nyquist plots for 1:0.010 CaTGS crystal at 30°C and 49°C
Figure 181: Comparison of Nyquist plots for 1:0.002 LaTGS crystal at 30°C and 49°C

Figure 182: Comparison of Nyquist plots for 1:0.004 LaTGS crystal at 30°C and 49°C
Figure 183: Comparison of Nyquist plots for 1:0.006 LaTGS crystal at 30°C and 49°C

Figure 184: Comparison of Nyquist plots for 1:0.008 LaTGS crystal at 30°C and 49°C
Figure 185: Comparison of Nyquist plots for 1:0.010 LaTGS crystal at 30°C and 49°C
Table 81: Relaxation frequency for pure, Ca and La doped TGS crystals

<table>
<thead>
<tr>
<th>System</th>
<th>Relaxation frequency ($f_r$) (Hz)</th>
<th>30°C</th>
<th>49°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TGS</td>
<td>129.38</td>
<td>19.61</td>
<td>31.33</td>
</tr>
<tr>
<td>1:0.002 CaTGS</td>
<td>125.32</td>
<td>128.30</td>
<td>8.17</td>
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<tr>
<td>1:0.004 CaTGS</td>
<td>67.18</td>
<td>1.03x10³</td>
<td>1.16x10³</td>
</tr>
<tr>
<td>1:0.006 CaTGS</td>
<td>2.65</td>
<td>148.32</td>
<td>357.66</td>
</tr>
<tr>
<td>1:0.008 CaTGS</td>
<td>798.87</td>
<td>1.54x10⁴</td>
<td>807.93</td>
</tr>
<tr>
<td>1:0.010 CaTGS</td>
<td>81.55</td>
<td>583.98</td>
<td>5.70x10³</td>
</tr>
<tr>
<td>1:0.002 LaTGS</td>
<td>2.08</td>
<td>70.96</td>
<td>1.49x10³</td>
</tr>
<tr>
<td>1:0.004 LaTGS</td>
<td>1.55</td>
<td>4.83</td>
<td>440.47</td>
</tr>
<tr>
<td>1:0.006 LaTGS</td>
<td>2.54</td>
<td>66.38</td>
<td>9.14</td>
</tr>
<tr>
<td>1:0.008 LaTGS</td>
<td>3.26</td>
<td>66.25</td>
<td>9.86</td>
</tr>
<tr>
<td>1:0.010 LaTGS</td>
<td>11.28</td>
<td>3.108</td>
<td>422.4</td>
</tr>
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