Chapter 1

Existing Information about Germanium Chalcogenides
1.1 INTRODUCTION

For more than 30 years, there has been a sustained academic interest and technical development effort directed at layered metal chalcogenides (LMCs) and their intercalation compounds. This in part is due to the intriguing structural and physical properties of these two-dimensional (2D) inorganic materials [1]. In the general case, these structures consist of infinite metal chalcogenide layers; within each layer the atoms are bound by strong covalent interactions, but the layers themselves interact only by weaker van der Waals forces [2]. For the most part, the metals involved are transition metals, although SnS$_2$ is a well-known example of a main-group LMC [3,4]

Metal chalcogenide (MCh) materials range from common oxides and sulphides, selenides, and tellurides, to complex compound or solid solution systems containing different metal or chalcogen elements in various oxidation states and varying proportions. Owing to their wide spectrum of properties, these materials relate to a large variety of existing and potential applications in electronics, optics, magnetics, solar energy conversion, catalysis, passivation, ion sensing, batteries, and fuel cells. [5].

Many of the chemical and physical properties of these materials derive from this anisotropic layered structure. Intercalation chemistry, the insertion of ions and/or molecules between individual LMC layers, is possible due to these weak interlayer bonding interactions. The highly anisotropic nature of the layered structure also leads to characteristic and often technologically useful mechanical, electrical, magnetic, and optical properties. On the other hand, since a broad range of metals and oxidation states is included in this structural class, a broad range of properties is also observed. Depending on the metal and the specific structure, LMCs may be semiconductors, semimetallic, or metallic [6,7]. The metallic chalcogenides may exhibit interesting electronic effects, such as charge density waves and superconductivity [8] Early technological interest was in part focused on the importance of the layered metal disulphides, MS$_2$, as the catalytic agent in hydro-processing or hydro-treating reactions of organic sulphur- and nitrogen-containing feed stocks. For the past several decades, MoS$_2$ and WS$_2$ in particular have been used as a hydrodesulphurization and denitrogenation catalysts in petroleum processing [9-11].
Other important applications have also been developed or proposed for these materials. For example, MoS$_2$ is currently an important material in high-temperature solid state lubrication [12, 13]. Other applications have not been realized but have involved considerable research and technical interest. For example, LMCs such as TiS$_2$, MoS$_2$, and NiPS$_3$ have also been explored as cathodic materials in lithium anode batteries [14-16].

Many of the MS$_2$ compounds are sufficiently conductive to allow for potential applications as conductive additives or use as other electro active components. In other cases, novel properties suggest potential application in new devices or other new roles for solid materials. For example, intercalation compounds derived from TaS$_2$, NbS$_2$, and MnPS$_3$ demonstrate interesting superconductivity and second-order-harmonic nonlinear optical properties [17,18].

1.1.1 The Chalcogens

It is common that the three heaviest elements of the sulphur sub-group, namely selenium, tellurium, and polonium, be collectively referred to as the “Chalcogens,” and the term chalcogen be addressed only for these elements – in practice, only for the chemically and technologically important selenium and tellurium; however, according to the official guides to inorganic nomenclature, the term applies equally to all the elements in Group 16 of the Periodic Table, thus being proper also for oxygen and sulphur. On the other hand, several textbooks imply that oxygen is excluded from the chalcogens. It was internationally accepted that the elements oxygen, sulphur, selenium, and tellurium will be called chalcogens and their compounds chalcogenides.

Metal chalcogenides have played a major role in the field of low-dimensional solids. It was the unravelling of the origin of the resistivity anomalies observed in layered transition MChs that stimulated the interest in low-dimensional inorganic materials. Metal clustering and low-dimensional structures are frequently found among transition MChs, as a consequence of the fact that, in contrast to the ionic 3D-type oxides, these compounds tend to form covalent structures, so that the reduced relative charge on the metal favours metal–metal bonding. In the metal-rich compounds, 3 preferred coordination polyhedra occur for the non-metal (chalcogen)
atoms. The linkage of these polyhedra takes place in such a way that they often end up with an arrangement identical to that known from isolated metal clusters. However, clusters are rarely isolated in the chalcogenide structures. They condense by sharing common vertices, edges, or faces, or more unusually they may be connected via significant chemical bonding between the vertices. They also form columns, in which the central metal atoms interact to give chains running in the same direction. In layered chalcogenides, which have enough $d$-electrons for significant M–M bonding in two dimensions, the dimensionality of M–M interactions is increased to two. Further, in certain cases, the cluster network is best regarded as a 3D metal framework, i.e., as a metal packing arrangement. It may be emphasized in this connection that the occurrence of M–M bonds in MChs has substantiated the use of classification schemes based on structural elements rather than oxidation numbers, rationalizing thus the coincidental integer values of the oxidation state of transition metals and consequently the apparent stoichiometries [19].

The layered transition metal dichalcogenides, although comprising a structurally and chemically well-defined family, display a number of remarkable characteristics, such as broad homogeneity ranges, order–disorder transitions, strong $d$–$p$ covalent mixing, and fast ionic diffusion. They cover actually a wide spectrum of electrical properties ranging from insulators like HfS$_2$, through semiconductors like MoS$_2$ and semi-metals like WTe$_2$ and TcS$_2$, to true metals like NbS$_2$ and VSe$_2$; they exhibit also intriguing magnetic and metal–insulator transitions, unusually high melting points, or superconductivity at high temperatures. In effect, this class of compounds has been most important in pioneering investigations on unusual electronic phenomena such as superconductivity, quantum size effects, and charge density waves (i.e., coupled fluctuations of electronic density and atomic positions along a conducting chain or layer). Moreover, their 2D nature is associated with very rich intercalation chemistry with many potential applications. For an extensive description of the various arrangements and polytypes in the layered MX$_2$ phases, the reader should consult the reviews of Whittingham [20] and Rouxel [21].

The concept of tailoring the properties of materials by intercalating guest species in a host crystal is not only of major academic interest because of the intriguing structural and electric properties of the as-formed intercalation phases, but
also of technological significance in various fields including battery and sensor development. Chalcogenide hosts are usually adequately conductive, so that the extent of intercalation of ionic species is affected and can be controlled by oxidation/reduction of the host lattice, conveniently carried out by electrochemical charge transfer of special interest to intercalation studies are complex non-stoichiometric systems, such as the so-called “misfit” layer chalcogenides that were first synthesized in the 1960s [22]. Typically, the “misfit compounds” present an asymmetry along the c-axis, evidencing an inclination of the unit cell in this direction, due to lattice mismatch in, say, the b-axis; therefore these solids prefer to fold and/or adopt a hollow fiber structure, crystallizing in either platelet form or as hollow whiskers. One of the first studied examples of such a misfit compound has been the kaolinite mineral.

1.1.2 Chalcogenide Glasses

The unique features of chalcogenide glasses, such as quasi-stability, photoconductivity, infrared transparency, non-linear optical properties, and ionic conduction, have led to a wealth of applications, several of which are commercially available or practically utilized [23].

By quasi-stability (or bi-stability) it is meant that these materials undergo an easily reversible thermally driven change from amorphous to crystalline phase, a phenomenon that can be exploited for electrical or optical switching purposes or for encoding binary information. Electrical switching in chalcogenide semiconductors came to prominence in the 1960s, when the amorphous Te_{48}As_{30}Si_{12}Ge_{10} system was found to display sharp, reversible transitions in electrical resistance above a threshold voltage, upon bias [24]. Local switching by optical means is already of great commercial significance in erasable high-density optical memories (CD-RW's) utilizing semiconductor lasers and chalcogenides such as GeSbTe in the form of films with a thickness of ∼15 nm. In these systems, data writing is done by means of laser light heating and data reading by measuring the difference in reflectivity of the laser light from each of the two phases. The reversibility of the transition between the amorphous and crystalline states is remarkable and has been shown to be stable over $10^{12}$ repeated read–write cycles. Alternatively, bringing on the amorphous–crystalline transformation by electrical means forms the basis of phase-change random-access
memory (PC-RAM), which operates much as the flash memory and magnetoresistive RAM (MRAM), as far as the electrodes are concerned, except that the memory bit cell consists of a bi-stable chalcogenide material. The phase change of CeSbTe glasses is accompanied by several orders of magnitude change in conductivity, thus providing a high reading signal-to-noise ratio [25].

On account of their photoconductive properties, chalcogenides glasses are used in applications such as photoreceptors in copying machines and X-ray imaging plates. Regarding purely optical applications, they are utilized for IR optical components such as lenses and windows and also IR-transmitting optical fibers. Chalcogenide fibers incorporating rare-earth ions, such as Er$^{3+}$, have been considered promising for optical amplifier applications. As exhibiting significant ionic conductivities, chalcogenide glasses are utilized for the fabrication of high-sensitivity ionic sensors. In this connection, lithium containing glasses have been investigated as solid-state electrolytes in all-solid-state batteries. Ionic transport in such materials can be useful also for data storage; a functional solid electrolyte consisting of crystalline metallic islands of Ag$_2$Se dispersed in an amorphous semiconducting matrix of Ge$_2$Se$_3$ was described recently [26]. Technologies exploiting phase-change and electrolytic chalcogenide devices are evolving convergently. Both technologies present exciting opportunities that are not restricted to memory applications, but include cognitive computing and reconfigurable logic circuits.

In third group if IV-VI compounds GeS and GeSe can be produced in both crystalline and amorphous forms [27]. In crystalline form they have an orthorhombic structure [28] and an exceptionally easy (001) cleavage planes perpendicular to c-axis [29]. This cleavage is so easy, in fact, that GeS and GeSe are expected to exhibit extreme anisotropy in their lattice vibration, optical and electronic properties [30] and perhaps show some characteristics features of the two dimensional or layer type semiconductors. [31-35].

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 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 staked on top of each other to form three-dimensional crystals. Several layered materials possess’s favourable 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 solids-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 devices 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 valance and conduction band width is reasonable magnitude due to rather strong metal chalcogenide hybridization; as a consequence the charge carrier nobilities are sufficiently large,
† The absorption constants are extraordinarily high, typically in the range $10^5$ cm$^{-1}$.

Therefore, energy conversion devices fabricated form these materials may be considered promising alternatives to more established solar cells. The elemental information about the material Ge, non metal S and chalcogen element (Se) used in present work for the synthesis of single crystals of GeS$_x$Se$_{1-x}$ ($x= 0, 0.25, 0.5, 0.75, 1$) are shown in Table 1.1.
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>VI</td>
<td>IV</td>
<td>IV</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>

† GERMANIUM (Ge)

It is a member of group IV elements. It is lustrous, hard silver metallic element. Ge is greyish – white element that has a metallic luster and posses 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 FCC crystal structure which is shown in below Figure 1.1.

Figure 1.1: The solid state structure of Germanium.

† 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 sulphate
minerals. At room temperature sulphur is a soft bright yellow solid. Crystallography of sulphur is complex. The orthorhombic crystal structure of sulphur is shown in to the Figure 1.2.

![Figure 1.2: The crystal structure of Sulphur.](image)

† **SELENIUM (Se)**

It is a member of group VI elements. It is covalent semiconductor. It has been metalized by application of pressure. At room temperature ‘Se’ is rhombohedra. Selenium exhibits both photovoltaic action, where light is converted directly in to electricity and photoconductive action where the electrical resistance decreases with increased illumination.

These properties make selenium useful in the production of the 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 used extensively in rectifiers. This solid is a p-type semiconductor and is useful in electronic and solid state applications. It has been used for photocopying for reproducing and copying documents, letters etc. ‘Se’ used by the glass industries to decolourised the glass and to make ruby coloured glasses and enamels and as 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 for lesser studied GeS$_x$Se$_{1-x}$ ($x = 0, 0.25, 0.5, 0.75, 1$) single crystals grown by Chemical Vapour Transport (CVT) technique using iodine as a transporting agent and examined the possibility of their use in fabrication of electronic devices. The work on GeS and GeSe has been reported but the intermediate compounds GeS$_{0.25}$Se$_{0.75}$, GeS$_{0.5}$Se$_{0.5}$ and GeS$_{0.75}$Se$_{0.25}$ are not reported yet. So in this chapter the general introduction on the existing information about the germanium monosulphide and germanium monoselenide has been provided as a guide line for the work described in this chapter.

### 1.1.3 Materials Synthesis

Usually, none of the members of the series GeS$_x$Se$_{1-x}$ ($0 < x < 1$) 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 Bridgeman or Bridgeman stockbarger technique.
- Vapour Transport in horizontal furnace.

Various microstructures and configurations are possible for useful solid materials, including bulk single crystals and epitaxial layers, polycrystalline articles or thin films with controlled grain size (including micro- and nanocrystalline phases), amorphous materials, composites, structured materials (e.g., multilayers,
superlattices), hybrids, and combinations thereof. Synthetic methods available for solid-state chemistry include the conventional direct combination high-temperature techniques, synthesis from fluxes and melts, vacuum/high-temperature deposition from gas phase, hydrothermal synthesis, and synthesis from solutions. Emerging approaches include synthesis of alloys from suspensions of pre-formed metal nanoparticles, synthesis of extended frameworks by directed assembly of large molecular building blocks, low-temperature synthesis of nanostructured metal oxides and chalcogenides, salt-inclusion synthesis, and a range of preparation techniques for porous materials [36].

Direct combination of chalcogen elements with most metals at temperatures 400 – 1,000 °C in the absence of air leads to the formation of MCh phases. For example, binary II–VI and IV–VI chalcogenides such as the selenides and tellurides of Cd, Hg, Pb, Sn, and Ge may be effectively prepared by mixing the elements in a quartz ampoule and heating to a temperature little above the melting point of the compound, in a rocking furnace. After reaction (for several hours) the ampoule is either quenched (giving amorphous phases) or slowly cooled to room temperature. Post-annealing of the product for 1–2 weeks under high vacuum without melting is usually required for the completion of the reactions. The nature of the products for a given reaction usually depends on the ratios of reactants, the temperature of the reaction, and other conditions.

Metal chalcogenides, apart from their technological significance in industrial applications, have played an important role in the development of new synthetic concepts and methods in the area of solid-state chemistry. A great example is alkali metal intercalation into TiS$_2$ first reported three decades ago, which highlighted the then-novel synthetic approach called “soft chemistry” (chimie douce). This low-temperature process allows for new compounds to be obtained while retaining the structural framework of the precursor. Related to this concept is the reactive flux method that has proven to be widely applicable to the preparation of multinary MChs, especially low-dimensional polychalcogenides with unprecedented structures [37]. We should underscore finally the developing approaches for low-temperature synthesis of MChs in small length (nanometric) scales, which have proved quite fruitful [38].
For the metallic elements of Group 14, all nine MX compounds (M: Ge, Sn, Pb; X: S, Se, Te) are known. Their crystalline structure can be viewed as distortion of the NaCl type to an extent depending on the components. The distortion amplitude is larger for the lighter compounds (GeS, SnS), which exhibit layer structures similar to that of the isoelectronic black phosphorus, and vanishes for the heavier compounds (GeTe, SnTe). The crystal symmetry of the layered structures involves corrugated planes of 3-coordinated covalently bonded atoms. This instability creates a gap at the Fermi energy and is responsible for the semiconducting nature of these compounds.

Various polymorphs have been reported for SnS with band gap widths in the range 1.0–1.5 eV, depending on the preparation method. The α-SnS (herzenbergite) is the most frequently occurring phase and is a p-type semiconductor with a direct optical transition at 1.3 eV and a high absorption coefficient (> 10⁴ cm⁻¹). The orthorhombic δ-SnS phase possesses a direct gap between 1.05 and 1.09 eV.

The lead compounds PbS, PbSe, PbTe are narrow-gap semiconductors that have been widely investigated for infrared detectors, diode lasers, and thermophotovoltaic energy converters. Their photoconductive effect has been utilized in photoelectric cells, e.g., PbS in photographic exposure meters. Integrated photonic devices have been fabricated by their heteroepitaxial growth on Si or III–V semiconductors. PbSe, with a direct gap lower than 0.3 eV, is widely used for manufacturing IR emitters, photodetectors, photoresistors, but also for laser diodes and thermovoltaic energy converters. Great attention has been paid to the investigation of the quantum size dependent properties of PbSe and therefore for production of relevant nanostructures. PbTe, with a similar band gap, makes a good candidate for photodetectors in the mid- and far-IR bands and mid-IR quantum-well laser diodes by providing high quantum efficiency, low noise level, and ability to tune peak wavelength by adjusting alloy composition (e.g., PbSnTe). PbTe and its derivative alloys are among the most efficient materials for thermoelectric power generation in the intermediate range of temperature (500–900 K) as they have high thermoelectric figure of merit combined with favourable material properties. However, the bulk material is not usually commercially available and the conductivity control is not easy.
Other binary metal compounds in this group include GeS$_2$, GeSe$_2$, SnS$_2$, SnSe$_2$, Sn$_2$S$_3$, and Sn$_3$S$_4$. Germanium disulfide, GeS$_2$, presents a unique structure consisting of a 3D framework of GeS$_4$ tetrahedral. SnS$_2$ has a CdI$_2$-type (C6) structure characterized by adjoining planes of weakly bound S atoms allowing a cleavage in [001] direction. Nominally it behaves as an n-type semiconductor with an indirect energy gap of 2.2 eV. Solid solutions Sn$_x$Se$_{2-x}$ are obtained over the entire composition range from SnS$_2$ to SnSe$_2$. These comprise also CdI$_2$-type layered semiconductors. Sn$_2$S$_3$ (orthorhombic symmetry) is a semiconductor with an optical band gap at ca. 0.95 eV.

Yabumoto [39] produced layers and polycrystalline blocks by sublimation of GeS in a stream of ammonia. Lider and Solovev [40] 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. [41]. Karbanov et al. [42] grew crystals of GeS with a volume up to 2 cm$^3$ by sublimation in vacuum while van der Dries and Lieth [43] grew GeS platelets by iodine transport. Stonchev and Vodenicharov [44] obtained powdered crystals of GeS by direct synthesis.

Starting from the year 1975, majority of the investigators [45, 46] have grown GeS single crystals following the method of vacuum sublimation introduced by Schonherr and Stetter [47]. 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, outguessed at 250 °C. The ampoules were pulled in to 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.

A few investigators [48-51] followed the method of static sublimation used by Bletskan et al. [52] for the growth of GeS in the form of single crystals. Valiukonis et al. [53,54] grew GeS single crystals by the Bridgman method. Lately Elkorashy [55, 56] used vapour transport method introduced by Schaefer [57] to grow single crystals of GeS. 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 [47] and static sublimation technique used by Bletskan et al. [52]. However, unlike GeS, majority of the workers have grown GeSe single crystals by 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. [58], Elkorashy [59-61] and valiukonis et al. [54] prepared GeSe single crystals by the Bridgeman technique. Ishihara et al. [58] and Taniguchi et al. [62] grew undoped GeSe crystals by the vacuum sublimation technique [47]. Zakharchuk et al. [63] & Zuev et al. [48] used static sublimation technique [52] to synthesized single crystals of GeSe. The vapour transport technique without any transporting agents was used for the growth of the GeSe single crystals [64-67]. Chemical vapour transporting technique was used for the growth of GeSe single crystals by Weidemeier et al. [68] and iodine as a transporting agent. Nagard et al. [69] also carried out growth of GeSe single crystals by CVT method using iodine as the transporting agent.

1.2 CRYSTAL STRUCTURE AND STRUCTURAL PROPERTIES

Structures of IV-VI compounds crystallise in several different crystal structures. In the 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 isotopic (B16) compounds GeSe, SnS and SnSe possess an orthorhombic crystal structure with space group Pnmc ($D_{2h}^{16}$). This structure, with a lower symmetry than the previous one, consist of double layers of atoms where each germanium 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) coordination (Figure 1.4).

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 1.6.
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.

![Diagram of GeSe crystal structure]

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

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.

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 $\bar{a}$, $\bar{b}$, $\bar{c}$ perpendicular to each other. The axes $\bar{a}$ and $\bar{b}$ ($a>b$) lie in the cleavage plane, the third one, $\bar{c}$, is perpendicular to this plan. It holds $a \approx b$ and c is much greater than both a and b which can be seen from Table 1.2.

The GeS/GeSe structure is in some respects related to that of NaCl type, in fact its lattice can be thought of as a deformed NaCl type [27]. Each atom forms six
dominant heteropolar bonds, the strongest of which are in three bonds of nearest neighbours in the same double layer.

![Figure 1.5: The primitive cell of GeS like compound.](image1)

Three weaker bonds are to further neighbours, two of which are in the same double layer, and one atom in the next layer [27]. The lattice parameters of GeS and GeSe are summarised in Table 1.2. The orthorhombic subgroup of IV-VI GeS compound consists of structures intermediate between three-dimensional and two-dimensional materials, constructed of two dimensional layers weakly bonded to each

![Figure 1.6: Unit cell of orthorhombic GeSe single crystal.](image2)
other to produce a three dimensional material. The intermediate compounds GeS$_x$Se$_{1-x}$
($x = 0.25, 0.5, 0.75$) are not yet reported.

1.3 OPTICAL PROPERTIES

Looking to the importance of optical band gap $E_g$ in device applications, a thorough investigation of optical parameters has been undertaken by the author in GeS$_x$Se$_{1-x}$ ($x = 0.25, 0.5, 0.75, 1$) single crystals grown using Chemical Vapour Transport (CVT) technique.

Table 1.2: Lattice Parameters of GeS and GeSe 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>[28]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.64</td>
<td>10.74</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.65</td>
<td>10.44</td>
<td>[45], [29], [71], [52], [72], [73], [56], [74], [75], [76], [55], [77], [66], [46], [78]</td>
</tr>
<tr>
<td></td>
<td>4.29 ± 0.01</td>
<td>3.64 ± 0.01</td>
<td>10.42 ± 0.03</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.64</td>
<td>10.47</td>
<td>[79], [49], [80], [81]</td>
</tr>
<tr>
<td></td>
<td>4.30</td>
<td>3.65</td>
<td>10.43</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>4.297</td>
<td>3.641</td>
<td>10.470</td>
<td>[83], [84]</td>
</tr>
<tr>
<td></td>
<td>4.29</td>
<td>3.64</td>
<td>10.42</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td>4.29</td>
<td>3.65</td>
<td>10.42</td>
<td>[86]</td>
</tr>
<tr>
<td>GeSe</td>
<td>4.38</td>
<td>3.82</td>
<td>10.79</td>
<td>[28], [65], [87], [67], [88], [70], [58], [81], [89], [59], [61], [60]</td>
</tr>
<tr>
<td></td>
<td>4.40 ± 0.008</td>
<td>3.85 ± 0.008</td>
<td>10.82 ± 0.01</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>4.375 ± 0.005</td>
<td>3.825 ± 0.005</td>
<td>10.80 ± 0.02</td>
<td>[64], [66]</td>
</tr>
<tr>
<td></td>
<td>4.390</td>
<td>3.827</td>
<td>10.824</td>
<td>[64], [66]</td>
</tr>
<tr>
<td></td>
<td>4.38</td>
<td>3.80</td>
<td>10.77</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>4.387 ± 0.008</td>
<td>3.387 ± 0.008</td>
<td>10.83 ± 0.015</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>4.39</td>
<td>3.83</td>
<td>10.8</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>4.39 ± 0.02</td>
<td>3.826 ± 0.007</td>
<td>10.827 ± 0.02</td>
<td>[69]</td>
</tr>
</tbody>
</table>

According to literature survey the band structure calculation for germanium and tin chalcogenides carried out [87] by equivalent orbital linear combination 

...
Chapter - I: Existing Information about Germanium Chalcogenides

The temperature dependence of the absorption edge of GeS within the range from 4.2 to 300 K has been studied by Wiley et al. [29, 75, 73] and Lider and Solovev [40]. Reflectivity of GeS has been studied by Wiley et al. [71], they used polarised light at room temperature (RT) and by Sobolev and Donetskikh [93] they used unpolarised light at 77 and 300 K. The Raman spectra of GeS at room temperature and also 20 to 300 K temperature range by Gregora and Stetter [45] and Wiley et al. [94]. Bletsken et al. [95] studied electroreflectance (ER) spectra of GeS at RT in the range from 1.4 to 2.2 eV. The reflective index of crystalline and amorphous GeS has been studied by Gregora et al. [84]. Kannewurf and Cashman [96] studied optical properties of GeSe near absorption edge in unpolarised light. Lukes [97] described optical properties of GeSe for cleaved (\(\vec{a} \parallel \vec{b}\) ) plane studied in polarised light in the range from 0.5 to 1.5 eV at room temperature. Vlachos et al. [65, 98] studied the absorption near the absorption edge (1.2 to 1.6 eV) in the temperature interval from 100 to 300 K. Zacharchuk et al. [99] reported the excitonic character of the absorption near the absorption edge studied at temperature from 4.2 to 300 K. Chandrasekhar and Zwick [87] have studied both infrared reflectivity in the range from 20 to 4000 cm\(^{-1}\) and Raman scattering from GeSe at room temperature. Infrared reflectivity in GeSe has also been reported by Siapkas et al. [100].

Tyagi et al. [51] 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 \(\vec{E} \parallel \vec{a}\) and \(\vec{E} \parallel \vec{b}\) in the range from 1.2 to 4.8 eV. According to the latest reports, Gashimzade et al. [81] carried out the band structure calculations for GeS and GeSe along with SnS and SnSe by equivalent-orbital linear combination of the atomic orbital method.

The other optical parameters of importance for device applications are the index of refraction ‘n’ and dielectric constant. Elkorashy [78, 61] 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 of cleavage. The real and
imaginary part of the complex dielectric constant \( (\varepsilon_r, \varepsilon_i) \) were calculated by him from the values of \( n \) and \( k \).

### 1.4 MAGNETIC PROPERTIES

From electrical and magnetic measurements on GeSe; Kyriakos et al. [101, 102] reported that this compound shows an antiferromagnetic behaviour with negative magnetoresistance effect. From their measurements, they determined a Neel temperature at 318K and observed that this above this temperature GeSe showed a ‘metallic’ behaviour with zero field resistivity. Kyriakos et al. [46] showed that similar to GeSe, GeS is also antiferromagnetic with Neel temperature around 455K. They [46] investigated the galvanomagnetic effects of GeS in the temperature range 293 – 423 K. Their results showed the existence of negative magnetoresistance and a kind of optical oscillation of both the magnetoresistance and the Hall Effect depending on both the temperature and the magnetic field. The negative magnetoresistance observed in GeS and GeSe was attributed to arise from localised moments located at impurity atoms, such as transition- metal atoms, which from antiferromagnetic clusters. These clusters are formed either at planner defects are at twin boundaries or between the double layers of germanium chalcogenides characteristic structure. Defects of this kind were verified in both GeS and GeSe by Karakostas [66]. The rapid oscillation of the magnetoresistance and Hall Effect was also explained to arise from the resonant defect states in the valance bands arising from the same defects which gave rise to the negative magnetoresistance.

### 1.5 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 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 [43, 103], or polycrystalline samples [104, 105]. The main conclusions which can be drawn from these measurements [43, 103-106] are:
GeS is always found to be p-type;

The room temperature resistivity is usually of the order of $10^3$ to $10^5\ \Omega\ \text{Cm}$ with considerable sample to sample variation;

Conduction is extrinsic at all temperature below $\approx 400^\circ\text{C}$;

A great variety of impurity and trapping levels are found in the band gap [107, 108]; and

It is exceptionally difficult to obtain good quality ohmic contacts needed for reliable electrical measurements.

Wiley et al. [109] 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 to 400 meV.

Bletskan and Indus [110] 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. [46] 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 valance band.

GeSe possesses a similar electronic structure as GeS in the sense that both of are p-type semiconductors. The study of the electrical properties of GeSe was first carried out by Asanabe and Okazaki [111]. From the temperature dependence of the electrical resistivity and the Hall coefficient they elucidated the existence of a shallow acceptor level and donor level close to the valance band. The donor level due to excess germanium atom was located about 0.2 eV above the valance band. This value was simply obtained from the temperature dependence of the Hall coefficient. The electrical parameters reported in the past has represented in the Table 1.3 and 1.4.

Ishihara and Nakada [88] measured the Hall coefficient and resistivity of GeSe between 320 and 1.5K. They estimated the ionisation energy of the acceptor from the temperature dependence of the Hall coefficient. The ionisation energy changed from 3.9 to 5.3meV according to the heat treatment given to the samples. There appeared
two activation energies corresponding to impurity conduction, the first one was at about 1.5 meV and the other one was at ~ 0.5 meV.

Table 1.3: The Electrical Parameters of GeS single crystals.

<table>
<thead>
<tr>
<th>Carrier Type</th>
<th>Carrier Concentration ‘P’ (cm⁻³)</th>
<th>Room Temp. Resistivity ‘ρ’ (Ω cm)</th>
<th>Hall coefficient ‘RH’ (cm³/c)</th>
<th>Mobility ‘μ’ (cm²/Vs)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>------</td>
<td>10⁸ - 10⁹</td>
<td>------</td>
<td>------</td>
<td>[112]</td>
</tr>
<tr>
<td>p</td>
<td>------</td>
<td>10³ - 10⁵</td>
<td>------</td>
<td>------</td>
<td>[107]</td>
</tr>
<tr>
<td>p</td>
<td>------</td>
<td>10⁶</td>
<td>------</td>
<td>------</td>
<td>[113]</td>
</tr>
<tr>
<td>p</td>
<td>------</td>
<td>10⁶ – 10⁹</td>
<td>------</td>
<td>------</td>
<td>[30]</td>
</tr>
<tr>
<td>p</td>
<td>------</td>
<td>7×10²</td>
<td>2×10⁴</td>
<td>30</td>
<td>[46]</td>
</tr>
<tr>
<td>p</td>
<td>3.4 ± 0.5×10¹⁸</td>
<td>5×10³</td>
<td>------</td>
<td>------</td>
<td>[114]</td>
</tr>
<tr>
<td>p</td>
<td>1.49 ×10⁹</td>
<td>3.82 × 10⁶</td>
<td>4.20×10⁹</td>
<td>182</td>
<td>[97]</td>
</tr>
</tbody>
</table>

The Value of 1.5 meV could be associated with the thermal excitation of holes from the Fermi level to a mobility edge in the upper band. Ishida et al. [67] carried out the resistivity ρ and the Hall coefficient RH measurements parallel to the layers of GeSe (p-type) single crystals between 77 K and 1.4 k in the carrier concentrations ranging from 7×10⁶ to 5×10¹⁷ cm⁻³. They found a metal- non-metal transition at carrier concentration of p ~ 4 × 10¹⁷ cm⁻³. The conductivity at this transition was ~ 20 mho cm⁻¹, which compared favourably well with three dimensional minimum metallic conductivity. Ishihara et al. [58] investigated anisotropy of electrical resistivity and Hall coefficient together with TEP in the temperature range of 78 to 300K in vapour grown p-type Ge₁ₓSe 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 range in GeSₓSe₁₋ₓ (x = 0, 0.25, 0.5, 0.75, 1) single crystals grown using vapour transport technique.
Table 1.4: The Electrical Parameters for GeSe single crystals

<table>
<thead>
<tr>
<th>Carrier Type</th>
<th>Carrier Concentration 'p' (cm(^{-3}))</th>
<th>Resistivity 'p' (Ωcm)</th>
<th>Hall Coefficient 'R_H' (cm(^3)C(^{-1}))</th>
<th>Mobility 'μ' (cm(^2)/V.s)</th>
<th>TEP (μV/K)</th>
<th>Effective mass</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>6.7 ×10(^{16})</td>
<td>1.2</td>
<td>1.6 ×10(^{4})</td>
<td>5.1 ×10(^{4})</td>
<td>5.3 × 10(^{1})</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>1.9 ×10(^{17})</td>
<td>6.1 ×10(^{3})</td>
<td>1.1 ×10(^{4})</td>
<td>1.3 ×10</td>
<td>70</td>
<td>0.20 m</td>
<td>[67]</td>
</tr>
<tr>
<td>p</td>
<td>2.7 ×10(^{17})</td>
<td>2.7 ×10(^{3})</td>
<td>7.9 ×10(^{2})</td>
<td>9.8 ×10(^{4})</td>
<td>429</td>
<td>0.004 m</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>2.8 ×10(^{17})</td>
<td>1.8 ×10(^{4})</td>
<td>5.3 ×10(^{3})</td>
<td>5.8 ×10(^{4})</td>
<td>50</td>
<td>6.2 m</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>7.2 ×10(^{16})</td>
<td>1.0 ×10(^{4})</td>
<td>5.3 × 10(^{1})</td>
<td>5.9 × 10(^{3})</td>
<td>467.8</td>
<td></td>
<td>[88]</td>
</tr>
<tr>
<td>p</td>
<td>1.4 ×10(^{17})</td>
<td>1.1 ×10(^{4})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>7.5 ×10(^{16})</td>
<td>5.0 ×10(^{1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>2.46 ×10(^{17})</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>3 ×10(^{18})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>4 ×10(^{15})</td>
<td>50-60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>6.2 ×10(^{14})</td>
<td>78.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>1.1 ± 0.6 ×10(^{6})</td>
<td>3 ×10(^{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref. [67], [88], [58], [72], [30], [69], [115], [114], [72], [30]
1.6 IMPORTANCE OF GeS AND GeSe 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 infrared detectors and emitters, narrow band gap compound crystals have potential applications in magneto resistive Hall effect and thermoelectric devices [116,117].

- 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 [48, 69, 118]. 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 their film particularly in the photoelectric properties [104, 119-122] and it has been suggested that the material could be used successfully as a photosensitive film in TV camera tubes [119,120]. GeS is also of great interest because of its possible use as a hologram recording material [123, 124].

- GeS has been of interest because of its outstanding properties as substrate for the layer – by – layer growth of epitaxial, single crystalline C$_{60}$ thin films [125]. A high friction coefficient of $\mu \approx 1.5$ was found for GeS [126]. 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 crystal as electrodes in these light emitting diode has been considered by Peisert et al. [127]. Synthesis of filamentary crystals of GeS doped with indium has found applications in various microinstruments e.g. tensometers, thermoresistors, accelerometers, photoresistance, Photocathodes etc [107]. Also GeS in the form of thin film has found its use as a basis for the fabrication of high efficiency transducers [128]. Moreover, Ag/Ge$_x$S$_{1-x}$ system works as a high resolution lithographic resist for UV applications, insensitive to visible light, this system has the advantage of being non-toxic and thermally stable [129].

- GeS has been used in the preparation of multicomponent chalcogenides useful in the development of cryogenic microelectronics [130]. 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 [131].

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, sensors and laser materials [132].

Among these metal selenides germanium monoselenide has particularly energy band gap close to the optimum value [69] 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 [92,133]. These films are objects of increasing importance in view of the possibilities for their application in solar cells, electronic switching and memory devices [134]. Additionally the Se containing films are chemically stable and water resistant [135], therefore, they can also be used for passivation.
REFERENCES


Chapter 1: Existing Information about Germanium Chalcogenides


Chapter 1: Existing Information about Germanium Chalcogenides


Chapter -1: Existing Information about Germanium Chalcogenides


