CHAPTER 1

EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES
1.1 INTRODUCTION:

Since the ancient times, Man had admired crystals for long as he appreciated beauty. Solid materials have played a vital role in the progress of mankind. While the stone-age caveman used sharp stones as weapons, later iron age heralded the emergence of materials as the key materials. At that time properties of naturally available materials were discovered by trial and error and then materials were put to use profitably. With this trial and error method gave the way to choice and selection of materials, once man realized that properties could be designed and materials with tailor-made characteristics could be synthesized.

Today, crystals are the pillars of modern technology. Without crystals there would be no electronics industry, no photonic industry, no fiber-optics communications, very little modern optical equipment and some very important gaps in conventional production engineering. Progress in crystal growth and epitaxial technology is highly demanded in view of its essential role for the development of several important areas as production of high efficiency photovoltaic cells and detectors for alternative energy and medicine and fabrication of light emitting diodes.

Solid materials can be classified according to a variety of criteria. Among the most significant of these is the description of a solid as being either crystalline or amorphous. Large natural crystals of a variety of solids have been known to man for thousands of years. Typical examples are quartz (SiO₂), rock salt (NaCl) the sulphides of metals such as lead and zinc and of course gemstones such as ruby (Al₂O₃) and diamond (C).

For many centuries the word "crystal" was applied specifically to quartz, it is based on the Greek word implying a form similar to that of ice. In current usage, a crystalline solid is one in which the atomic
arrangement is regularly repeated and which is likely to exhibit an external morphology of planes making characteristic angles with each other if the sample being studied happens to be a single crystal. When two single crystals of the same solid are compared, it will usually be found that the sizes of the characteristic plane "faces" are not in the same proportion the "habit" varies from crystal to crystal. On the other hand, the interfacial angles are always the same for crystals of a given material.

Many of the metal chalcogenides, compounds of metals and nonmetals with S, Se or Te are important in the new technologies [1]. These chalcogenides considered as "high - tech" materials have many applications, including the following:

- tribology (high temperature lubricants)
- semiconductors, thin films, glasses, photoresists, photomicrography (electronics)
- intercalation of alkali and other metals (battery technology)
- catalysis (dehydro sulphurisation)
- solar energy conversion
- extractive metallurgy (de-sulphurisation as practiced in steel industry)
- corrosion in sulphur containing atmospheres (e.g. H₂S).

Among these metal chalcogenides, the binary IV – VI layered compounds formed with Ge as cations and S, Se and Te as anions form a very interesting class of semiconductors.

In third group of IV-VI compounds GeS and GeSe can be produced in both crystalline and amorphous forms [2]. In crystalline form they have an orthorhombic structure [3] and an exceptionally
easy (001) cleavage planes perpendicular to c-axis [4]. This cleavage is so easy, in fact, that GeS and GeSe are expected to exhibit extreme anisotropy in their lattice vibrational, optical and electronic properties [5] and perhaps show some characteristic features of the two dimensional or layer type semiconductors [6-10].

It would appear, therefore, that GeS and GeSe provide an excellent opportunity for investigating the relations among structure, bonding and the electronic properties of solids with comparisons possible between:

➢ crystalline and amorphous forms

➢ two and three dimensional structures

➢ members of the isomorphic series GeS, GeSe, SnS and SnSe

➢ Structurally different compounds GeS, GeTe and GaS.

Structure of these layered materials can be described as solid containing molecules which are in two dimensions extends to infinity and which are loosely stacked on top of each other to form three-dimensional crystals. Several layered materials posses favorable semiconducting properties and have attracted attention as a new class of solar cell materials. Significant optical-to-electrical/chemical energy conversion efficiencies have been obtained in solid-state photovoltaic and photoelectrochemical cells. The potential of this class of materials has not been fully explored yet but appears to be limited mainly by the availability of suitable materials. Attempts have therefore been made to produce good quality crystals and thin films of the layered semiconductors for photoelectronic device applications. Several approaches including a novel extension of molecular beam epitaxy for the preparation of layered materials are being actively pursued to produce high quality single crystals and thin films.
The metal chalcogenides, on the other hand, exhibit promising properties for quantum solar energy conversion because:

- The band gap is typically in the range of 1 to 2 eV and therefore ideally fit for the solar spectrum,
- The valence and conduction band width is of reasonable magnitude due to rather strong metal chalcogenide hybridization; as a consequence the charge carrier mobilities are sufficiently large,
- The absorption constants are extraordinarily high, typically in the range $10^5 \text{ cm}^{-1}$.

Therefore, energy conversion devices fabricated from these materials may be considered promising alternatives to more established solar cells.

**Table 1.1** The atomic number, atomic weight, group, period, density and melting point of Ge, S and Se elements.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ge</th>
<th>S</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>IV</td>
<td>VI</td>
<td>VI</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>8,18,4</td>
<td>2,8,6</td>
<td>8,18,6</td>
</tr>
<tr>
<td>Atomic No.</td>
<td>32</td>
<td>16</td>
<td>34</td>
</tr>
<tr>
<td>Atomic Weight (gm)</td>
<td>72.64</td>
<td>32.065</td>
<td>78.96</td>
</tr>
<tr>
<td>Density (gm cm⁻³)</td>
<td>5.323</td>
<td>2.07</td>
<td>4.79</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>938.4</td>
<td>115.8</td>
<td>221</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>2820</td>
<td>444.7</td>
<td>685</td>
</tr>
</tbody>
</table>

The elemental information about the metal Ge, non-metal S and chalcogen element (Se) used in the present work for the synthesis of single crystals of Ge₅ₓSe₁₋₅ₓ (x = 0, 0.25, 0.5, 0.75, 1) are as shown in Table 1.1.
• **Germanium (Ge):**

It is a member of group IV elements. It is lustrous, hard, silver metallic element. Ge is grayish-white element that has a metallic luster and possesses the same crystal structure that the diamond. In addition, it is important to note that Germanium is a semiconductor with electrical properties between those of metal and insulator. Ge has F.C.C. crystal structure which is shown in the figure 1.1.

![Figure 1.1 The solid state structure of Germanium.](image)

• **Sulphur (S):**

It is a member of group VI elements. It is an abundantly available, multivalent non metal element. It can be found as the pure element or as sulphide and sulfate minerals.

![Figure 1.2 The crystal structure of sulphur](image)
At room temperature sulphur is a soft bright yellow solid. Crystallography of sulphur is complex. The orthorhombic crystal structure of sulphur is shown in the figure. 1.2

- **Selenium (Se):**

  It is a member of group VI elements. It is a covalent semiconductor. It has been metallized by application of pressure. At RTP Se is rhombohedral. They are also metastable monoclinic forms of Se based on Se₅ rings, similar to S₈.

![Figure 1.3 The solid state structure of selenium.](image)

Selenium exhibits both photovoltaic action, where light is converted directly into electricity and photoconductive action where the electrical resistance decreases with increased illumination. These properties make selenium useful in the production of photocells and exposure meters for photographic use, as well as solar cells. Selenium is also able to convert a.c. electricity to d.c. and is extensively used in rectifiers. This solid is a p-type semiconductor and is useful in electronic and solid-state applications.

It has been used in photocopying for reproducing and copying documents, letters, etc. Se used by the glass industry to decolourise glass and to make ruby coloured glasses and enamels and as

---

**CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.**
photographic toner and additive for stainless steel. The solid-state structure of selenium is shown in figure 1.3.

Author has chosen to work on the synthesis and characterization of lesser studied GeS_xSe_1-x (x = 0, 0.25, 0.5, 0.75, 1) single crystals and examined the possibility of their use in fabrication of electronic devices. The work on GeSe and GeS has been reported but the intermediate compounds GeS_0.25Se_0.75, GeS_0.5Se_0.5 and GeS_0.75Se_0.25 are not reported yet. So in this chapter the general introduction on the exciting information about germanium monosulphide and germanium monoselenide has been provided as a guideline for the work described in this thesis.

1.2 OCCURRENCE AND SYNTHESIS

Usually, none of the members of the series GeS_xSe_1-x (0 < x < 1) is known to occur naturally and so has to be synthesized in the laboratory. Among various crystal growth techniques monocrystalline Germanium sulphoselenide can be grown by the following methods:

- Sublimation of the material in a vertical furnace
- Czochralski and Bridgman or Bridgman Stockbarger technique
- Vapour transport in a horizontal furnace.

A brief description of the various attempts made by earlier workers using the methods outlined above to grow GeS single crystals is presented below:

Yabumoto [11] produced layers and polycrystalline blocks by sublimation of GeS in a stream of ammonia. Lider and Solovev [12] obtained small platelets of GeS in evacuated silica ampoules after annealing GeS close to the melting point. Polycrystalline blocks of GeS were obtained by slow cooling of molten GeS by Okhotin et al. [13]. Karbanov et al. [14] grew crystals of GeS with a volume upto 2 cm³ by

Starting from the year 1975, majority of the investigators [4, 17-30] have grown GeS single crystals following the method of vacuum sublimation introduced by Schonherr and Stetter [31]. The growth of GeS single crystals was carried out in a vertically arranged furnace. The size of the growth ampoule was about 20 mm in diameter and 120 mm in length. The growth ampoules were filled with 20g GeS chunks. They were evacuated, outgassed at 250°C and sealed off at 10^-6 torr. A slight constriction at the tip prevented the crystal from dropping during growth. High quality crystals were obtained for maximum temperatures between 520 and 580°C. The ampoules were pulled into the upper zone with a rate less than r = 0.2 mm/h. The temperature of the lower zone was constant over a sufficient length so that the source material evaporated with the same temperature during the whole growth process. The growth temperature was about 40°C below the evaporation temperature. Further details of the entire growth process can be obtained from [31].


A critical survey of the existing information on GeSe indicated that similar to GeS, Germanium monoselenide single crystals have been grown by Bridgman technique, vacuum sublimation technique introduced by Schonherr and Stetter [31] and static sublimation technique used by Bletskan et al. [36]. However, unlike GeS, majority of the workers have grown GeSe single crystals by the vapour
transport technique either using no transporting agent or using iodine as the transporting agent. A brief description of the various attempts made by these investigators is given below.

Ishihara et al. [41], Elkorashy [42-44] and Valiukonis et al. [37] prepared GeSe single crystals by the Bridgman technique. Ishihara et al. [41] and Taniguchi et al. [29] grew undoped GeSe crystals by the vacuum sublimation technique [31]. Zakharchuk et al. [45] & Zuev et al. [32] used static sublimation technique [36] to synthesize single crystals of GeSe.

The vapour transport technique without any transporting agents was used for the growth of the GeSe single crystals[46-49].

Chemical vapour transport technique was used for the growth of GeSe single crystals by Weidemeier et. al [51] and iodine as a transporting agent. Nagard et al. [52] also carried out growth of GeSe single crystals by a CVT method using iodine as the transporting agent.

1.3 CRYSTAL STRUCTURE AND STRUCTURAL PROPERTIES

Structures of IV-VI compounds crystallise in several different crystal structures. In this lead chalcogenides or SnTe adopt the NaCl structure where each atom is in octahedral co-ordination of six atoms of the other type. On the other hand, GeS together with its isotropic (B16) compounds GeSe, SnS and SnSe possess an orthorhombic crystal structure with space group $P_{nmc}$ ($D_{2h}^{16}$). This structure, with a lower symmetry than the previous one, consists of double layers of atoms where each Ge atom is coordinated by two S/Se atoms in the plane of the layer and one additional S/Se atom at a short distance, perpendicular to this plane, in the same double layer (2+1) co-ordination (Fig 1.4). A prominent feature of the GeS / GeSe structure,
is, however, its layer character, since this structure results from stacking of double GeS / GeSe layers and look like pseudo-bidimensional because inter-layer bondings are weaker than intralayer bondings.

Figure 1.4 Layered structure of GeS/GeSe projected in (001) plane.

The primitive cell of GeS and GeSe contains eight atoms and covers two adjacent double layers which can be seen form figure 1.5. The primitive cell of the GeS / GeSe compounds can be seen in figure. 1.5.

The unit cell of GeSe single crystal is shown in figure 1.6 For the structure of GeSe, S is to be replaced by Se in this figure. In this structure, each Ge atom is surrounded by six S atoms (and vice versa) in distorted octahedral arrangement. Within a double layer, each atom has three nearest neighbours. The character of bonds between the atoms inside a double layer is represented by a mixture of the homopolar and heteropolar bonds and that between the layers is represented by the bonds of the van der Waals type.

CH. 1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.
Owing to the layered structure these materials (GeS and GeSe) show strongly anisotropic properties. Both GeS and GeSe are from the CH. 1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.

Figure 1.5 The primitive cell of GeS like compound.

Figure 1.6 Unit cell of orthorhombic GeSe single crystal.

Owing to the layered structure these materials (GeS and GeSe) show strongly anisotropic properties. Both GeS and GeSe are from the
crystallographic point of view characterized by three axes $\tilde{a}, \tilde{b}, \tilde{c}$ perpendicular to each other. The axes $\tilde{a}$ and $\tilde{b}$ ($a > b$) lie in the cleavage plane, the third one, $\tilde{c}$, is perpendicular to this plane. It holds $a \approx b$ and $c$ is much greater than both $a$ and $b$ which can be seen from table 1.2.

**Table 1.2** Lattice parameters of GeSe and GeS single crystals.

<table>
<thead>
<tr>
<th>Material</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeS</td>
<td>4.40</td>
<td>3.65</td>
<td>10.44</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.64</td>
<td>10.74</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.65</td>
<td>10.44</td>
<td>[4],[17],[19],[23],[24],[30],[36],[38],[39],[48],[53],[56],[59],[60],[61]</td>
</tr>
<tr>
<td>GeS</td>
<td>4.29±0.01</td>
<td>3.64±0.01</td>
<td>10.42±0.03</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.64</td>
<td>10.47</td>
<td>[20],[27],[33],[62]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.641</td>
<td>10.470</td>
<td>[57],[58]</td>
</tr>
<tr>
<td></td>
<td>4.29</td>
<td>3.64</td>
<td>10.42</td>
<td>[25]</td>
</tr>
<tr>
<td>GeSe</td>
<td>4.38</td>
<td>3.82</td>
<td>10.79</td>
<td>[3],[41],[47],[49],[50],[62],[66],[67]</td>
</tr>
<tr>
<td></td>
<td>4.40±0.008</td>
<td>3.85±0.008</td>
<td>10.82±0.01</td>
<td>[42],[43],[44],[64]</td>
</tr>
<tr>
<td></td>
<td>4.375±0.005</td>
<td>3.825±0.005</td>
<td>10.80±0.02</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>4.390</td>
<td>3.827</td>
<td>10.824</td>
<td>[46],[48]</td>
</tr>
<tr>
<td></td>
<td>4.38</td>
<td>3.80</td>
<td>10.77</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>4.387±0.008</td>
<td>3.837±0.008</td>
<td>10.83±0.015</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>4.39</td>
<td>3.83</td>
<td>10.8</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>4.39±0.02</td>
<td>3.826±0.007</td>
<td>10.827±0.02</td>
<td>[52]</td>
</tr>
</tbody>
</table>

The GeS / GeSe structure is in some respects related to that of the NaCl type, in fact its lattice can be thought of as a deformed NaCl type [2]. Each atom forms six dominant heteropolar bonds, the strongest of which are in three bonds to nearest neighbours in the

*CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.*
same double layer. Three weaker bonds are to further neighbours, two of which are in the same double layer, and one to an atom in the next layer [2]. The lattice parameters of GeS and GeSe are summarised in table 1.2. The orthorhombic subgroup of IV – VI GeS compounds consists of structures intermediate between three-dimensional and two dimensional materials, constructed of two dimensional layers weakly bonded to each other to produce a three dimensional material. The intermediate compounds GeS\textsubscript{x}Se\textsubscript{1-x} (x=0.25, 0.5, 0.75) are not yet reported.

1.4 OPTICAL PROPERTIES

Looking to the importance of optical band gap $E_g$ in device applications, a thorough investigation of optical parameter has been undertaken by the author in GeS\textsubscript{x}Se\textsubscript{1-x} (x= 0, 0.25, 0.5, 0.75, 1) single crystals grown using direct vapour transport technique.

According to the literature survey the band structure calculation for germanium and tin chalcogenides carried out [66] by equivalent orbital linear combination method. The temperature dependence of the absorption edge of GeS within the range from 4.2 to 300K has been studied by Wiley et al. [4, 24, 56] and Lider and Solovev [73]. Reflectivity of GeS has been studied by Wiley et al. [19], they used polarised light at room temperature (RT) and by Sobolev and Donetskich [74] they use unpolarised light at 77 and 300K. The Raman spectra of GeS at room temperature and also 20 to 300K temp. range by Gregora and Stetter [17] and Wiley et al. [76]. Bletskan et al. [75] studied the electroreflectance (ER) spectra of GeS at RT in the range from 1.4 to 2.2 eV. The refractive index of crystalline and amorphous GeS has been studied by Gregora et al. [58].

In these papers [27, 28] almost 60 papers related mostly to GeS, especially its optical properties are quoted. Lukes [77] has discussed
the temperature dependence of dielectric function from the study of thermoreflectance spectra of GeS.

Kannewurf and Cashman [78] studied optical properties of GeSe near the absorption edge in unpolarised light. Lukes [79] described optical properties of GeSe for cleaved (\(\overline{a}||\overline{b}\)) plane studied in polarised light in the range from 0.5 to 1.5 eV at RT. Vlachos et al. [47, 80] studied the absorption near the absorption edge (1.2 - 1.6 eV) in the temperature interval from 100 to 300K. Zacharchuk et al. [81] reported the excitonic character of the absorption near the absorption edge studied at temperatures from 4.2 to 300K. Chandrasekhar and Zwick [66] have studied both infrared reflectivity in the range from 20 to 4000 cm\(^{-1}\) and Raman scattering for GeSe at RT. Infrared reflectivity in GeSe has also been reported by Siapkas et al. [82].

Tyagi et al. [35] have studied the ER spectra in GeSe for both polarizations in the cleavage plane at RT in the range from 1.1 to 2.5 eV. Lukes et al. [83] have also reported TR spectra in GeSe obtained at 100 and 320 K for the orientations \(\overline{E}||\overline{a}\) and \(\overline{E}||\overline{b}\) in the range from 1.2 to 4.8 eV.

According to the latest reports, Gashimzade et al. [62] carried out the band structure calculations for GeS and GeSe along with SnS and SnSe by equivalent-orbital linear combination of the atomic orbitals method.

The other optical parameters of importance for device applications are the index of refraction 'n' and dielectric constant. Elkorashy [61, 44] measured the refractive index 'n' for GeS and GeSe single crystals by the interference method in the transparency region. He calculated the extinction coefficient 'k' from the measured absorption coefficient. He performed the measurements at room temperature using plane polarised light with the plane of polarisation parallel to the a – and b- crystallographic axes which lie in the plane.

---

CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.
of cleavage. The real and imaginary parts of the complex dielectric constant ($\varepsilon_r$, $\varepsilon_i$) were calculated by him from the values of $n$ and $k$.

1.5 MAGNETIC PROPERTIES

From electrical and magnetic measurements on GeSe; Kyriakos et al. [85-86] reported that this compound shows an antiferromagnetic behaviour with a negative magnetoresistance effect. From their measurements, they determined a Neel temperature at 381K and observed that above this temperature GeSe showed a 'metallic' behaviour with zero field resistivity. Kyriakos et al. [30] showed that similar to GeSe, GeS is also antiferromagnetic with a Neel temperature around 455K. They [30] investigated galvanomagnetic effects of GeS in the temperature range 293-423K. Their results showed the existence of negative magnetoresistance and a kind of rapid oscillation of both the magnetoresistance and the Hall effect depending on both the temperature and the magnetic field. The negative magneto resistance observed in GeS and GeSe was attributed to arise from localised moments located at impurity atoms, such as transition- metal atoms, which form antiferromagnetic clusters. These clusters are formed either at planar defects or at twin boundaries or between the double layers of germanium chalcogenide's characteristic structure. Defects of this kind were verified in both GeS and GeSe by Karakostas [48]. The rapid oscillation of the magneto resistance and the Hall effect was also explained to arise from the resonant defect states in the valence bands arising from the same defects which gave rise to the negative magnetoresistance.

1.6 ELECTRICAL PROPERTIES

It appears from the literature that majority of germanium monosulphide and germanium monoselenide compounds in the form of single crystals, polycrystalline and thin film form have been reported as p-type semiconductors. The electrical properties of GeS,
however, have remained poorly characterized, since most of the earlier electrical measurements were either done on crystallites of ill defined orientation [15, 87], or polycrystalline samples [126, 127]. The main conclusions which can be drawn from these measurements [15, 87, 88] are:

- GeS is always found to be p-type;
- The room temperature resistivity is usually of the order of $10^3$ to $10^5 \, \Omega \cdot \text{cm}$, with considerable sample to sample variation;
- Conduction is extrinsic at all temperatures below $\approx 400^\circ\text{C}$;
- A great variety of impurity and trapping levels are found in the band gap [22, 89] and
- It is exceptionally difficult to obtain good quality ohmic contacts needed for reliable electrical measurements.

Wiley et al. [90] extended the results on electrical behaviour of GeS further by carrying out electrical conductivity measurements in GeS single crystals by two probe and four probe techniques in the temperature range 77 to 500 K. They concluded from their measurements that activation energies of 240 meV and 400 meV.

Bletskan and Indus [91] while studying the temperature dependence of electrical conductivity in filamentary crystals of In doped GeS obtained a value of thermal activation energy as equal to 0.97 eV. In the later studies Kyriakos et al. [30] while investigating galvanomagnetic effects of orthorhombic GeS crystals in the temperature range 293-423 K observed a kind of rapid oscillation in the Hall coefficient which depended both on temperature and magnetic field. This rapid oscillation in Hall coefficient was attributed to the resonant defect states in the valence band.

CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.
GeSe possesses a similar electronic structure as GeS in the sense that both of them are p-type semiconductors. The study of the electrical properties of GeSe was first carried out by Asanabe and Okazaki [93]. From the temperature dependence of the electrical resistivity and the Hall coefficient they elucidated the existence of a shallow acceptor level and a donor level close to the valence band. The donor level due to excess germanium atoms was located about 0.2 eV above the valence band. This value was simply obtained from the temperature dependence of the Hall coefficient. The electrical parameters reported in past has been represented in table 1.3 and 1.4.

**Table 1.3** The electrical parameters of GeS single crystals

<table>
<thead>
<tr>
<th>Carrier type</th>
<th>Carrier concentration</th>
<th>Room temp.</th>
<th>Hall coefficient</th>
<th>Mobility 'μ'</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>---</td>
<td>10^5 to 10^7</td>
<td>----</td>
<td>----</td>
<td>[21]</td>
</tr>
<tr>
<td>p</td>
<td>---</td>
<td>10^2-10^5</td>
<td>----</td>
<td>----</td>
<td>[89]</td>
</tr>
<tr>
<td>p</td>
<td>10^6</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>[94]</td>
</tr>
<tr>
<td>p</td>
<td>10^6-10^9</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>[5]</td>
</tr>
<tr>
<td>p</td>
<td>7×10^2</td>
<td>2×10^4</td>
<td>30</td>
<td>[30]</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>3.4±0.5×10^{18}</td>
<td>5×10^3</td>
<td>----</td>
<td>----</td>
<td>[95]</td>
</tr>
<tr>
<td>p</td>
<td>1.49×10^9</td>
<td>3.82 × 10^6</td>
<td>4.20×10^9</td>
<td>182</td>
<td>[113]</td>
</tr>
</tbody>
</table>

Ishida et al. [49] carried out the resistivity ρ and the Hall coefficient R_H measurements parallel to the layers of GeSe (p-type) single crystals.

*CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.*
between 77 K and 1.4K in the carrier concentrations ranging from $7 \times 10^{16}$ to $5 \times 10^{17}$ cm$^{-3}$. They found a metal-nonmetal transition at the carrier concentration of $p \sim 4 \times 10^{17}$ cm$^{-3}$. The conductivity at this transition was $\sim 20$ mho cm$^{-1}$, which compared favourably well with a three dimensional minimum metallic conductivity.

Ishihara et al. [41] investigated anisotropy of electrical resistivity and the Hall coefficient together with the TEP in the temperature range of 78 to 300K in vapour grown p-type Ge$_{1-x}$Se crystals in which $x$ was of the order less than 0.005. They obtained the effective masses of holes along the a-, b- and c- crystallographic axes as 0.20 m, 0.37m and 6.2m respectively where m is the electron mass.

Inspired by this work and looking to the fact that detailed studies on electrical property measurements in different temperature ranges is lacking in GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$); author has carried out an in depth study of the electrophysical measurements in GeS$_x$Se$_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) single crystals grown using direct vapour transport technique. The results of these investigations are presented in Chapters 4 and 5.
<table>
<thead>
<tr>
<th>Carrier type</th>
<th>Carrier concentration 'p' cm⁻³</th>
<th>Resistivity 'p' Ω cm</th>
<th>Hall coefficient 'RH' cm³C⁻¹</th>
<th>Mobility 'μ' cm²/V.s</th>
<th>TEP μV/K</th>
<th>Effective mass</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>6.7x10¹⁶</td>
<td>1.2</td>
<td>1.6x10⁻¹</td>
<td>5.1x10⁴</td>
<td>---</td>
<td>---</td>
<td>[49]</td>
</tr>
<tr>
<td>p</td>
<td>1.9x10¹⁷</td>
<td>6.1x10⁻¹</td>
<td>1.1x10⁻¹</td>
<td>1.3x10</td>
<td>---</td>
<td>---</td>
<td>[50]</td>
</tr>
<tr>
<td>p</td>
<td>2.7x10¹⁷</td>
<td>2.7x10⁻¹</td>
<td>7.9x10⁻²</td>
<td>9.8x10⁻¹</td>
<td>---</td>
<td>---</td>
<td>[41]</td>
</tr>
<tr>
<td>p</td>
<td>2.8x10¹⁷</td>
<td>1.8x10⁻¹</td>
<td>5.3x10⁻²</td>
<td>5.8x10⁻¹</td>
<td>---</td>
<td>---</td>
<td>[41]</td>
</tr>
<tr>
<td>p</td>
<td>7.2x10¹⁶</td>
<td>1.0x10⁴</td>
<td></td>
<td></td>
<td>---</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>1.5x10¹⁷</td>
<td>1.6x10³</td>
<td></td>
<td></td>
<td>---</td>
<td>467.8</td>
<td>[41]</td>
</tr>
<tr>
<td>p</td>
<td>1.4x10¹⁷</td>
<td>1.1x10³</td>
<td></td>
<td></td>
<td>---</td>
<td>7.0x10³</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>3x10¹⁸</td>
<td>7.5x10⁻¹</td>
<td></td>
<td></td>
<td>---</td>
<td>5.3x10³</td>
<td>[41]</td>
</tr>
<tr>
<td>p</td>
<td>5.0x10⁻¹</td>
<td>5.0x10⁻¹</td>
<td></td>
<td>5.9x10³</td>
<td>467.8</td>
<td>7.0x10³</td>
<td>[41]</td>
</tr>
<tr>
<td>p</td>
<td>2.46x10⁻¹</td>
<td></td>
<td></td>
<td></td>
<td>---</td>
<td>0.20 m</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>3x10¹⁸</td>
<td></td>
<td></td>
<td></td>
<td>---</td>
<td>0.37 m</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>4x10¹⁵</td>
<td>50-60</td>
<td></td>
<td></td>
<td>---</td>
<td>20-25</td>
<td>[5]</td>
</tr>
<tr>
<td>P</td>
<td>6.2x10¹⁴</td>
<td>78.2</td>
<td></td>
<td>1.45 x 10³</td>
<td>429</td>
<td>50</td>
<td>0.004 m [112]</td>
</tr>
<tr>
<td>P</td>
<td>1.1±0.6x10¹⁶</td>
<td>3x10²</td>
<td></td>
<td></td>
<td>---</td>
<td>---</td>
<td>[95]</td>
</tr>
<tr>
<td>P</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td>---</td>
<td>370</td>
<td>[53]</td>
</tr>
<tr>
<td>P</td>
<td>3x10¹⁸</td>
<td></td>
<td></td>
<td>5x10¹⁴</td>
<td>---</td>
<td>70</td>
<td>[5]</td>
</tr>
</tbody>
</table>

**Table 1.4** The electrical parameters for GeSe single crystal
1.7 IMPORTANCE OF GeSe AND GeS SINGLE CRYSTALS

➢ The properties of IV-VI semiconducting compounds are useful for infrared detection as sensors of thermal radiation and as wide band gap detectors in the areas of lasers, radar and laser communication. In addition to infrared detectors and emitters, narrow band gap compound crystals have potential applications in magneto resistive Hall effect and thermoelectric devices [97,70].

➢ Among these IV-VI compounds, bulk crystals as well as thin photosensitive films of germanium monosulphide and germanium monoselenide are of special interest in optoelectronics [32, 52, 84].

➢ Germanium monosulphide is particularly interesting because it is the least anisotropic member of the IV-VI group and so represents an intermediate state between a true layer structure and a three dimensional crystal. Increasing interest has been shown in GeS and its films particularly in the photoelectric properties [88,98-101] and it has been suggested that the material could be used successfully as a photosensitive film in TV camera tubes [98, 99]. GeS is also of great interest because of its possible use as a hologram recording material [102, 96].

➢ GeS has been of interest because of its outstanding properties as substrate for the layer-by-layer growth of epitaxial, single crystalline C₆₀ thin films [103]. A high friction coefficient of \( \mu \approx 1.5 \) was found for GeS [104]. In recent years there has been growing interest in the field of organic light emitting diodes (OLEDs). The role played by cleaved GeS (001) single crystals as electrodes in these light emitting diodes has been considered by Peisert et al. [105].
Synthesis of filamentary crystals of GeS doped with indium has found applications in various microinstruments e.g. tensometers, thermoresistors, accelerometers, photo resistances, photocathodes etc [91]. Also GeS in the form of thin films has found its use as a basis for the fabrication of high efficiency transducers [92]. Moreover, Ag/Ge\(_x\)S\(_{1-x}\) system works as a high resolution lithographic resist for U-V applications, insensitive to visible light, this system has the advantage of being non-toxic and thermally stable [106].

GeS has been used in the preparation of multicomponent chalcogenides useful in the development of cryogenic microelectronics [107]. Germanium sulphide glasses work as interesting materials which can be used as sensitive media for optical recording as light guides, as high resolution inorganic photoresistors or antireflection coatings [71].

Metal selenides have attracted considerable attention because of their interesting properties and potential applications. They have been widely used as thermoelectric cooling materials, optical filters, optical recording materials, solar cell materials, superionic materials and sensor and laser materials [108]. Among these metal selenides, Germanium monoselenide has particularly energy band gap close to the optimum value [52] for solar energy conversion which makes them of some interest for photovoltaic applications.

Films of germanium monoselenide (GeSe) and off-stoichiometric GeSe are very attractive for IR optical devices [69, 109]. These films are objects of increasing importance in view of the possibilities for their application in solar cells, electronic switching and memory devices [110]. Additionally the Se containing films are chemically stable and water resistant [111], therefore, they can also be used for passivation.

CH. 1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.
REFERENCES


CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.

CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.


---

CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.

CH. 1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.
CH.1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.


---

CH. 1. EXISTING INFORMATION ABOUT GERMANIUM CHALCOGENIDES.