CHAPTER V

ELECTRICAL PROPERTIES OF GLS, GZS, TGZC AND LT SINGLE CRYSTALS

5.1 Introduction

A perfect order for the arrangement of atoms/molecules throughout the crystalline material exists only in an ideal crystal. All crystals contain large number of various defects or imperfections. In a real crystal a large number of atoms will be misplaced. This is due to the fact that the presence of defects upto a certain concentration helps in the reduction of free energy with a corresponding increase in the entropy [1]. The commonly observed defects due to the misplacement of atoms/molecules producing vacancies are Schottky defect and Frenkel defect [2]. The crystal imperfections caused by the transfer of atoms from the lattice sites in the interior to the lattice site at the surface of the crystal is known as Schottky defect. In Frenkel defect an atom is transferred from a lattice site to an interstitial position, a position normally not occupied by an atom. In thermal equilibrium a certain number of lattice vacancies are always present in the crystal. The concentration of the vacancies increases as the temperature increases. The point defects such as Schottky defect and Frenkel defect influence the optical and electrical properties of ionic crystals. The study of the ionic conductivity is an important tool for the investigation of the lattice defects in the crystal.

The electric field distribution within the crystal can be identified by the study of dielectric properties of the crystals. The different polarization mechanisms in solids such as atomic polarization of the lattice, orientation polarization of dipoles, space charge polarization, electronic and ionic polarization can be easily understood by studying the dielectric constant as a function of frequency and the
change of dc conductivity with temperature [3]. Space charge polarization occurs because of the accumulation of charges at the structural interfaces [4]. The contributions of each of these polarization effects depend upon the chemical composition, crystal structure, perfection, frequency of the applied field and temperature. A study of the frequency dependence of dielectric constant gives information about the contributions of polarization in the crystalline solids [5-7]. The abrupt changes in dielectric properties with change in temperature indicate possible structural transitions taking place in solids [8, 9].

5.2 Conduction Mechanisms in Crystalline Solids

The current due to the excitation of electrons from the valance band to the conduction band is negligibly small for nonconducting/dielectric crystalline materials [10]. The conduction process in these materials can be explained by

(i) Schottky- Richardson mechanism, which explains the conduction as due to the electrons emitted from the cathode [11].

(ii) Poole- Frenkel mechanism, which explained the conduction as due to the liberation of electrons from the traps of the bulk material [12].

(iii) Fowler-Nordheim mechanism, which explains conduction as due to the tunneling [13].

(iv) Space charge limited conduction [14] etc.

5.2.1 Schottky Mechanism

The current in a material may be due to the thermal activation of electron over the metal insulator interface barrier. The applied electric field reduces the height of the barrier and hence helps to increase the current in the medium. The Schottky-Richardson current voltage relationship is expressed as:

\[ J = AT^2 \exp \left( - \frac{\varphi_s}{kT} + \beta_{SR} E^{1/2} \right) \]

\[ \beta_{SR} = \left( \frac{2e}{kT} \frac{e}{n \varepsilon_0 d} \right)^{1/2} \] is the field lowering factor.
\[ \log J = \log AT^2 - \frac{\varphi_e}{kT} + \beta_{SR}E^{1/2} \]

So the \( \log J \) versus \( E^{1/2} \) plot referred to as Schottky plot should be a straight line with a positive slope.

### 5.2.2 Poole-Frenkel Mechanism

Enhanced electrical conduction in low mobility solids resulting from thermal emission of carriers over a field lowered barrier surrounding donor-like (or acceptor-like) localized level is known as Poole-Frenkel conduction \[12\]. The effect arises in the presence of ionizable donors with an activation energy \( W_d \) which exerts a Coulombian force which normally neutralize them. In the presence of a field \( E \) (the electric field intensity at the metal/dielectric interface) the effective ionization energy for emission in the direction of the field is lowered by the amount

\[ W = e\beta_{PF}E^{1/2} \]

Where the Poole-Frenkel coefficient \( \beta_{PF} \) is given by\[15\]:

\[ \beta_{PF} = \left( \frac{e}{n\varepsilon_0} \right)^{1/2} \]

Where \( e \) is the magnitude of the electronic charge and \( \varepsilon_0 \) is the dielectric constant.

The current–voltage relationship for Poole-Frenkel mechanism is expressed as, \[16\]:

\[ J = J_0 \exp \left\{ e \left( \beta_{PF}E^{1/2} - \Phi_{PF} \right)/kT \right\} \]

\( \Phi_{PF} \) is the height of trap potential well.

Hence, the field dependent conductivity is expressed as

\[ \sigma = \sigma_0 \exp \left( e\beta_{PF}E^{1/2} / kT \right) \]

Or, \( \log \sigma = \log \sigma_0 + \beta_{PF}E^{1/2} / kt \)
So that the Poole–Frenkel mechanism is characterized by the linearity of $\log \sigma$ versus $E^{1/2}$ plots with a positive slope.

### 5.2.3 Fowler-Nordheim Mechanism

Fowler-Nordheim relation for current density [13] indicating the presence of tunneling current is given by is:

$$J=AV^2\exp\left(-\frac{\varphi}{V}\right)$$

so that, $\log \left(\frac{J}{V^2}\right) = \log A - \left(\frac{\varphi}{V}\right)$

The log ($J/V^2$) versus 1/V plot is expected to be linear with negative slope.

### 5.3 Experimental

The grown crystals of GLS, GZS, TGZC and LT, cut into rectangular shapes with 1mm thickness were polished. The flat opposite faces were coated with quick drying silver paste to establish better ohmic contact. The crystal was then placed inside the crystal holder with pressure contacts. The crystal holder along with the crystal was then placed inside an oven attached with a temperature controller. The temperature inside the oven was measured using a Pt 100 thermocouple. The electrodes were then connected in series with a DC voltage source and a KIETHLEY meter, model 236, to measure the current with high accuracy. Before starting the observations each sample was heated at 70°C for about 20 minutes to remove the absorbed moisture. For measurements the temperature of the sample was fixed at a constant value for about 20 minutes so that the crystal attains the same temperature. Voltage was varied from 0 to 100 volts and for 20 different voltages the corresponding currents were noted using an interfaced computer set up. The procedure was repeated for different temperatures. The average values of three trials for each temperature were noted. The measurements were conducted for all the four crystals. The results are presented in...
the form of log I-log V characteristics. The conduction mechanism present in the crystals was analyzed using Schottky, Poole-Frenkel and Fowler-Nordheim plots.

5.3.1 log I-log V characteristics

The current as a function of voltage for the samples at different temperatures are plotted and is shown in Fig.5.1. For all the four materials the dependence of current on the voltage could be represented as \( I \propto V^n \) with the value of \( n \) greater than 1. This shows that the conduction is non-ohmic in nature.

![Fig.5.1 LogV-LogI Plots](image-url)
The space charge limited current mechanism cannot be used to explain the conduction in these materials since the slope of the graph is less than 2. For space charge limited current mechanism the slope of the plot should be around 2 [17]. In the case of GLS, GZS and TGZC crystals the current decreased with increase in temperature. In the case of LT crystal the current initially increased up to 40°C and then decreased upto 60°C and after that increased upto 100°C. The decrease in the conductivity may be due to the reduction of charge carriers [18] or due to the loss of water molecules in the crystal [19].

5.3.2 Schottky plots

The field intensity (E) and the corresponding current density (J) were calculated in each case. The log J vs E\textsuperscript{1/2} graph which represents the Schottky plots were plotted for the grown crystals and are shown in Fig.5.2.

![Schottky plots](image_url)
The Schottky plots of GLS, GZS, TGZC and LT above the applied voltage of 10V can be considered as linear with positive slope. This indicates that the Schottky-Richardson mechanism can be applied to explain the conduction process in all these four materials. Moreover the dependence of current on temperature will be strong in the case of Schottky-Richardson mechanism. The plots are shown in Fig.5.2.

5.3.3 Poole-Frenkel plots

The Log $\sigma$ vs $E^{1/2}$ plots for the grown crystals are shown in Fig 5.3. It shows positive slope for all the four materials. This indicates the absence of Poole-Frenkel mechanism in the conduction of these materials.

![Poole-Frenkel plots](image)

Fig.5.3. Poole-Frenkel plots
5.3.4 Fowler-Nordhiem plot

The Fowler–Nordhiem plots for GLS, GZS, TGZC and LT were drawn with 1000/V along the X-axis and Log \( J/V^2 \) along the Y-axis. The graphs are shown in Fig.5.4. The graphs are showing positive slopes for all the four materials. This indicates the absence of Fowler–Nordhiem mechanism in the conduction process of these materials.

![Fowler-Nordhiem plots](image)

Fig.5.4. Fowler- Nordhiem plots

5.4 Dielectric constant

Dielectrics are basically insulating materials. They are also used in capacitors to increase the capacitance by placing them in between the plates of the capacitor. The capacitance of the capacitor without the dielectric medium in between \( (C_o) \) is given by
\[ C_0 = \varepsilon_0 \frac{A}{d} \]

Where \( \varepsilon_0 \) is the absolute permittivity, \( A \) the cross sectional area and \( d \) the separation between the plates.

When the dielectric medium is kept in between the plates the capacitance of the capacitor increases to

\[ C = \varepsilon_0 \varepsilon_r \frac{A}{d} \]

Where \( \varepsilon_r \) is the dielectric constant and \( d \) is the thickness of the medium.

For practical applications the medium should have a high value for its dielectric constant and a low dielectric loss. The dielectric constant or relative permittivity \( \varepsilon_r \) of a material depends on the degree of polarization or charge displacement that occurs in the material. The polarizability, \( \alpha \), of the dielectric is represented as \( \mathbf{p} = \alpha \mathbf{E} \) where \( \mathbf{p} \) is the dipole moment induced by the local electric field, \( \mathbf{E} \). The polarizability of the medium (\( \alpha \)) is the total effect of the electronic polarizability \( \alpha_e \), ionic polarizabilty \( \alpha_i \), dipolar polarizability \( \alpha_d \) and the space charge polarizability \( \alpha_s \)

\[ \alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s \]

The electronic polarization is caused by a slight displacement of the negatively charged electron cloud in an atom relative to the positively charged nucleus. The ionic polarizabilty arises from a slight relative displacement or separation of anions and cations in a solid. It is the principal source of polarization in ionic crystals. Dipolar polarizability arises in materials that contain permanent electric dipoles. These dipoles may change their orientation and they tend to align themselves with an applied electric field. The effect is usually very temperature dependent since the dipoles may be frozen at low temperature. The space charge polarizability occurs in materials that are not perfect dielectrics but in which some long range charge migration may occur.
The polished crystal applied with silver paste on a pair of opposite faces is kept inside the crystal holder. It was kept inside the constant temperature enclosure attached with a temperature controller. The leads from the electrodes were connected to a KIETHLEY meter. A Pt100 thermocouple was used to measure the temperature of the sample. The capacitance values were measured for different frequencies of 1 KHz, 10 KHz and 100 KHz by changing the temperature from 30°C to 80°C.

5.4.1 Dielectric constant with Temperature.

The variation of dielectric constant with temperature was studied by measuring the capacitance of the samples at different temperatures starting from room temperature. The corresponding dielectric constants were calculated using the equation \( \varepsilon = \frac{Ct}{(\varepsilon_0 A)} \) where \( t \) is the thickness, \( A \) the area of the sample and \( \varepsilon_0 \) is the permittivity of free space. The measurements and the calculations were repeated for different frequencies. The plots in Fig.5.5 shows the variation of the dielectric values with temperature. The dielectric values of GLS, GZS and TGZC crystals remained nearly the same for all the temperatures studied for the same frequency. But the dielectric constant decreased with increase in frequency. LT crystals showed a decrease in dielectric values with increase in temperature for the same frequency. The dielectric constant decreased with increase in frequency. The high values of the dielectric constants of the samples may be due to the presence of all the four polarizations. The decrease in the value of dielectric constant with increase in frequency may be due to the reduction in the effect of some of the polarizations at high frequencies.

At high temperatures the expansion of the crystal decreases the number of ions per unit volume of the material and this changes the polarizability. This may be the reason for the observed variation of dielectric constant of LT with temperature. There were no abrupt variations observed in the dielectric constant of
the crystals with in the temperatures studied indicating the absence of any phase transition.

5.4.2 Dielectric constant with frequency

The dielectric constants calculated for a constant temperature were plotted as a function of log of the frequency values. Graphs are plotted for different temperatures. Fig. 5.6 shows the dielectric constant vs log f graphs.
The graphs of GLS and GZS showed a continuous decrease in the dielectric constant with frequency. For TGZC and LT the graphs show an initial decrease and then an increase. Frequency dependence of dielectric constant indicates the presence of space charge effect in addition to electronic and atomic conduction in the sample. The applied field in the crystal produces a local displacement of electrons in the direction of the field which in turn gives rise to the polarization. As the frequency increases at some stage the space charge fails to sustain and comply with the field and hence the polarization decreases giving rise to a decrease in value of $\varepsilon$ [20].
5.5 Photoconductivity

Photoconductivity is the increase in electrical conductivity of semiconductors and insulators due to increase in the charge carriers, which are produced by the excitation of electrons by the incident light of sufficiently high energy. The phenomenon in which the conductivity decreases due to the presence of the light is called negative photoconductivity. Photoconductivity finds application in photoconductors, which uses the radiation controlled electrical resistance, light detectors, light controlled switches, television cameras etc.

Leads were connected to opposite phases of well-polished thin single crystals using silver paste. One of the crystals was then connected in series with a dc power supply and KEITHLEY meter. The sample was covered with a black
cloth and the voltage was varied from 0 to 100 volt (1000 volts/cm). The dark currents for different voltages were recorded. The sample was then irradiated using a powerful halogen lamp. The voltage and the photocurrents were recorded for the same voltage range.

The same procedure was repeated for different samples. The voltage – current plots are shown in Fig. 5.7.

The photocurrent of the samples were less than the dark current in the whole range of voltage applied, which showed the negative photoconducting nature of the samples. This may be due to the reduction in the number of charge carriers or due to the decrease in the lifetime of the charge carriers in the presence of the radiation [21].

As per the Stockmann model [22] there are two energy levels in the forbidden energy gap of the material. One of which is between the Fermi level and the conduction band and the other is close to the valance band. The second state captures the electrons from the conduction band and holes from the valance band. This reduces the number of charge carriers in the conduction band and hence the current decreases in the presence of the radiation.

5.6 Conclusion

The dc conductivity and the capacitance of the samples were measured for different temperatures. The frequency response of the dielectric constant and the photoconductivity were studied. The dc conductivity measurements indicate that Schottky-Richardson mechanism which explains the conduction as due to the electrons emitted from the cathode is suitable to explain the conductivity in the studied crystals. The increase in temperature decreases the conductivity of the samples. The decrease in the conductivity may be due to the reduction in the number of charge carriers in the crystal. The dielectric measurements showed that the dielectric constant of the samples change inversely with the frequency. There were no considerable changes taking place in the values of $\varepsilon$ with increase in
temperature, ruling out any phase transitions within the temperature range studied. The materials showed negative photoconductivity. This may be due to the reduction in the number of charge carriers or due to the decrease in the life-time of the charge carriers in the presence of radiation.
References


160
