Chapter 3

DC Electrical Conductivity and Phase Transition Studies of Lithium Hydrazinium Sulphate Single Crystal
3.1 Literature Review

During recent years fast ion conducting solids have been the subject of extensive research. These materials find potential application in high energy density batteries, specific electrodes and sensors, display devices and various other electrochemical systems. Protonic conductors made up a class of fast ion conductors in which charge transfer is a result of the movement of $H^+$ ions. Proton conducting solids are particularly relevant to $H^2$. $O^2$ fuel cells and water electrophoresis devices [1]. This chapter deals with the DC electrical conductivity of the proton conductor Lithium Hydrazine Sulphate single crystal.

Lithium Hydrazine Sulphate is a ferroelectric crystal having practical importance, despite its low spontaneous polarization. Its coercive field is advantageously low. Its spontaneous polarization is about equal to that of Rochelle salt; and it is much lower than that of glycine [2]. The compound Lithium Hydrazine Sulphate (LiN$_2$H$_5$SO$_4$) was first prepared by Sommer and Weise in 1916 [3]. The abbreviation LHS is used for this compound hereafter. LHS was first shown to be a proton conductor by Vanderkooy et al [4]. The magnetic resonance absorption studies were conducted by Cuthbert and Petch [5].
Since the discovery of its ferroelectric behavior by Pepinsky [2] in 1958 LHS has been the subject of numerous experimental investigations. M R Anderson and I D Brown questioned this ferroelectric behavior [6]. The crystal structure of LHS was studied using X-ray diffraction method by I D Brown [7] and later by Jan H Van Den Hende and Henri Buotin [8]. Later Brown et al [9] refined the crystal structure data of LHS using X-ray diffraction method. Again the structure was refined using Neutron diffraction technique by V M Padmanabhan and R Balasubramanian [10]. Molecular reorientation study of this crystal was conducted by MacClement et.al [11] using proton resonance absorption study to resolve the contradictory conclusion drawn from the magnetic resonance and neutron diffraction studies, about the hindered rotation of NH$_3$ group, because of the important role the hydrogen atoms play in the ferroelectric behavior of LHS. Spectroscopic studies like Raman photometry was conducted by Krishnan & Krishnan [12], and IR measurement was carried out by Warrier & Narayanan [13]. Roger Frech and Scott H Brown reinvestigated the low temperature Raman spectra and room temperature IR spectra of LHS [14]. Later they extend their studies over a temperature range 15K to 300 K [15].

The structure of LHS at room temperature is found to be orthorhombic with the space group Pna2$_1$. The unit cell has dimension a =8.99Å, b= 9.94Å and c= 5.18Å and contain four formula units. The fig 3.1 shows the unit cell. The density of the crystal is 1.966 gcm$^{-3}$. The Lithium and Sulphur atoms are at the center of the tetrahedra of oxygen atoms [7]. The tetrahedra share corner oxygen atoms to form three-dimensional framework. Each oxygen atom is bonded to one lithium atom and to one sulphur atom, so that every LiO$_4$ tetrahedra is surrounded by four SO$_4$ tetrahedra and vice versa. The morphology of the crystal is shown in fig 3.2. The neutron diffraction study suggests that the SO$_4$ tetrahedron is slightly distorted. The distortion is not as much as that observed by Van Den Hende & Boutin. An interesting feature in the structure of LHS is the existence of the infinite chains of hydrogen bonds in the direction of the c-axis [10] as shown in fig 3.3. Hydrogen atoms of the NH$_2$ group of the N$_2$H$_5$ ion are ordered inside the crystal and NH$_2$ group is linked by one hydrogen bond to the oxygen of the SO$_4$ ion and by the other to the adjacent NH$_2$ group. The neutron diffraction study also suggests
Fig 3.1: Unit cell visualization of LHS crystal in the a-b plane

Fig 3.2: Morphology of the LHS crystal
that there is no hindered rotation of hydrogen atoms of the NH$_3$ group, as reported by Cuthbert & Petch. But in a more detail investigation by MacClement et al. [11] and R R Knispel & Petch [16] concluded that the hydrogen atoms in the NH$_3$ group is rigid at room temperature but it undergo hindered rotation about the N -N axis, as the temperature increases. The electrical properties are related to the movement of Protons within this chain. One proton from each -NH$_2$ group contributes a link to the chain of N-H--N bonds while the other proton in the NH$_2$ group and the proton of the -NH$_3^+$ group form N-H--N bonds to the oxygen of the SO$_4^{2-}$ tetrahedra.

The interesting electrical properties of LHS have been described briefly by Pepinsky et al. The spontaneous polarization is found to increase with temperature in the range -10 to +70° C [2]. Cuthbert & Petch [5] have shown that at room temperature the crystal conduct electricity strongly along c axis and this conduction increases very rapidly with temperature. The existence of ...N-H....N-H....N-H chains permits the transfer of protons along the hydrogen bond from one N atom to the next and thus the large electrical conductivity which occur along the c-axis [4]. The thermal expansion study by S Devanarayan & K R K Easwaran [17] on Lithium Hydrazinium Sulphate, shows anomalous behavior in the expansion coefficients between -160°C and -60°C and also in the neighborhood of +130°C. These anomalies are explained as due to
homomorphous transitions in which there is a reorientation of the \(-\text{NH}_2\) group about the N-N axis or a re-alignment of the \(-\text{NH}_2\) group. The thermal diffusivity of LHS in different crystallographic directions, in the temperature range from 20 to 70°C were conducted by T. Krajewski and M. Stachowiak [18].

LHS has been considered as a member of the ferroelectric sulfate family because it exhibits what appears to be hysteresis loop in the c-axis dielectric constants, although no conclusive evidence for a ferroelectric phase transition has been found. The electrical conduction of LHS is due to the translational motion of proton has been investigated by some authors [1, 4, 19, 20]. The conductivity along c-axis is about \(10^3\) times as great as along a- and b-axes at room temperature and has the value of \(2 \times 10^8\ \text{ohm}^{-1}\ \text{cm}^{-1}\) and an activation energy of 0.75 eV at 298K [4]. Similar results have been obtained from electrical conductivity measurements on deuterated LHS [21]. Hugo Schmidt et al [22] have proposed a one-dimensional partially blocked channel model for the unusual electrical properties of this material and the hysteresis loop is interpreted as arising from a saturation of the ac conductivity. Temperature dependence of the real part of the high frequency dielectric constant measured between \(-200^\circ\text{C}\) to \(+200^\circ\text{C}\) do not carry any signature of a ferroelectric transition. Salman et al [20] measured the complex impedance in the frequency range between 20 Hz and 500 kHz from 290 K to 485 K and suggested the existence of a structural change at about 433K.

Godfrey et al [23] measured the temperature dependence of all six diagonal elastic constants at high temperature and reported that the anomalous behavior of these constants in the 410 K- 440 K temperature ranges is attributed to a phase transition occurring near 425 K. But in a more recent investigation on the electrical conductivity at high temperature by T. Fukami [24] suggest that there is no indication of a structural phase transition in this temperature range.

Thus it has been suggested by some groups that there exist a structural phase transition at high temperature and some group suggest the existence of structural phase transition has not yet been confirmed. Even though electrical conductivity in LHS crystal along c-axis has been understood well, the conductivity along a- and b-axis has scarcely
given in the literature. The aim of the present study is to check the existence of any phase transition by measuring the electrical properties.

3.2 Experimental Details

3.2.1 Crystal Growth

Single crystals of Lithium Hydrazinium Sulphate were grown from aqueous solution by slow evaporation method.

The reaction is

\[ \text{Li}_2\text{CO}_3 + 2(2\text{NH}_2)\text{H}_2\text{SO}_4 \rightarrow 2\text{LiN}_2\text{H}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O} \]

Large size crystal of very good quality having dimension 30mm $\times$ 30mm $\times$ 20mm was obtained after 45 days. The solubility of the LHS is found to increase linearly with temperature and almost saturate at 50°C. The fig 3.4 shows the solubility curve and fig 3.5 shows the photograph of the grown crystal.

![Solubility curve of the Lithium Hydrazinium Sulphate crystal](image)

3.2.2 Cutting and Polishing

The interfacial angles are measured using a contact goniometer. By knowing the lattice parameters and crystal system one can construct a stereographic plot by using the computer program 'Jcrystal'. The natural faces of the sample have been identified by
the method as discussed in chapter 2. The stereographic projection of the crystal is depicted in the fig 3.6 with possible faces. The morphology of the grown crystal is shown in fig 3.2. The measured and computed interfacial angles are shown in table 3.1. The measured angles were well in agreement with the calculated values when the faces of the crystal were correctly identified. After identifying the crystallographic axes the crystals were cut into required dimension along different direction and then polished well. The methods of cutting and polishing were described earlier.

<table>
<thead>
<tr>
<th>Interfacial angle between</th>
<th>Computed angle</th>
<th>Measured angle (± 1°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face 1</td>
<td>Face 2</td>
<td></td>
</tr>
<tr>
<td>1 0 0</td>
<td>1-1 0</td>
<td>42.12</td>
</tr>
<tr>
<td>1 0 0</td>
<td>1 1 0</td>
<td>42.12</td>
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<tr>
<td>1 0 0</td>
<td>1 0 -2</td>
<td>73.92</td>
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<td>1 0 -2</td>
<td>-1 0 -2</td>
<td>180.0</td>
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<td>1 0 2</td>
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</tr>
<tr>
<td>1 0 -2</td>
<td>1 -1 0</td>
<td>78.15</td>
</tr>
</tbody>
</table>

Table 3.1: Values of Measured and Computed interfacial angles of LHS crystal

3.2.3 Measurement of dc Conductivity

The prepared sample was mounted on a conductivity cell. The whole cell was kept in the temperature circulator bath. Temperature is varied in steps. The rate of temperature rise was 0.5°C/min in the vicinity of the transition temperature and 1°C/min in the other region. DC conductivity can be measured with the help of a Keithley programmable electrometer. Current through the sample was noted by applying a voltage of 10V.
Fig 3.5: Photograph of the Grown LHS crystal
Fig 3.6: Stereographic projection of LHS crystal projected at 001 direction
3.3 Results and Discussion

3.3.1 DC electrical Conductivity along a, b and c-axes

The results of the investigation of electrical conductivity along a, b and c-axes of the LHS crystal are shown in figs 3.7 and 3.8. It shows a plot of Temperature Vs conductivity.

Fig. 3.7: DC conductivity of LHS along a and c-axes.

Fig. 3.8: DC conductivity of LHS crystal along b-axis.

From the nature of the curve it can be seen that the conductivity increases with temperature with some amount of anomalies at certain temperatures. This anomaly is found at around 420 K. After 420 K the conductivity increases rapidly with temperature.
The experiment is repeated several times for several sample so as to ensure the presence of conductivity anomaly. The value of conductivity is found to be $1.01 \times 10^{-8} \text{ cm}^{-1} \Omega^{-1}$ at 373 K.

The result of the dc conductivity studies along b-axis is shown in fig 3.8 with certain amount anomaly. The value of conductivity increases rapidly after 420 K. The conductivity anomaly is observed at around 423K. The occurrence of this anomaly can also be observed when the experiment is repeated for several times on several samples. The value of conductivity along b-axis is $1.86 \times 10^{-10} \text{ cm}^{-1} \Omega^{-1}$ at 373 K. A slope change was observed at 425K for all successive runs.

The variation of conductivity with temperature along c-axis for the LHS crystal is shown in fig 3.7. Fig shows some amount of anomaly at around 410 K and 428 K. Conductivity anomalies are also observed at around 426K when the experiment was repeated for several times. A slope change was observed at around 420K for all experimental runs. The value of conductivity remains almost constant upto 420K and increases very rapidly after 420K. The value of conductivity along c-axis is found to be $1.06 \times 10^{-7} \text{ cm}^{-1} \Omega^{-1}$ at 373K.

The activation energies of the LHS crystals can be found using the plot of $1000/T$ Vs $\ln \sigma$. The plot of $1000/T$ Vs log of conductivity gives a straight line, which can be

![Plot of 1000/T Vs lnσ for a, b and c-axes.](image)

Fig 3.9: Plot of 1000/T Vs lnσ for a, b and c-axes.
represented by an Arrhenius relation

\[ \sigma = \sigma_0 \exp \left( -\frac{E}{K_B T} \right) \]

Fig 3.9 shows the plot of \( \frac{1000}{T} \) Vs \( \ln \sigma \) along a, b and c- axes. The activation energies are calculated from the slope of the curve and it has the values 1.04eV, 1.20eV and 0.97eV for a, b and c-axes respectively. Again the activation energies for the conduction process of the LHS crystal can be calculated along a, b and c axes for the successive runs and it is tabulated in table 3.2.

<table>
<thead>
<tr>
<th>Activation energy (eV)</th>
<th>a-axis</th>
<th>b-axis</th>
<th>c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; run</td>
<td>1.12</td>
<td>1.22</td>
<td>0.86</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; run</td>
<td>1.12</td>
<td>1.26</td>
<td>0.97</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; run</td>
<td>1.11</td>
<td>1.16</td>
<td>0.824</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; run</td>
<td>1.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Activation energies along different axes for different experimental trials

3.4 Discussion

The temperature variation of dc electric conductivity along a, b and c-axes has been measured. As can be noted from figures 3.7 & 3.8 that the crystal shows a minor electrical conductivity anomaly at around 425K. A slope change was observed along a, b and c axes for LHS crystal at around 425K. In order to confirm the presence of these anomalies the experiments were repeated for several times for several samples. In all experimental trials the conductivity shows anomalous changes near 425K. These anomalies are rather small in magnitude and reveal themselves only under close examination of the curve. But from the above figs it can be noted that the conductivity is almost constant upto 420K and increases very rapidly as the temperature increases. These measurements indicated that the Hydrazinium ion is rigid only at very low temperatures. As the temperature is raised the \(-\text{NH}_3\) group was found to undergo hindered rotation about the N-N axis. Above 425 K the Hydrazinium ion appeared to tumble about several axes. This is in good agreement with the earlier work carried out by MacClement et al [11]. The exponential increase in the value of conductivity is also reported by Vandoorkey et al [4]. The crystal conducts electricity strongly along c-axis. The result shows that the value of conductivity along c-axis is very much higher.
compared to other two axes as suggested earlier [2,4]. The activation energy calculated from the dc electric conductivity study gives the value of 1.04eV, 1.2eV and 0.97eV along a, b and c- axes. The activation energy reported earlier (0.85eV along c axis) was also good conformity with the present study. A decrease in the conductivity was observed upto 375K along a, b and c-axis, (as shown in fig 3.9) in the first run, indicate that there may be impurities and will decomposes when it was heated at 373 K. Thus for good conductivity result the sample should be annealed for one hours at 373 K.

3.5 Conclusion

In this chapter the results of the dc electrical conductivity of Lithium Hydrazinium Sulphate single crystal have been reported. Large size single crystals of LHS have been grown. The photograph of the grown crystal is depicted. The crystal faces are identified and cut along different axes in required dimension.

Results of the electrical conductivity measurements showed anomalies in the temperature variation of dc conductivity at around 425K. These anomalies are explained as due to a weak phase transition in the LHS crystal near 425K. The experiments are repeated for several times and for several samples. Previous investigation results in thermal expansion study and NMR study and temperature variation of Elastic constant study are found to be consistent with the present inference of this phase transition. AC electrical conduction study and dielectric studies are carried out to establish the phase transition in the crystal and the results are discussed in the next chapter.
References


