CHAPTER 4

ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x = 0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
4.1 INTRODUCTION

Study of electrical conduction is one of the important characteristics of semiconductor materials required not only for practical applications but also for the interpretation of various physical phenomena. Electrical conductivity is an elegant experimental tool to probe the structural defects and internal purity of crystalline solids. The profound changes which occur in physical and chemical nature of a material essentially give information through its conductivity data.

It appears from the literatures that majority of germanium monosulphide and germanium monoselenide compounds in the form of single crystals having application in various electrical and optoelectronic devices. All these applications find their base in electrical and optical properties of the material. Therefore, it becomes interesting to characterize the grown crystals for these properties. The investigation of the electrical properties of the grown crystals is presented in this chapter and various electrical characterization methods are discussed in brief.

4.2 MEASUREMENT OF TEMPERATURE DEPENDENT ELECTRICAL RESISTIVITY OF GeS_xSe_1-x (x= 0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.

4.2.1 Basic principle and experimental procedure

There are many conventional methods for measuring resistivity. These methods are unsatisfactory for semiconductors because the metal semiconductor contacts are usually rectifying in nature. Also the injection of minority carrier happens due to one of the current carrying contacts. An excess concentration of minority carriers will affect the potential of other contacts and modulate the resistance of the material.
For the study of variation in resistivity with temperature of the grown crystals a high temperature measurement set has been designed and developed in University Shophesticsted Instrumentation Centre (USIC), Sardar Patel University. Using this experimental set up, resistance of sample has been measured from room temperature to 723K temperature in the step of 10K and for each step the corresponding resistivity can been calculated. To avoid excessive heating of the sample chamber, it is cooled by circulating cold water around it with the help of tubes. Photograph of the sample holder and the simplified schematic block diagram of the whole experimental set up is shown in figure 4.1 & 4.2

**Figure 4.1** Experimental setup for high temperature resistivity measurement
The crystal is mounted in the sample holder which is then inserted in the sample chamber and closed at the top. Introducing this assembly in vertical tabular furnace. The temperature of the sample is raised using variac. The temperature of the sample is measured with the help of Cr-Al thermocouple kept in vicinity of the sample which is connected to the digital temperature controller which can control and display the acquired temperature. Starting from room temperature (303 K), the temperature of the sample is increased slowly from room temperature to 723 K, in steps of 10 K and at each step the corresponding value of the resistivity of the sample is measured.
calculated. The cross section of the whole experimental set up is shown in figure 4.3

**Figure 4.3** Cross section of the set up for high temperature resistivity measurements

4.2.2 **High temperature electrical resistivity measurement**
**perpendicular to c-axis (Along to the basal plane)**

The experimental set up explained above has been used to study the variation of resistivity with temperature. These measurements were carried out on as grown crystals GeS\textsubscript{x}Se\textsubscript{1-x} (x= 0, 0.25, 0.5, 0.75) perpendicular to c-axis. These crystals having thickness 't' along the c-axis and this immediately allow any electrical measurement perpendicular to c-axis.

The resistivity at different temperature is the calculated using the following formula

\[ \rho = \frac{Rbt}{l} \]  \hspace{1cm} 4.1

Where \( r \) is the measured resistance, \( b \) is the width of sample, \( t \) is the thickness and \( l \) is the length of the sample respectively and \( R \) is the measured resistance.
4.2.2.1 Results and discussions

The measured resistance as a function of temperature are shown graphically in figure 4.4 for GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75) single crystals. The graph shows that the resistance monotonically decreases with increasing temperature mostly for all the samples. This shows that the grown materials are semiconductor in nature. In GeS\textsubscript{0.5}Se\textsubscript{0.5} and GeS\textsubscript{0.75}Se\textsubscript{0.25} single crystals the resistance decreases upto 523K and then the resistance increases upto 560K then again it gradually decreases. The change in resistance as the function of temperature is interpreted using resistivity plot. The variation of electrical resistivity as a function inverse of temperature in the temperature range 303K to 723K for all the samples are shown in figure 4.5. The entire curve is divided into three regions and activation energy has been calculated for each region from slope of the straight line. Although the samples exhibit semiconducting nature, ln\rho \rightarrow 1/T curve is not perfectly linear throughout.

Figure 4.4 (a) Variation of resistance as a function of temperature for GeSe single crystals along the basal plane.
Figure 4.4 (b) Variation of resistance (R) as a function of temperature (T) for GeS_{x}Se_{1-x}(x=0.25, 0.5, 0.75) single crystals along the basal plane.
Using the following Arrehenius relation [1-2], activation energy for all samples for each step-in figure 4.6.

\[ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) \]

where \( E_a \) is the activation energy required in process, \( k \) is the Boltzmann constant, \( T \) is the sample temperature, \( \rho_0 \) is the preexponential factor, \( \rho \) is the electrical resistivity the evaluated temperature.

The calculated values of activation energies are given in table 4.1. The nature of the graphs clearly gives an indication that GeS\(_x\)Se\(_{1-x}\) (x=0, 0.25, 0.5, 0.75) single crystals possesses semiconducting nature, as the resistivity decrease with temperature. In general the semiconductor exhibits the intrinsic behavior at higher temperature whereas extrinsic behavior at lower temperature.

![Figure 4.5 (a) Variation of ln\( \rho \) vs. inverse of temperature for GeSe single crystals along the basal plane.](image)
Figure 4.5 (b) Variation of ln$p$ vs. inverse of temperature for Ge$_x$Se$_{1-x}$
($x=0.25$, $0.5$, $0.75$) single crystals along the basal plane.

CH.4. ELECTRICAL PROPERTIES OF Ge$_x$Se$_{1-x}$ ($x=0$, $0.25$, $0.5$, $0.75$, $1$) SINGLE CRYSTALS.
In figure 4.5(a) & (b) in the first region majority charge carriers are the impurity atoms which may present in the interstitial sites or loosely bound to the crystal lattice. They contribute to the major part of conduction over a wide range of temperature. Hence the conduction mechanism is dominated by the extrinsic carriers which are shown in second region. These charge carriers is nothing but the impurity ions trapped in the crystal lattice or sitting on the interstitial sites during the crystal growth. For GeS$_{0.5}$Se$_{0.5}$ and GeS$_{0.75}$Se$_{0.25}$ crystals from 523K the resistivity increases up to 573K which actually a result of the transition of the conduction mechanism from extrinsic to intrinsic behavior, which is normal feature of any doped semiconductor.

4.2.3 **High temperature electrical resistivity measurement parallel to c-axis (Normal to the basal plane)**

The high temperature resistivity parallel to c-axis has been measured using the method explained above. The experimental set is as shown in figure 4.1. The resistivity measured for entire samples from room temperature to 723K temperature, in step of 10 K.

The resultant change in resistance as a function of temperature is measured. From the values of resistance at different temperature the resistivity is determined using the formula:

\[
\rho = \frac{RA}{t}
\]

where 'A' is area and 't' is the thickness of the sample.

4.2.3.1 **Results and discussion**

The high temperature resistivity measurements were carried out on the same as grown crystals of Ge$_x$Se$_{1-x}$ (x=0, 0.25, 0.5, 0.75) parallel to c-axis. A similar nature of the plot of resistance versus temperature is also observed for normal to the basal plane as shown in figure 4.6 (a) & (b). From these graphs one can notice that there
exhibits conduction anisotropy, as judge from the noticeable change in the magnitude of resistance. And in GeS_{x}Se_{1-x} (x=0, 0.25, 0.5, 0.75) single crystals as the content of sulphur increases the material becomes more resistive.

To analyze the conduction mechanism ln\rho vs. inverse of temperature has been plotted which is shown in figure 4.7(a) & (b) for GeSe and GeS_{x}Se_{1-x} (x= 0.25, 0.5, 0.75) single crystals respectively. The low temperature electrical resistivity is always influenced by some important phenomenon like the nearest neighbour hoping process of the carriers, the presence of excitons and their influence in conduction mechanism. According to Pollak and Knotek [3]. The electrical resistivity may find a dominance of the neighbour hoping of carriers which results decreases in activation energy. Knotek and Pollak [4] also explained influence of excitonic mechanism on the activation energy of materials. According to them the activation energy decreases as the temperature decreases due to excitonic mechanism. In this present investigation from figure 4.7 (a) & (b) we can say the there is linear variation in resistivity with temperature. Using the slope of three different regions the activation energy has been calculated using the equation given below and mentioned in table 4.1.

\[ E_a = 2.303 \times k_B \times 10^{3} \times \text{slope (eV)} \]  

where \( k_B = 8.602 \times 10^{-5} \text{ eV/K} \)

From the value of activation energy we can say that the activation energy goes on decreasing at lower temperature for all the sample of GeS_{x}Se_{1-x} (x=0, 0.25, 0.5, 0.75, 1). This shows the clear indication of the influence of excitonic mechanism on the electrical conduction for all the samples.
From the above discussion it is observed that the resistivity of all the samples is found to be different along different direction which is due to the layered structure of each compound. [5]. Along the basal plane the resistivity is found to be low where as along c-axis it is supposed to be high. This is because of the layers of GeS$_x$Se$_{1-x}$ (x=0, 0.25, 0.5, 0.75) single crystals along these axis bound to each other with weak van-der-Wall forces which facilitates very low conduction. Therefore it shows a high value of electrical resistivity [6]. The easier conduction in such crystals is along the basal plane which shows the anisotropic behavior in different direction.

**Figure 4.6(a)** Plot of resistance (R) as a function of temperature (T) for GeSe normal to the basal plane.
Figure 4.7(a) Plot of lnρ vs. 1/T (K⁻¹) for GeSe crystals normal to the basal plane

Table 4.1 The values of activation energies perpendicular to c-axis and parallel to c-axis for GeSₓSe₁₋ₓ (x = 0, 0.25, 0.5, 0.75) single crystal

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. Range</th>
<th>Along a-b axis</th>
<th>Temp. Range</th>
<th>Along c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeSe</td>
<td>303 - 483</td>
<td>0.038</td>
<td>303 - 383</td>
<td>0.133</td>
</tr>
<tr>
<td></td>
<td>493 - 773</td>
<td>0.113</td>
<td>393 - 493</td>
<td>0.171</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>503 - 723</td>
<td>0.212</td>
</tr>
<tr>
<td>GeS₀.₂₅Sᵉ₀.₇₅</td>
<td>308-478</td>
<td>0.100</td>
<td>308 - 413</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>483-638</td>
<td>0.438</td>
<td>418 - 553</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>643-723</td>
<td>1.491</td>
<td>558 - 723</td>
<td>1.645</td>
</tr>
<tr>
<td>GeS₀.₅Sᵉ₀.₅</td>
<td>304-428</td>
<td>0.161</td>
<td>308 - 368</td>
<td>0.189</td>
</tr>
<tr>
<td></td>
<td>433-533</td>
<td>0.120</td>
<td>373 - 543</td>
<td>0.491</td>
</tr>
<tr>
<td></td>
<td>538-723</td>
<td>0.407</td>
<td>553 - 723</td>
<td>1.743</td>
</tr>
<tr>
<td>GeS₀.₇₅Sᵉ₀.₂₅</td>
<td>308-448</td>
<td>0.262</td>
<td>303-398</td>
<td>0.348</td>
</tr>
<tr>
<td></td>
<td>453-593</td>
<td>0.375</td>
<td>403-528</td>
<td>0.828</td>
</tr>
<tr>
<td></td>
<td>598-723</td>
<td>1.393</td>
<td>533-723</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Activation energy (eV)
Figure 4.7(b) Plot of \( \ln p \) vs. \( 1/T \) (K\(^{-1}\)) for Ge\( _x \)Se\( _{1-x} \) (x=0, 0.25, 0.5, 0.75) crystals normal to the basal plane.

CH. 4. ELECTRICAL PROPERTIES OF Ge\( _x \)Se\( _{1-x} \) (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
4.2.4 Anisotropy

For the single crystals belonging to the layered structure family, the anisotropy of the transport properties is an interesting phenomenon. The single crystals of the layered materials behave extremely two-dimensionally as far as their mechanism is concerned. They are very difficult to handle because planes slide easily along the layers held together by the very weak van der Walls bonding. Intuitively and inquisitively enough; one might also expect similar anisotropies in the electrical properties i.e. the conductivity or mobility.

Although layered compounds are indeed anisotropic, there is a great variation in the anisotropy ratio among them. In some cases, anisotropy factors of upto $10^6$ have been reported [7]. The measurements of resistivity along the basal plane $\rho_\perp$ and normal to the basal plane $\rho_\parallel$ in the temperature range 303 K to 423 K were used to determine the anisotropy ratio for the single crystal of $\text{GeS}_x\text{Se}_{1-x}$ ($x = 0, 0.25, 0.5, 0.75$). The anisotropy behavior with temperature is shown in figure 4.8 (a) & (b).

![Variation of log\(y\) with temperature for GeSe single crystal.](image)

**Figure 4.8(a)** Variation of log\(y\) with temperature for GeSe single crystal.

CH.4. ELECTRICAL PROPERTIES OF $\text{GeS}_x\text{Se}_{1-x}$ ($x = 0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
Figure 4.8(b) Variation of logy with temperature for GeS\textsubscript{x}Se\textsubscript{1-x} (x=0.25, 0.5, 0.75)
The anisotropy ratio $\gamma$ can be defined as,

$$\gamma = \frac{\rho_{||}}{\rho_{\perp}}$$

From figure 4.8 (a) & (b) it is seen that the anisotropy ratio depends on temperature for as grown crystals. The high value of anisotropy factor is because of layer type growth of these crystals in which the normal covalent bonding is observed along the basal plane where as weak van-der-Wall bonding appears along the c-axis [8].

4.3 THERMO ELECTRIC POWER MEASUREMENT (TEP)

4.3.1 Introduction

In the early 1960s a requirement of autonomous sources of electrical power arose from the exploration of space, advances in medical physics and the exploitation of earth's resources in increasingly hostile and inaccessible locations. Thermoelectric generators are ideally suitable to such applications.

During the last decade there has been a worldwide search for new materials with higher thermoelectric figure of merit and attempts to improve the thermoelectric properties of the known compounds. It is anticipated that the successful development of such materials will lead to new fields of applications for thermoelectric devices and related technologies based on bulk crystals and films. However, the improvement of thermoelectric materials requires a detailed knowledge of all the factors, which determines their properties.

One of the parameters that determine the potential usefulness of any semiconducting material is its thermal energy gap. The thermal energy gap is most often estimated from the resistivity measurements, but this method requires four probes or two probes ohmic contacts and relatively high temperatures. Recently Goldsmid and Sharp [9]
have shown that the measurement of the Seebeck coefficient as a function of temperature on any novel semiconductor is one of the simplest ways of estimating its band gap. Among the electronic transport properties, the thermoelectric power is one of the most sensitive methods of studying the variation in the Fermi levels. It is one of the independent method of determining the carrier sign, density and mobility in semiconductors. Thermoelectric effects have been widely used to analyze the properties of metals and semiconductor in thermal equilibrium [10, 11]. Thermoelectric measurements are used frequently in the study of semiconductors because of the information that they can provide on free carrier concentration, effective mass of the carriers and importantly the scattering mechanism. It also provides the determination of the carrier sign, density and position of Fermi levels in semiconductor [11]. Also, the thermoelectric effect offers a distinctive advantage over other methods because the measured thermoelectric voltage is directly related to the carrier concentration, which makes these measurements simpler even for low mobility materials [12]. The investigation of the thermoelectric power (TEP) of thermoelectric material can yield valuable information about electric-band structure and potentially significant contribution from different interaction mechanism to the transport technique. Many researchers have observed thermoelectric effect in technologically important [13].

Good thermoelectric can convert heat directly into electric energy with a reasonable efficiency provided a substantial temperature gradient exists and the material has a high thermoelectric figure of merit (ZT) [14].

Recently a semiconducting material (Zn4Sb3) has been developed [15], which is relatively inexpensive and can be used in more efficient thermoelectric generators for waste heat recovery and automobile industry applications.
Looking to the recent importance of thermoelectric power generation outlined above and in [16], it is worthwhile to carry out a systematic study of the thermoelectric properties of semiconducting materials, which have physical properties similar to known efficient thermoelectric materials. In this context, author has put his efforts in carrying out a similar study on the single crystal of GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75, 1) because of the fact that metal chalcogenides have attracted considerable attention for their use as thermoelectric cooling materials [17]. In this section, author has reported systematic measurements of the thermoelectric power (s) of the as grown compounds of GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75, 1) as a function of temperature. The variation of thermoelectric power (s) with temperature has also been used to determine the effective mass and concentration of charge carriers present in the as grown crystals.

4.3.2 Experimental procedure

To measure the Seebeck coefficient as a function of temperature for the samples used in the present investigations, a differential temperature controller developed by Scientific Solutions, Mumbai [18] was used. The thermoelectric power measurements on all the samples were carried out with thermoelectric power set-up TPSS-200. The experimental system is shown in figure 4.9. It consists of two blocks:

(a) Sample holder with heaters with pick up probes and
(b) Electronic circuit controlling temperature and temperature gradient across the sample.

The sample holder consists of two low power heaters A and B (15 Watt each). The temperature T of the heater A is measured by thermocouple (TC\textsubscript{1}) and the temperature gradient \(\Delta T\) between A and B is measured by differential temperature sensor (TC\textsubscript{2}). Both the thermocouples are of K type.
The sample under investigation is mounted directly on the heaters, and is held by two pick up probes, which are of copper. These probes also measure the Seebeck voltage developed across the two ends of the sample.

The second block consists of temperature indicator, proportional controller and two-heater control circuit which drive the two heaters A and B. With the help of this electronic control circuit it is possible to generate a stable temperature gradient between the two heaters. It is possible to control the temperature from 298 K to 573 K and $\Delta T$ of $\pm 10$ K simultaneously with better than $\pm 1$ K stability. The problem usually encountered in making thermoelectric power measurements are stray thermal emfs. In the present instrument these have been eliminated by providing choice of selection of temperature gradient in the range of 1 K to 10 K. The sample and the electronic circuit have been incorporated into one unit. Use of low power heaters and electronic controllers makes the operation very easy and Seebeck coefficient of the sample can be measured conveniently.

**Figure 4.9** The thermoelectric power measurements system TPSS-200

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
When any isolated conducting material is subjected to a temperature gradient an electrical potential (voltage) is generated within it. This is known as the absolute Seebeck effect (ASE). The absolute Seebeck coefficient (ASC), is defined as the instantaneous rate of change of the ASE with respect to temperature at a given temperature i.e.

\[ \text{ASC} = \left[ \frac{d}{dt} \text{(ASE)} \right]_T \]

4.6

The least complicated example of the way in which this phenomenon is used is to form a thermocouple composed of two dissimilar conductors or thermo elements, by electrically joining one set of their ends. The greatest application of the Seebeck effect is in thermoelectric thermometry. This results from the fact that thermoelectric circuits convert thermal energy into electrical energy. Thermocouples composed of standardized metallic conductors are very widely used for the accurate, sensitive and reliable measurement and control of temperature.

The well-known Peltier effect is the complimentary effect to the Seeback effect. In the Peltier effect there is a reversible change in the heat content at an interface between dissimilar conductors that results from the flow of current across it. The Peltier effect finds its applications in thermoelectric devices for refrigeration and power generation. The possibility of using thermoelectric phenomena in the generation of electricity was considered as early as in 1885 by Rayleigh, who first calculated the efficiency of a thermoelectric generator.

4.3.3 Results and discussion

The variation of 'S' of GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75, 1) crystals at different temperatures is shown in figure 4.10. The seebeck coefficient is observed to be positive for GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75,
1) single crystals over the entire temperature range revealing p-type nature of all the samples.

To study the temperature dependence of the thermoelectric power of a p-type semiconductor the expression by Perluzzo et al. [19-20] can be used

\[ S = -\frac{k}{e} \left[ A + \frac{E_F}{kT} \right] \] 4.7

where \( k \) is the Boltzmann constant, \( e \) is the electronic charge, \( E_F \) is the separation of the Fermi level from the top of the valence band, \( A = (5/2) - s \) is the constant that varies from 0 to 4, depending on the dominant scattering process and may be assumed to be a measure of the kinetic energy transported by carriers [21].

The carrier concentration of the crystals essentially depends upon \( E_F \). For a small temperature range \( E_F \) is fairly constant and hence from equation (4.3), if the TEP is plotted against the reciprocal of temperature (\( T^{-1} \)) a straight line is expected.

From the slope and intercept of that line \( E_F \) and \( A \), can be determined. The fact that \( E_F \) is fairly constant implies that the carrier concentration ‘p’ is not changing with temperature. Therefore, equation 4.7 can be expressed as [22]

\[ S = -\frac{k}{e} \left[ A + \ln \left( \frac{N_A}{p} \right) \right] \] 4.8

where \( N_A \) is the effective density of states and is given by

\[ N_A = 2 \left[ 2 \pi m^*_h kT / h^3 \right]^{1/2} \] 4.9

CH. 4. ELECTRICAL PROPERTIES OF GeS\(_x\)Se\(_{1-x}\) (\( x = 0, 0.25, 0.5, 0.75, 1 \)) SINGLE CRYSTALS.
where \( m_h^* \) is the effective mass of holes. Using the values of carrier concentration from Hall effect measurements at room temperature.

The effective density of states for all samples of GeS\(x\)Se\(1-x\) (\(x=0, 0.25, 0.5, 0.75, 1\)) can be calculated with the help of formula

\[
p = N_A \exp\left(-\frac{E_F}{kT}\right)
\]

where \( E_F \) is the Fermi energy obtained earlier, \( k \) is the Boltzmann constant and \( T \) is the room temperature. The values of effective density of states thus obtained are shown in Table 4.2.

Using these values of effective density of states in expression 4.10, the effective masses of holes (\( m_h^* \)) for all samples of GeS\(x\)Se\(1-x\) (\(x=0, 0.25, 0.5, 0.75, 1\)) have been evaluated and are listed in Table 4.2. As the content of sulphur increases the change in Fermi energy and \( m_h^*/m_e \) is shown in figure 4.11.

Table 4.2 Evaluated values of \( E_F \), \( A \), \( m_h^* \) and \( s \) for GeS\(x\)Se\(1-x\) (\(x=0, 0.25, 0.5, 0.75, 1\)) single crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_F ) (eV)</th>
<th>( A )</th>
<th>( m_h^* )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeSe</td>
<td>0.071</td>
<td>2.49</td>
<td>0.687 ( m_e )</td>
<td>0.344</td>
</tr>
<tr>
<td>GeS(<em>{0.25})Se(</em>{0.75})</td>
<td>0.048</td>
<td>2.49</td>
<td>0.101 ( m_e )</td>
<td>0.257</td>
</tr>
<tr>
<td>GeS(<em>{0.5})Se(</em>{0.5})</td>
<td>0.045</td>
<td>2.49</td>
<td>0.064 ( m_e )</td>
<td>0.198</td>
</tr>
<tr>
<td>GeS(<em>{0.75})Se(</em>{0.25})</td>
<td>0.039</td>
<td>2.49</td>
<td>6.6E-07 ( m_e )</td>
<td>0.141</td>
</tr>
<tr>
<td>GeS</td>
<td>0.013</td>
<td>2.49</td>
<td>2.9E-05 ( m_e )</td>
<td>0.069</td>
</tr>
</tbody>
</table>
Figure 4.10 Variation of thermoelectric power ‘S’ with and inverse of temperature (1/T) for all the single crystals.

CH.4. ELECTRICAL PROPERTIES OF GeS_xSe_1-x (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
Figure 4.11 Variation in Fermi energy and \( m^*_h / m_e \) with ‘x’ (‘x’ is the content of sulphur in \( \text{GeS}_x\text{Se}_{1-x} \) \( x=0, 0.25, 0.5, 0.75, 1 \) single crystals)

From figure 4.11 we can conclude that as the content of sulphur increases the Fermi energy and \( m^*_h / m_e \) decreases simultaneously.
4.4 HALL EFFECT MEASUREMENTS

4.4.1 Hall effect measurement system

The Lake Shore 7504 Series Hall Effect / Electronic Transport Measurement System [23] shown in figure 4.12 is designed to measure electronic properties of electrically conductive materials. The system consists of advanced, integrated hardware and software. 7504 Series system which is easy to operate using the Lake Shore Hall Measurement System Software. The Hall System Software controls system instrumentation during an experiment and determines sample resistance, resistivity, Hall coefficient, Hall mobility and carrier concentration. It also control magnetic field during the measurements. Variation in temperature is made possible with the help of Lakeshore temperature controller (340) coupled with the Closed Cycle Refrigerator (CCR 75014).

Figure 4.12 The Lake Shore 7504 Series Hall Effect / Electronic transport Measurement System
The system consists of electromagnet which can produce a magnetic field of maximum 10 kG, with 4 inch air gap between the two pole pieces. The necessary current is being supplied by the magnetic power supply (LS 689) with current and voltage limits of 0 to ± 32 V respectively. The Model 450 is an extremely accurate full-featured gaussmeter that covers a wide range of magnetic fields and applications. The instrument provides easy-to-use front panel programming and a vacuum fluorescent alphanumeric display. This alphanumeric format allows for message-based front panel operation. Most operations can be performed and monitored through the front panel keypad and message display. The Model 450 measures fields in either gauss (G) or tesla (T). Set magnetic field can be varied manually or with auto ranging. The gaussmeter measures both DC and AC magnetic field values. In DC operation, the display shows the DC field at the probe with the sign followed by the appropriate filed units. In AC operation, the display shows a Peak or RMS value for the field at the probe.

Figure 4.13 Sample holder built upon PCB contains four pressure contacts.

Sample holder is built on PCB which contains in built four pressure contact probes made up of Stainless Steel, heater and Cr-Al

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
thermocouple as shown figure 4.13. The thermocouple and heater are directly connected with the power supply in series. The temperature can be controlled and displayed with the help of temperature controller model DTC-07DP ASABA made in USIC, Sardar Patel University. At particular temperature all the Hall parameters has been measured under a magnetic field of ± 3kG.

4.4.2 van der Pauw resistivity measurements

Electrical properties of the materials play an important role in determining the behavior of solid state devices and thereby their potential for such applications. Investigation regarding electrical behavior of GeS$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystals grown by direct vapour transport technique have been reported to be highly depended on growth conditions [24]. Hall Effect measurement is a unique tool to provide the information about basic material parameters needed to find the suitable of its application. Figure 4.13 Lakeshore - 7504 complete Hall effect measurement system.

The theoretical foundation of the Hall measurement evaluation for irregularly shaped samples is based on the conformal mapping develop by van der Pauw [25-26]. He showed how the resistivity, carrier concentration and mobility of a flat sample of arbitrary shape can be determined without knowing the current pattern, if the following conditions are satisfied.

(a) The contacts should be sufficiently small,
(b) The contacts should be at the circumference of the sample
(c) The sample should be uniformly thick and
(d) The sample should be contain no isolated holes

Van der Pauw suggested different geometries of the samples such as circular, square, rectangle and cross. The cross structure is
generally used for films and other bulk crystals. According to the investigation made by Daniel W. Koon [27-30] for different geometries, the preferred geometry is square rather than circle to reduce the effect of contact lead placement errors in the transport parameters such as resistivity and Hall coefficient. The square shape is the most convenient sample shape to fabricate and this will also reduce the effect of errors in the van der Pauw method arising from either the size or the displacement of contacts leads from the edge of the sample. The lead placement in the square sample must be near the corners in order to minimize errors.

It is easy to show that for four contacts on the boundary of a semiconductor plane sheet the resistance $R_{12,34}$, $R_{23,41}$ satisfy the relationship:

$$\exp\left(-\frac{\pi R_{12,34} t}{\rho}\right) + \exp\left(-\frac{\pi R_{23,41} t}{\rho}\right) = 1 \quad 4.11$$

By knowing $t$, $R_{12,34}$, $R_{23,41}$ the above equation can be solved for the resistivity of the material [31-32] and rewritten as

$$\rho = \frac{\pi t}{\ln 2} \left(\frac{R_{12,34} + R_{23,41}}{2}\right) F \quad 4.12$$

Where, $R_{12,34} = \frac{V_{34}}{I_{12}}$

The current $I$ enters the sample through contact 1 and leaves through contact 2 and $V_{34} = V_4 - V_3$ is the voltage between contact 4 and 3. $R_{34,41}$ is similarly defined. The quantity 'F' is a transcended function given as,
\[
R_r = \frac{V_{43}I_{23}}{I_{12}V_{14}} = \frac{R_{12,34}}{R_{23,41}}
\]

or

\[
R_r = \frac{I_{12}V_{14}}{V_{43}I_{23}} = \frac{R_{23,14}}{R_{12,43}}
\]

And \(F\) is calculated by solving the equation,

\[
\frac{R_r - 1}{R_r + 1} = F \cdot \frac{\exp\left[\frac{\ln(2)}{2}\right]}{\arccosh\left(\frac{\ln(2)}{2}\right)}
\]

\(F=1\), when \(R_r = 1\), which occurs with symmetrical samples like circles or squares, when the constants are equally spaced and symmetrical.

For each measurement point in a Hall experiment up to 32 individual resistance measurements are required.

(i) Hall resistance measurements for +ve magnetic field, +B (4 measurements)
(ii) Zero field resistance measurements (8 measurements).
(iii) Resistivity measurements for +ve magnetic field, +B (8 measurements)
(iv) Hall resistance measurements for -ve magnetic field, -B (8 measurements)
(v) Resistivity measurements for -ve magnetic field, -B (8 measurements)

In the present investigation the experiments has been conducted with a magnetic field of \(\pm 3\)KG.

By knowing thickness ‘\(t\)’ of the sample and measurements of voltage and current with polarity reversal across the contacts, the resistivity for geometries A and B can be calculated from the following equations [31-32].

---

CH.4. ELECTRICAL PROPERTIES OF GeSe\(_x\)Se\(_{1-x}\) (\(x=0, 0.25, 0.5, 0.75, 1\)) SINGLE CRYSTALS.
\[ \rho_A = \frac{\pi f_A}{\ln(2)} \left\{ \frac{V_{12,43}^+ - V_{12,43}^- + V_{23,14}^+ - V_{23,14}^-}{I_{12}^+ - I_{12}^- + I_{23}^+ - I_{23}^-} \right\} [\Omega \cdot m, \Omega \cdot cm] \]

\[ \rho_B = \frac{\pi f_B}{\ln(2)} \left\{ \frac{V_{34,21}^+ - V_{34,21}^- + V_{41,23}^+ - V_{41,23}^-}{I_{34}^+ - I_{34}^- + I_{41}^+ - I_{41}^-} \right\} [\Omega \cdot m, \Omega \cdot cm] \]

where \( V_{12,43}^\pm \) indicate a voltage measured across terminals 4 and 3, when a positive current flows in to terminal 1 and out of terminal 2.

\( I_{12}^\pm \) denotes +ve forward current measured between contacts 1 and 2.

The Geometrical factor \( f_A \) and \( f_B \) are functions of resistance ratios \( Q_A \) and \( Q_B \), respectively, given by:

\[ Q_A = \frac{R_{12,43}^- - R_{12,43}^+}{R_{23,14}^- - R_{23,14}^+} = \left( \frac{V_{12,43}^+ - V_{12,43}^-}{I_{12}^+ - I_{12}^-} \right) \left( \frac{I_{23}^+ - I_{23}^-}{V_{23,14}^+ - V_{23,14}^-} \right) \]

\[ Q_B = \frac{R_{34,21}^- - R_{34,21}^+}{R_{41,23}^- - R_{41,23}^+} = \left( \frac{V_{34,21}^+ - V_{34,21}^-}{I_{34}^+ - I_{34}^-} \right) \left( \frac{I_{41}^+ - I_{41}^-}{V_{41,23}^+ - V_{41,23}^-} \right) \]

If either \( Q_A \) or \( Q_B \) is greater than one, then use the reciprocal instead. The relationship between \( f \) and \( Q \) is expressed by the transcendental equation

\[ Q -1 \frac{Q+1}{Q+1} = f \cosh^{-1} \left\{ \frac{1}{2} \exp \left[ \frac{\ln 2}{f} \right] \right\} \]

which can be solved numerically.

The two resistivities must agree \( Q_A \) and \( Q_B \) should agree to within ±10%. If they do not, then the sample is too inhomogeneous, or anisotropic, or has some other problem. If they do agree, the average resistivity is given by
\[ \rho_{av} = \frac{\rho_A + \rho_B}{2} \left[ \Omega \cdot \text{m}, \Omega \cdot \text{cm} \right] \]

Similarly with the help of same measurements of voltage and current along with the magnetic field reversal, the two Hall coefficient are calculated by the following equations.

\[
R_{HC} = \frac{t[m]}{B[\text{gauss}]} \frac{V_{31,42}^+ (B) - V_{31,42}^- (B) + V_{31,42}^- (B) - V_{31,42}^+ (B)}{I_{31}^+ (B) - I_{31}^- (B) + I_{31}^- (B) - I_{31}^+ (B)} \left[ \text{m}^3 \cdot \text{C}^{-1} \right] \tag{4.20}
\]

\[
= 10^8 \frac{t[\text{cm}]}{B[\text{gauss}]} \frac{V_{31,42}^+ (B) - V_{31,42}^- (B) + V_{31,42}^- (B) - V_{31,42}^+ (B)}{I_{31}^+ (B) - I_{31}^- (B) + I_{31}^- (B) - I_{31}^+ (B)} \left[ \text{cm}^3 \cdot \text{C}^{-1} \right] \tag{4.21}
\]

and

\[
R_{HD} = \frac{t[m]}{B[\text{gauss}]} \frac{V_{42,13}^+ (B) - V_{42,13}^- (B) + V_{42,13}^- (B) - V_{42,13}^+ (B)}{I_{42}^+ (B) - I_{42}^- (B) + I_{42}^- (B) - I_{42}^+ (B)} \left[ \text{m}^3 \cdot \text{C}^{-1} \right] \tag{4.22}
\]

\[
= 10^8 \frac{t[\text{cm}]}{B[\text{gauss}]} \frac{V_{42,13}^+ (B) - V_{42,13}^- (B) + V_{42,13}^- (B) - V_{42,13}^+ (B)}{I_{42}^+ (B) - I_{42}^- (B) + I_{42}^- (B) - I_{42}^+ (B)} \left[ \text{cm}^3 \cdot \text{C}^{-1} \right] \tag{4.22}
\]

These two should agree to within ± 10% If they do not, then the sample is too inhomogeneous, or anisotropic, or has some other problem. If they do, then the average Hall coefficient can be calculated by

\[
R_{Hav} = \frac{R_{HC} + R_{HD}}{2} \left[ \text{m}^3 \cdot \text{C}^{-1}, \text{cm}^3 \cdot \text{C}^{-1} \right] \tag{4.23}
\]

From the average value of resistivity and Hall coefficient the hall mobility can be calculated using the equation
\[ \mu_H = \frac{R_{Hav}}{\rho_{av}} \left[ m^2 \cdot V^{-1} \cdot s^{-1}, cm^2 \cdot V^{-1} \cdot s^{-1} \right] \]

where \( \rho_{av} \) zero field resistivity.

The effective charge carriers concentrations can be calculated by using the formula

\[ \eta_e = \frac{1}{R_H \cdot e} \]

4.4.3 Experimental procedure

GeS\(_x\)Se\(_{1-x}\) (\(x=0, 0.25, 0.5, 0.75, 1\)) single crystals were grown by direct vapour transport techniques described in chapter 2. For Hall measurements the ohmic contacts on such a crystals along the basal plane were prepared. The contact was made from S.S pressure contacts onto the basal plane of the crystal in PCB as shown in figure 4.13. For the verification of the ohmic contacts of different pairs for all the samples van der pauw method is used. After the verification of ohmic contacts the measurement has been started at room temperature to the 120°C temperature under a fixed magnetic field of 1, 2 and 3KG using Lake Shore Hall measurement system 7504 and the data were stored as spreadsheet in the computer memory. The results have been reported from room temperature to 120°C temperature.

4.4.4 Results and Discussion

For van der Pauw samples, connection 1 and 3 are opposite to each other (as are contacts 2 and 4). Measuring \( R_{12} \), \( R_{12} \) sends the excitation current from the switch card down cable 1 and back on cable 2. The voltage is measured between the same cables, so the resistance measured includes the cable resistance, contact resistance at both contacts, and the sample resistance between the two contacts.

CH.4. ELECTRICAL PROPERTIES OF GeS\(_x\)Se\(_{1-x}\)(x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
The voltage measured across the same contacts used to supply current (e.g. $R_{13, 13}$ or $R_{24, 24}$) will tell us the voltage levels at the current source and other instruments connected to the switch card. Use the voltages measured in this test to keep within the limits of our measurement configuration.

Ohmic contacts are required for accurate Hall effect measurements. It is recommended that we test the current-voltage characteristics between contacts to verify ohmic behavior before making Hall effect measurements on unknown sample. With experience, we have found that some samples almost always have ohmic contacts and do not require contact testing.

Measuring both $R_{13, 13}$ and $R_{24, 24}$ tests all four contacts on a van der Pauw sample and is the minimum number of tests required to determine if all four contacts are ohmic. If one or more of the contacts is non-ohmic, additional test may be required to identify the bad contact(s). We have tested $R_{12, 12}$, $R_{23, 23}$, $R_{34, 34}$ and $R_{14, 14}$ to verify ohmic behavior of all contacts. The Ohmic nature of the electrical contacts made on the entire sample using I-V characteristic as shown in 4.14 (a), (b), (c), (d) and (e) have been verified before extracting the Hall parameters. In order to get the linear nature of the prepared electrical contacts, the contacts have been annealed under different conduction.

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
Figure 4.14 (a) Plot I-V characteristic between R12,12 and R23,23 contacts of GeSe single crystal.
Figure 4.14 (a) Plot I-V characteristic between R34,34 and R41,41 contacts of GeSe single crystal.
Figure 4.14 (b) Plot I-V characteristic between R12, 12 and R23, 23 contacts of GeS$_{0.25}$Se$_{0.75}$ single crystal.

**CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.**
Figure 4.14 (b) Plot I-V characteristic between R34,34 and R41,41 contacts of GeS_{0.25}Se_{0.75} single crystal.
Figure 4.14 (c) Plot I-V characteristic between R12,12 and R23,23 contacts of GeS$_{0.5}$Se$_{0.5}$ single crystal.
Figure 4.14 (c) Plot I-V characteristic between R34,34 and R41,41 contacts of GeS$_{0.5}$Se$_{0.5}$ single crystal.
Figure 4.14 (d) Plot I-V characteristic between R12,12 and R23,23 contacts of Ge$_{0.75}$Se$_{0.25}$ single crystal.
Figure 4.14 (d) Plot I-V characteristic between R34,34 and R41,41 contacts of GeS$_{0.75}$Se$_{0.25}$ single crystal.
Figure 4.14 (e) Plot I-V characteristic between R12,12 and R23,23 contacts of GeS single crystal.
Figure 4.14 (e) Plot I-V characteristic between R34,34 and R41,41 contacts of GeS single crystal
Figure 4.16 (a) Variation of Hall resistivity with temperature at 1kG magnetic field for GeS_{x}Se_{1-x} (0, 0.25, 0.5, 0.75, 1) single crystal.
Figure 4.16 (b) Plot of carrier concentration as a function of temperature at 1kG for Ge$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal.
Figure 4.16 (c) Plot of Hall coefficients $R_h$ as a function of temperature at 1kG for GeS$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal.

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0$, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
Figure 4.16 (d) Plot of mobility as a function of temperature for GeS$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal at 1 kG.
Figure 4.17(a) Plot of carrier resistivity as a function of temperature at 2kG for Ge$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal
Figure 4.17 (b) Plot of carrier concentration as a function of temperature at 2kG for GeSₓSeₙ₋ₓ (0, 0.25, 0.5, 0.75, 1) single crystal.
Figure 4.17 (c) Plot of Hall coefficient $R_H$ as a function of temperature at 2kG for GeS$_x$Se$_{1-x}$ ($0, 0.25, 0.5, 0.75, 1$) single crystal.

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
Figure 4.17 (d) Plot of Hall mobility as a function of temperature at 2kG for GeS_xSe_{1-x} (x=0, 0.25, 0.5, 0.75, 1) single crystal.
Figure 4.18 (a) Plot of carrier resistivity as a function of temperature at 3 kG for Ge$_x$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal
Figure 4.18(b) Plot of carrier concentration as a function of temperature at 3 kG for Ge$_x$S$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystal.
Figure 4.18 (c) Plot of Hall coefficients $R_H$ as a function of temperature at 3 kG for all single crystal.

CH.4. ELECTRICAL PROPERTIES OF Ge$_x$Se$_{1-x}$ ($x=0$, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
After the confirmation of the ohmic nature experiments were conducted for Hall parameters. The change in the Hall parameters with temperature and with magnetic field has been shown in figure 4.15 and 4.16 - 4.18 (a), (b), (c), (d) for 0kG, 1kG, 2kG, 3kG respectively. From the analysis the value of positive value of Hall coefficient clearly indicates the all the compound of GeS_xSe_1-x (0, 0.25, 0.5, 0.75, 1) are p-type and majority charge carriers in them are holes and all of them remain p-type nature even their temperature are raised. From 4.16 (a) & (b), 4.17(a) & (b) & and 4.18 (a) & (b) it has been observed that as the content of sulphur increase the material becomes more resistive, the value of carrier resistivity increases with increase in magnetic field and it decreases with increase in temperature. The carrier concentration increases with the
temperature this is due to the excess number of charge carriers made available as the temperature increases and this is because of decreases in resistivity. The content of sulphur decreases the value of \( n \) increases and there is countable effect on it of magnetic field for the entire sample. The mobility decreases with temperature this is due to the increases in the concentration of charge with rise in temperature.

4.5 HIGH PRESSURE MEASUREMENT

4.5.1 Introduction

High pressure science is an exciting area of research. In the past three decades this field has grown rapidly as a research tool and also in the development of other new technologies. There has been a considerable interest in the study of the high pressure behavior of solids because of academic, technological and geophysical reasons [33-41]. The academic interest owes its origin to the fact that at high pressure, nature of the interatomic forces in matter change considerably. These changes in solids can be studied in greater detail to reveal several new features of the interatomic forces, which are responsible for their diverse physical properties. In addition the high pressure studies are also of great importance to visualize the mechanism governing the structural changes and to reveal solid state properties associated with different structure. Under extreme pressure fluid lubricants squeeze out from between mating surfaces causing high friction and wear. With lamellar solids shearing takes place more easily when loads are high. So lamellar solids are well suited to extreme pressure lubrication.

The technological interest lies in the synthesis of super hard materials like diamond, cubic boron nitride and their polycrystalline sintered compacts. All these materials are strategic to a country's economic and industrial development. Considerable interest has also been shown by the geophysicists in high-pressure studies to explore...
the inner mantle of the earth where most of the matter is expected to be confined under very high pressures and temperatures. Under normal conditions solids exhibit a particular crystal structure for which the total energy is minimum. However, on application of high pressure, the atomic arrangements in solid changes, resulting in changes in interatomic distances and crystal structure. Such a structural phase transition can be noticed experimentally by observing the X-ray diffraction pattern, electrical resistivity and optical properties at different pressures. In this context it will be of great importance to study the physical behaviour of lamellar solids like GeS_xSe_{1-x} (0, 0.25, 0.5, 0.75, 1) under extremely high pressure. In the present work, author aims to use the resistance measurements at different pressure to study the possibility of phase transitions in GeS_xSe_{1-x} (0, 0.25, 0.5, 0.75, 1) single crystals.

A brief review of high pressure science and methods for the generation and measurement of high pressure up to 10 GPa has been given in this chapter.

4.5.2 Practical method of pressure generation

A complete working of pressure generation system will require the pressure vessel, pressure transmitting medium, seals etc. but also an arrangement to apply load on piston which is necessary to generate pressure. The Teflon cell technique is often used to generate pressure up to 4 GPa [42]. Various types of piston cylinder apparatus have been employed for the generation of high pressure [43]. Because of a comparatively trouble free performance, large sample volume and very high temperature capability the modified piston cylinder apparatus [44-45] have been extensively used for synthesis of materials such as diamond and cubic boron nitride. These devices can be used to generate the pressure up to 15 GPa and temperature up to 3273 K.

CH.4. ELECTRICAL PROPERTIES OF GeS_xSe_{1-x} (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
The piston-cylinder type apparatus can give truly hydrostatic pressure, but the maximum pressure is limited to about 7 GPa. To achieve higher pressure, one must use a different principle, namely that of massive support as shown in figure 4.19. A sharp tip made of high strength material is pressed against an equally hard surface with the sample in between. The stress of the order of \( F/A \), where \( F \) is the force with which the tip is pressed and \( A \) is the area on which the force \( F \) is supported, is generated. The highest stress that can be achieved is limited by the yield or the fracture strength of the tip material depending on whether the tip deforms plastically or by fracture.

The form in which the Bridgman opposed anvil system uses this principle is shown in figure 4.20. The anvils are pressed against each other and sample is kept in between.

![Diagram](force_sample_hard_surface)

**Figure 4.19** The principle of "massive support" to generate high pressure.
The frictional forces acting between the anvil face and the gasket material prevent the extrusion of the material and the high pressure is transmitted to the substance under investigation. Naturally, the nature of the gasket material is important, because when a solid transmitting medium is used, the pressure inside is not truly hydrostatic. However, talc plastically deforms and flows at high pressure and so the uni axial component of the stress is quite small.

The Bridgman opposed anvils are used upto about 100 kbar. With lateral support for the tungsten carbide anvils one can go to about 150 kbar and with slight modification as suggested by Drickamer, the pressure can be raised to 300 kbar. For higher pressure, the diamond anvil arrangement is needed.

The diamond anvil apparatus works on the same principle as the Bridgman anvils. This was first introduced by Valkanberg, 1964 and refined later on by Block et al., 1976.
4.5.2.1 Bridgman anvils

Maximum static pressures have now been achieved with the diamond anvil cell. From the mechanical point of view it is a Bridgman anvil cell as shown in figure 4.21, made of the strongest material: diamond. There is also a broad class of apparatus based on the same principle. The Bridgman anvil cell itself is traditionally made to tungsten carbide and works up to 20 GPa [46]. All the cells have two main parts: anvils and gasket. We consider the cells first from the general point of view of finding the conditions for achieving of the highest pressure.

![Schematic diagram of a Bridgman anvil](image)

**Figure 4.21** Schematic diagram of a Bridgman anvil

When a substance is compressed between anvils, the pressure achieved is much higher than in piston-cylinder vessels, for the following reasons:

The material of the anvils is working mainly under compression and very hard materials such as diamond, tungsten carbide (WC) and...
sapphire can be used, which have compressive yield strengths three or more times the tensile yield strength.

Pressure much greater than tensile yield strength are generated when anvils are made in the form of a truncated cone, because the loaded area is supported by the surrounding material. The limiting case of 'massive support' is realized in hardness measurements when the compressed volume of a material is supported by a half-space of the material. The principle of 'massive support' was formulated by P. Bridgman. This phenomenological observation is supported by calculations.

Multiplication of pressure occurs, which means that the pressure between the anvils is not uniform and maximal pressure in the centre of the anvils may be much higher than the mean pressure over the anvil $P = \frac{F}{S}$, where $F$ is the applied load and $S$ is the contact area.

A cell was designed [47] which is typically consists of WC anvils with a pyrophyllite or pipestone (catlinite) gasket with the sample in the centre surrounded by a solid pressure medium. Pressures above 10 Gpa are achieved [48]. A variety of such cells have been developed [49-50].

A. Gasket

Bridgman introduced a gasket into the cell. Material squeezed between the anvils is not extruded completely even at the highest pressure. The high-pressure volume-the part of the gasket with the sample and high-pressure medium- is supported by the gasket, made of plastic or compressible material. In this case catlinite and pyrophyllite gaskets are good in many respects: they are soft but strengthened under pressure, they are plastic but also compressible, which allows pressure to be increased without significant extrusion of

CH.4. ELECTRICAL PROPERTIES OF GeS<sub>x</sub>Se<sub>1-x</sub> (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
the gasket, and finally they are insulators, which is convenient for electrical measurements.

Pyrophyllite-like materials in practice do not provide lateral support in the ordinary Bridgman cell. This is achieved in the Drickamer cell [51]. Pressure in tungsten carbide (WC) cell was restricted to ~10 GPa and measurements were limited mainly to resistivity methods.

If we compare the anvil cell with the piston-cylinder vessel, anvils can be considered as well-supported pistons, and the gasket as the cylinder. The gasket can retain the high-pressure medium at very high pressures because anvils compressing the gasket (ends of cylinder) generate additional forces (friction), which reinforce the cylinder. The friction component predominates at a small thickness of the gasket (relative to the diameter).

4.5.3 RESISTANCE MEASUREMENT USING BRIDGMAN ANVIL CELL

Hydrostatic cells commonly imply piston-cylinder cells. A photograph of the high-pressure set-up is shown in figure 4.22. The Bridgman anvils consist of a tungsten carbide cylindrical piece, one face of which is ground in a tapered form ending with a flat anvil surface. In a typical anvil, the anvil has a diameter of 100 mm; the WC cylinder is of 25 mm diameter with the flat surface of 10 mm and the taper angle about 10°. The anvil face experiences a high pressure but the material is heavily supported to prevent a failure of the material. Thus the anvil faces can support pressures in excess of 10 GPa. The anvils are pressed against each other four leads electrical resistivity measurements can be done as shown in figure 4.23. The sample is enclosed with talc disc and surrounded by pyrophyllite gasket. The frictional forces acting between the anvil face and the
gasket materials prevent the extrusion of the material and the high pressure is transmitted to the substance under investigation and the results have been discussed in the next section.

Figure 4.22 The high pressure set-up used for the measurement of resistance using Bridgman opposed anvils up to 10 GPa.

Single crystals of GeS_xSe_{1-x} (0, 0.25, 0.5, 0.75, 1) are layer-type semiconductor compounds grown by direct vapour transport technique. For the room temperature measurement of resistance as a function of pressure, up to 10 GPa, the sample was set at the centre of the talc disc on the lower anvil. The schematic diagram of the experimental arrangement for the resistance measurement with pressure is shown in Figure 6.7. The pressure was generated by a hydraulic press on the Bridgman type tungsten carbide opposed anvil apparatus with insitu Bismuth pressure calibration. The samples were contained in a pyrophyllite gasket with talc as pressure transmitting medium. A four-probe method was used to evaluate the resistance of these samples. Stainless steel wires of thickness 50 μm were used. For the measurements of resistance, suitable current (≈1-10 mA range)
was passed through outer leads and the voltage drop across the inner leads was measured.

Figure 4.23 Schematic diagram of the four probe arrangement for the measurements of resistance as the function pressure.

4.5.4 RESULTS AND DISCUSSION

The variation of resistance with pressure for GeS<sub>x</sub>Se<sub>1-x</sub> (0, 0.25, 0.5, 0.75, 1) single crystals are shown in figure 4.24 respectively. For all the cases, it is seen that the resistance decreases gradually with increase in pressure up to maximum value attained. The results of variation of electrical resistance do not show presence of any phase transition up to 8GPa. The resistance was measured in several independent runs on these crystals as a function of pressure and was found to be reproducible.
Figure 4.24 (b) Plot of Log R as a function of pressure in GPa in GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) single crystals.

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) SINGLE CRYSTALS.
Figure 4.24(a) Plot of Log R as a function of pressure in GPa GeS$_{x}$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystals.

In these crystals, the valence band and conduction band are separated by narrow energy band gap. When pressure increases, the separation of bands decreases and the charge carriers of chalcogen element (selenium) from valence band contribute to the carriers of conduction band and the sample becomes more conducting. This explains the decrease of resistance with increase in pressure in figure 4.24. Thus, the decrease in resistance is probably attributed to the charge carriers of valance band contributing to the conduction band carriers. From figure we can say the in GeS$_{x}$Se$_{1-x}$ (0, 0.25, 0.5, 0.75, 1) single crystals.
single crystals the content of sulphur increase the resistance of the compound increase but in all the sample the resistance decreases monotonously as the pressure increases.

4.6 MEASUREMENT OF DIELECTRIC PROPERTIES

4.6.1 Introduction

An interesting group of compounds which has received increasing attention from the fundamental as well as the industrial point of view in recent years. The study of dielectric properties of solids often gives good insight into the electric field distribution within the solids. Studying the dielectric constant as a function of frequency and temperature, the various polarization mechanisms in solids can be understood. Considerable work in this filed has been carried out by several workers [52-58]. A careful study of the GeS_xSe_{1-x} (x=0, 0.25, 0.5, 0.75, 1) suggests to study the variation of dielectric constant and loss factor of crystalline GeS_xSe_{1-x} (x=0, 0.25, 0.5, 0.75, 1) single crystals with respect to frequency and temperature.

The present chapter embodies an indepth analysis of the variation of dielectric parameters of GeS_xSe_{1-x} (x=0, 0.25, 0.5, 0.75, 1) single crystals in the frequency range 200 Hz to 1 MHz using LCR meter model Agilent 4284 A and temperature range 303K to 523K.

4.6.2 High temperature LCR measurement set up

The grown crystals or pallets were employed. The geometrical dimension of all the samples were measured using a traveling microscope and the thickness has been measured using micrometer screw. The dielectric measurements were carried out using the standard two electrode method. The specimen was mounted in between two flat stainless steel parallel electrodes of a specially designed sample holder. Both the upper and lower base of the holder...
can be screwed in for proper contact of the sample with the electrode. The sample holder was enclosed in a specially built resistance heating furnace which is capable to provide temperature upto 625K. The whole measurement setup is shown in figure 4.25.

To measure all dielectric parameters Automation and Controlling software ‘LABVIEW’ is used. The parameters like the thickness and area of the sample, starting and ending temperature and frequency as well as desired steps to increase temperature and frequency has been set in software. These input data are essential in order to measure dielectric parameters at desired temperature and frequencies. The digital temperature controller DT84848 is used to monitor the preferred temperature of the specimen. When preferred temperature is achieved HP4284A LCR meter will scan all the frequencies and resultant data is feeded in the storage device.

**Figure 4.25** High temperature LCR experiment set up
4.6.3 Experimental details

The grown single crystals of GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75, 1) by direct vapor transport technique were mounted in the sample holder. The capacitance and the dissipation factor were measured in the frequency range 100 Hz to 1 MHz with different temperature from room temperature to 523K, in the step of 50K temperature using 4284A LCR meter. From capacitance and dissipation factor all the other parameter can be calculated.

The dielectric constant $\varepsilon'$ of the sample was calculated using the formula

$$\varepsilon' = \frac{C}{C_0}$$  \hspace{1cm} (4.26)

where $C$ is measured capacitance and $C_0$ is calculated by the given equation

$$C_0 = \frac{\varepsilon_0 A}{t}$$  \hspace{1cm} (4.27)

where $\varepsilon_0$ is the permittivity of free space (8.854 X 10\textsuperscript{-12} Fm\textsuperscript{-1}), 'A' and 't' are the area and thickness of the samples respectively.

The dielectric loss tangent was computed as

$$\tan \delta = fD$$  \hspace{1cm} (4.28)

where $D$ is the dissipation factor and $f$ is the frequency in kHz

The resistivity has been determined using the formula

$$\rho_{ac} = \frac{1}{\sigma_{ac}} = \frac{1}{\omega \varepsilon_0 \varepsilon^{'\prime}} = \frac{A}{2\pi fC t \tan \delta}$$ \hspace{1cm} (4.29)

where $\omega = 2\pi f$, $\varepsilon_0$ is free space permittivity and $\varepsilon^{'\prime}$ ($=\varepsilon' \tan\delta$) is the dielectric loss factor, $f$ is applied frequency, $C$ and $\tan\delta$ are the measured capacitance and dielectric loss.
4.6.4 Results and discussions

The variation of capacitance, dielectric constant, loss tangent \( \tan \delta \), a.c.resistivity, a.c.conductivity and the imaginary part of permittivity of the as grown Ge\( S_x Se_{1-x} \) \((x=0, 0.25, 0.5, 0.75, 1)\) crystals with different frequency and from 303 K to 523 K temperature, in the step of 50K temperature, have been shown in figure 4.26 – 4.30 (a), (b), (c), (d) and (e).

As one can see that dielectric behavior is frequency dependent. The capacitance is increases with temperature and it decreases with increasing frequency for all the Ge\( S_x Se_{1-x} \) \((x=0, 0.25, 0.5, 0.75, 1)\) crystals. Because at lower temperature the mobility of ions is very low and so is the conductivity, resulting a lower value of capacitance. With temperature, the mobility of charge carries increases, resulting the increase in space charge polarization and capacitance both.
Figure 4.26 (a) Variation of Capacitance and dielectric loss with frequency and temperature for GeSe single crystal.
Figure 4.26 (b) Variation of dielectric constant and a.c. resistivity with frequency and temperature for GeSe single crystal.
**Figure 4.26 (c)** Variation of a.c. conductivity and imaginary part of permittivity with frequency and temperature for GeSe single crystal.
Figure 4.27 (a) Variation of capacitance and dielectric loss with frequency and temperature for Ge$_{0.25}$Se$_{0.75}$ single crystal.
Figure 4.27 (b) Variation of dielectric constant and a.c. resistivity with frequency and temperature for GeS$_{0.25}$Se$_{0.75}$ single crystal.
Figure 4.27 (c) Variation of a.c. conductivity and imaginary part of permittivity with frequency and temperature for GeS$_{0.25}$Se$_{0.75}$ single crystal
Figure 4.28 (a) Variation of capacitance and dielectric loss with frequency and temperature for GeS$_{0.5}$Se$_{0.5}$ single crystal.
Figure 4.28 (b) Variation of dielectric constant and a.c. resistivity with frequency and temperature for GeS_{0.5}Se_{0.5} single crystal
Figure 4.27 (c) Variation of a. c. conductivity and imaginary part of permittivity with frequency and temperature for GeS$_{0.5}$Se$_{0.5}$ single crystal
Figure 4.29 (a) Variation of capacitance and dielectric loss with frequency and temperature for GeS$_{0.75}$Se$_{0.25}$ single crystal.
Figure 4.29 (b) Variation of dielectric constant and a.c. resistivity with frequency and temperature for GeS$_{0.75}$Se$_{0.25}$ single crystal.
Figure 4.29 (c) Variation of a. c. conductivity and imaginary part of permittivity with frequency and temperature for GeS$_{0.75}$Se$_{0.25}$ single crystal.
Figure 4.30 (a) Variation of capacitance and dielectric loss with frequency and temperature for GeS single crystal.
Figure 4.30 (b) Variation of dielectric constant and a. c. resistivity with frequency and temperature for GeS single crystal
From figure 4.26-4.30(b) the dielectric constant is observed to be high at lower frequency and it systematically decreases with increasing frequency upto 600 kHz and then after it nearly becomes frequency independent for GeS\textsubscript{x}Se\textsubscript{1-x} (x=0, 0.25, 0.5, 0.75, 1) crystals.
The dielectric constant of solids is known to consist of contribution from electronic, ionic, dipolar and space charge polarization exhibits itself prominently at lower frequency. This polarization is known to arise from defects or impurities present, grain boundaries etc. [59-60] and also due to creation and distribution of dipoles either within the bulk or at the surface of the crystals. Hence the higher values of the dielectric constant at lower frequency in the present investigation may be because of a large amount of space charge polarization [61-63]. Less frequency dependence value of $\varepsilon$ is taken as static dielectric constant. This indicates the probable presence of ionic and electrical polarization, since the concentration of crystals defects controlling the space charge polarization negligible. The dispersion of $\varepsilon$ with frequency can be attributed to the Maxwell-Wagner type interfacial polarization i.e the fact that inhomogeneities give rise to a frequency dependence of conductivity because charge carriers accumulate at the boundaries of less conducting regions, there by creating interfacial polarization.

The temperature is also found to exhibit an interesting influence on the dielectric properties. The value of $\varepsilon$ increases with temperature for all the samples. From the Figure 4.26-4.30(b) one can notice that at low temperatures the variation in dielectric constant is much less frequency dependent, while at higher temperatures the increase in dielectric constant is stronger and much more frequency dependent. This is due to lattice expansion, polarizability of the constituent ions due to increase in temperature and available volume together with the increase of atomic polarizability [64]. The faster increase with temperature is contributed by the thermally generated charge carriers. In most of the semiconducting compounds the number of charge carriers increase with temperature while the mobility decreases with rise in temperature. These changes are probably impeded by trapping a space charge there by building up polarization which results in
macroscopic field distortion [65]. This leads to a large increase in $\varepsilon'$. And also the lattice defect concentration can rise with temperature, making the space charge polarization dominant and hence the $\varepsilon'$ increases with temperature. The changes in $\varepsilon'$ with temperature are of similar nature at all the frequencies.

While from all the figures we can say the as the content of sulphur increases in GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) crystals the dielectric constant of the sample increases.

Figure 4.26-4.30 (a) shows the variation in dielectric loss tan$\delta$, it increases with increasing frequency and it in also increases consistently with temperature for GeSe, GeS$_{0.75}$Se$_{0.25}$ and GeS. While for GeS$_{0.5}$Se$_{0.5}$ and GeS$_{0.25}$Se$_{0.75}$ it decreases with temperature and frequency. For many materials it has been observed that the dielectric loss decreases as frequency increases [66-67] The response of the normal materials to applied fields depends on the frequency of the applied fields. In fact, polarization of material does not respond instantaneously to an applied filed so the permittivity is often treated as a complex function of frequency. The change in complex dielectric constant with frequency is shown in figure 4.26-4.30(c). This indicates that as the frequency increases the value of imaginary part of the permittivity decreases. But it increases with temperature for GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) crystals. The observed decrease in $\varepsilon'$ values with frequency and increase in $\varepsilon'$ with temperature, which are the common features of all the compositions and it can be on explained on similar arguments as for $\varepsilon'$.

The conductivity of all the materials is increases with temperature and frequency both while at lower frequency it is much more independent of frequency. The resistivity decreases with frequency and temperature both with can be seen from figure 4.26-
4.30 (b) & (c). So at higher temperature GeS$_x$Se$_{1-x}$ ($x=0$, 0.25, 0.5, 0.75, 1) all single crystals become more conducting so its resistivity decreases with temperature. At lower frequency the increase in conductivity is more rapid and at higher frequency the conductivity increases very slowly.

4.7 CONCLUSIONS

- The electrical resistivity is increases as the content of sulphur increases. The value of resistivity along the basal plane is higher then that of the normal to the basal plane. There is no any transition in any single crystals upto 723K temperature. All the material shows anisotropy behaviour.

- The positive sign of the seebeck coefficient shows that all the materials having p-type semiconducting nature. The scattering parameter and Fermi energy has been calculated for all the samples.

- The positive values of hall coefficient in all the samples indicate that they have p-type semiconducting nature with majority charge carriers as holes. The change in hall parameters with increase in temperature upto 120°C has been duly explained in the text.

- The electrical resistivity monotonously decreases with increase in pressure up to 8 GPa for all the samples which shows the semiconducting behavior of all the samples.

- The variation in dielectric parameters with temperature and applied frequency have been observed and explained in detail in the text.

CH.4. ELECTRICAL PROPERTIES OF GeS$_x$Se$_{1-x}$ ($x=0$, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
REFERENCES


CH.4. ELECTRICAL PROPERTIES OF GeSxSe1-x (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.


CH.4. ELECTRICAL PROPERTIES OF GeS_xSe_1-x (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.
CH.4. ELECTRICAL PROPERTIES OF GeSₓSe₁₋ₓ (x=0, 0.25, 0.5, 0.75, 1) SINGLE CRYSTALS.