Chapter 1

Introduction and Existing Information about Transition Metal Chalcogenides

The use of crystals dates back as far as there are records of history itself. They were used in Biblical times, throughout Ancient Egypt, Rome and date to all ancient cultures. Crystal in fact came from the period in history when the earth was forming. The heating and cooling of the planet formed the magnificent crystalline objects we have today. Over the years, uses of crystals have not really changed and they are still being used in the same way as the ancients.
1.1 INTRODUCTION

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering Physics, Chemistry, Material science, Chemical engineering, Metallurgy, Crystallography, Mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals. The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

Transition metal chalcogenides: oxides, sulfides, selenides and tellurides are important technological materials. The potential is increasingly being recognized, with recent advanced applications of transition metal chalcogenides including: solar energy conversion, solar control coating, microelectronic devices, catalysts, sensors, optical fiber and laser sources [1-4]. The family of the TMDCs forming $\text{TX}_2$ is composed of the transition metals (groups 3-12 of the periodic table) $T$ like titanium or zirconium and chalcogenides (group 16) $X$ like selenium, sulphur or tellurium. The most well-known TMDC is MoS$_2$ which has found an application as solid lubricant
and also promising for photovoltaic is e.g. zirconium disulfide (ZrS$_2$) which is a subject of active research in HU group EES [1]. The TMDCs typically grow in layered crystals similar to graphite. Their electronic properties range from metals like VSe$_2$ to insulators like HfS$_2$ [2].

It is common that the three heaviest elements of the sulfur 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 sulfur. On the other hand, several textbooks imply that oxygen is excluded from the chalcogens, this probably being the consequence of having discussed the chemistry of oxygen [5].

The term “chalcogen” was proposed around 1930 by Werner Fischer [6], when he worked in the group of Wilhelm Biltz at the University of Hannover, to denote the elements of group 16. It was quickly accepted among German chemists, and it was Heinrich Remy who recommended its official use in 1938 while being a member of the Committee of the International Union of Chemistry (later IUPAC) for the Reform of the Nomenclature of Inorganic Chemistry. Following this, it was internationally accepted that the elements oxygen, sulfur, selenium, and tellurium will be called chalcogens and their compounds chalcogenides. The term derives from the Greek terms χαλκός meaning copper and γεννάω meaning giving birth, and it was meant in the sense of “ore-forming element” (cf. “hydrogen” similarly originating from υδωρ meaning water; also “oxygen”, etc.).

The chemistry of soluble metal chalcogenide complexes, either containing chalcogen–chalcogen bonds or only chalcogen–metal, has been studied extensively primarily for sulfur, and after the mid-1970s for selenium and tellurium as well. Metal–sulfur systems have a long chemical history in all aspects, but from the 1960s the interest in the related complexes was renewed, owing to their significance in bioinorganic chemistry and to hydrodesulfurization and other catalytic processes.
The early progress in the identification of the many possible coordination modes available for sulfide ligands has been summarized neatly by Vahrenkamp [7]. A large number of synthetic molecular transition metal complexes with either terminal or bridging sulfide ligands have been reported and their catalytic activity has been reviewed [8-9]. The coordination modes and structural types of soluble metal selenides and tellurides, synthesized in solution or in the solid state, have been sorted and described in the seminal review by Ansari and Ibers [10]. An excellent introduction to the synthetic and structural coordination chemistry of inorganic selenide and telluride ligands, covering all the facts up to 1993, can be found in Roof and Kolis [11], with the emphasis on compounds of mostly molecular nature.

Metal chalcogenides have played a major role in the field of low-dimensional solids. It was the unraveling of the origin of the resistivity anomalies observed in layered transition metal chalcogenides that stimulated the interest in low-dimensional inorganic materials. Metal clustering and low-dimensional structures are frequently found among transition metal chalcogenides, 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 favors metal–metal bonding. In the metal-rich compounds (actually those containing M–M bonds) 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. 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 metal chalcogenide 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 [12].

The complexes in which metal clusters are coordinated by chalcogenide or polychalcogenide ligands occupy a special position among the so-called inorganic or high-valence clusters, the most characteristic being those of 4d- and 5d-metals of groups V-VII. Currently, the chalcogenide cluster chemistry of the main group and d-transition metals is firmly established. The area has been the subject of several reviews [13-14]. A recent survey of new and older results for the early transition metal-chalcogenides has been given by Fedorov et al. [15]. Considerably less developed is the cluster chemistry of the lanthanoids. Ionic lanthanides form comparatively unstable compounds with S, Se, and Te, so that as-composed clusters are rare [16].

From TMDC titanium dieseline (TiSe$_2$), two compounds TiS$_x$Se$_{2-x}$ and TiTe$_x$Se$_{2-x}$ are derived, the later were chosen as TiS$_2$ and TiTe$_2$ which are also members of the TMDC family having very similar crystal and electronic structures but a bigger band gap for TiS and a band overlap for TiTe$_2$. TiSe$_2$ is a very interesting subject studying CDWs, as it is a semiconductor with a very small band gap [17] allowing to investigate the necessity of a positive or negative band gap for the phase transition by tuning the band gap size with band gap engineering. Additionally, its crystal structure makes physisorption experiments possible, since it does not have dangling bonds in the c direction - (001) surface which could react with the adsorbed molecules. The electronic structures are very similar as well; the relative position of the valence and conduction band is the main relevant difference here. While TiTe$_2$ is a semimetal with a band overlap also referenced as negative gap, TiSe$_2$ is a small-gap semiconductor and TiS$_2$ a semiconductor with a bigger gap. Similar to TiSe$_2$, there exists conflicting results about the nature of the band gap for TiS$_2$. While theoretical calculations are ranging from semi-metal [18] to a gap of 2 eV [19], experimental results also indicate semi-metallic [20] or semiconducting behavior. In the work of Thürm [21], TiS$_2$ is found to be a semiconductor, yet he did not determine the exact size of the band gap. So the experimental value of 0.3 eV from Chen et al. [22] will be used though this is considered as a lower bound. Some other TMDCs also
show CDW phase transitions as their low dimensionality favors CDWs [23]. However, neither TiS\textsubscript{2} nor TiTe\textsubscript{2} which are important for the understanding of the ternary compounds, show a CDW phase. In some high temperature superconductors this phenomenon appears as well, sometimes in combination with spin density waves. This close relation to superconductivity was even more emphasized by the discovery of a competing superconducting state in TiSe\textsubscript{2} induced by pressure [24] or Cu intercalation [25].

Particularly, the layered transition metal dichalcogenides (TMDCs) have received much attention of researchers which is going on accelerated because of vast variety of their electronic and optical properties [26-36]. During past few decades these materials have been widely studied from both theoretical as well as application point of view. Following the energy crisis in the early 1970s, considerable efforts were made in the investigation of new semiconductors for interfacial solar energy conversion devices [31-35]. The semiconducting layered TMDCs form a major class of materials that have been investigated for energy conversion in Photo-electrochemical (PEC) cell and solid state (p-n and schottky) solar cell. Many compounds of this class are also investigated almost exclusively as dry and solid lubricants in high vacuum devices, nuclear reactors, rotating anode X-ray etc. The electronic configurations of d-bands are brought about by crystal structure (coordination) changes, non-stoichiometry and valency changes and large variations or transitions in the electronic properties are observed [30].

1.2 OCCURRENCE AND SYNTHESIS

Since none of the ZrSTe, TiSTe and TiSeTe (amorphous or single crystal) is known to occur naturally, all of them are required to be synthesized in the laboratory for characterization. For the growth of compound single crystals, various growth techniques are available at present. These include both, growth from the melt as well as growth from the vapor. The well-known method over the years for the growth of transition metal chalcogenides includes Bridgeman and vapor transport techniques.

We have successfully employed the chemical vapor transport technique for the growth of the single crystals of ZrSTe, TiSTe, and TiSeTe. Table 1.1 summarizes the
information and physical properties of constituent elements of ZrSTe, TiSTe, and TiSeTe compounds.

Table 1.1 The elemental information.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Zirconium (Zr)</th>
<th>Titanium (Ti)</th>
<th>Sulphur (S)</th>
<th>Tellurium (Te)</th>
<th>Selenium (Se)</th>
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<tr>
<td>Atomic Number</td>
<td>40</td>
<td>22</td>
<td>16</td>
<td>52</td>
<td>34</td>
</tr>
<tr>
<td>Atomic weight (g·mol⁻¹)</td>
<td>91.22</td>
<td>47.86</td>
<td>32.06</td>
<td>127.6</td>
<td>78.96</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Kr] 4d² 5s²</td>
<td>[Ar] 3d¹ 4s²</td>
<td>[Ne] 3s² 3p⁴</td>
<td>[Kr] 4d⁰ 5s² 5p⁴</td>
<td>[Ar] 4s² 3d⁰ 4p⁴</td>
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<td>Electrons per shell</td>
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<td>2, 8, 6</td>
<td>2,8,18,18,6</td>
<td>2, 8, 18, 6</td>
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<tr>
<td>Phase</td>
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<td>Solid</td>
<td>solid</td>
<td>solid</td>
<td>solid</td>
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<tr>
<td>Density (near room temperature) (g·cm⁻³)</td>
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<td>4.54</td>
<td>2.07</td>
<td>6.24</td>
<td>4.39</td>
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<td>Melting point (K)</td>
<td>2125</td>
<td>1933</td>
<td>388.36</td>
<td>722.8</td>
<td>494</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>4650</td>
<td>3560</td>
<td>717.8</td>
<td>1261</td>
<td>958</td>
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<tr>
<td>Heat of fusion (J·mol⁻¹) × 10³</td>
<td>20.9</td>
<td>15.45</td>
<td>1.727</td>
<td>17.49</td>
<td>6.69</td>
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<tr>
<td>Heat of vaporization (J·mol⁻¹) × 10³</td>
<td>581.6</td>
<td>429</td>
<td>45</td>
<td>50.6</td>
<td>95.48</td>
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<td>Oxidation states</td>
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<td>6, 4, 2, 1, -2 (strongly acidic oxide)</td>
<td>4, 2, -2 (strongly acidic oxide)</td>
<td></td>
</tr>
<tr>
<td>Electronegativity (Pauling scale)</td>
<td>1.33</td>
<td>1.54</td>
<td>2.58</td>
<td>2.1</td>
<td>2.55</td>
</tr>
<tr>
<td>Ionization energies (J·mol⁻¹) × 10³</td>
<td>1ˢᵗ : 6.84</td>
<td>1ˢᵗ : 6.82</td>
<td>1ˢᵗ : 999.6</td>
<td>1ˢᵗ : 9.009</td>
<td>1ˢᵗ : 941.0</td>
</tr>
<tr>
<td></td>
<td>3ʳᵈ : 22.99</td>
<td>3ʳᵈ : 7.491</td>
<td>3ʳᵈ : 3357</td>
<td>3ʳᵈ : 27.96</td>
<td>3ʳᵈ : 2973.7</td>
</tr>
</tbody>
</table>
Atomic radius
(cm) × 10⁻⁸
2.16 2 100 1.42 115
Covalent radius
(cm) × 10⁻⁸
1.45 1.32 102 1.36 116
van der Waals
radius
(cm) × 10⁻¹⁰
N/A N/A 180 206 190
Electrical
resistivity
(293 K) (Ω·cm)
43.3×10⁻⁶ 40×10⁻⁶ >10²³×10⁻⁶ 10⁸×10⁻⁶ 10⁶
Thermal
conductivity
(300 K)
(W·cm⁻¹·K⁻¹) × 10⁻³
227 219 205 235 519

1.3 CRYSTAL STRUCTURE

Binary metal chalcogenides of great variety occur, since with a given chalcogen many metals and metalloids form several compounds and sometimes long series of compounds. Although complex structures are not unusual, for a large part the binary compounds belong or relate to the very basic structural types and may be approached easily in a descriptive manner. “Three-dimensional” structures, commonly the cubic NaCl (rock salt; RS) and zinc blende (ZB), or the hexagonal NiAs and wurtzite (W) types, as well as “2D” layer-lattice varieties related to the CdI₂ type, are the major structure types observed.

Most transition elements react with chalcogen atoms to give dichalcogenides MX₂ with a precise 1:2 stoichiometry, crystallizing in either 2D or 3D structures, as originating from the competition between cationic d levels and anionic sp levels. The “2D” layered structures, which can be formulated as M⁴⁺(X⁻)₂, consist of sandwiched sheets of the X–M–X form, separated by a “van der Waals” gap between the X layers of adjacent sheets. Inside the sheets, the coordination of the metal ions is
sixfold, either octahedral (as in the 1T polytype, which is more commonly denoted as the CdI$_2$ structure) or a body-centered trigonal prism (2H polytype).

Two-thirds of the about 60 MX$_2$ compounds assume layered structures, found in particular for all the early transition metals of groups IV-VII (with the exception of manganese). The non-layered MX$_2$ compounds assume a quite different structure motif and occur exclusively in group VIII and beyond. Most of these materials are composed of infinite “3D” networks of metal atoms and discrete X$_2$ units with an X-X distance almost equal to that expected for an X-X single bond.

The layered transition metal dichalcogenides, although comprising of 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 refer the reviews of Whittingham [37] and Rouxel [38]. Noteworthy also is the extensive compilation of early data on layered MX$_2$ given by Wilson and Yoffe [39], who worked out a group-by-group correlation of transmission spectra of the compounds to available electrical and structural data and produced band models in accord with a molecular orbital approach.

Solid solutions are very common among structurally related compounds. Just as metallic elements of similar structure and atomic properties form alloys, certain chemical compounds can be combined to produce derivative solid solutions, which
may permit realization of properties not found in either of the precursors. The combinations of binary compounds with common “anion” or common “cation” element, such as the “isovalent alloys” of IV–VI, III–V, II–VI, or I–VII members, are of considerable scientific and technological interest as their solid-state properties (e.g., electric and optical such as type of conductivity, current carrier density, band gap) modulate regularly over a wide range through variations in composition. A general descriptive scheme for such alloys is as follows [40].

Structurally group V transition metal dichalcogenides can be regarded as strongly bonded X-M-X layers or sandwiches which are loosely coupled to one another by weak van der Waals type force. Within a single X-M-X sandwich, the M and X atoms form two dimensional hexagonal arrays. Depending on the relative alignment of the two X atom sheets within a single X-M-X sandwich two distinct two-dimensional structures can be obtained. In one, the metal atoms are octahedrally coordinated by six neighboring X atoms whereas in the other, the coordination of the metal atoms is trigonal prismatic variations in the stacking sequence and the registry of successive X-M-X symmetries respectively [41]. Low dimensional crystals are of great interest because of their particular properties related to the crystalline anisotropy [42].

The 2D layered structures of Group IV-VI transition metal dichalcogenides MX₂ (M = Ti, Zr, Hf, Nb, Ta, Mo, W) as well as of the ternary alkali metal/3d-metal systems AMX₂ (A = alkali metal; M = Ti, V, Cr, Mn, Fe, Co, Ni) are capable of intercalating various guest species. The most well investigated is the intercalation of alkali metals (A) to dichalcogenide hosts, resulting in the formation of AₓMX₂ phases (0 < x ≤ 1; M = Ti, Zr, Hf, V, Nb, Ta, Mo,W; X = mainly S, Se), which, in effect, have served for fundamental studies of the intercalation-induced structural changes and charge transfer. Transition metal derivatives of layered sulfides and selenides are also known, forming intercalates of the type MₓMX₂ (M’ = 3d transition metal, M = Nb, Ta; X = S, Se). Interestingly, ditellurides form metal-rich layer compounds rather than intercalation phases, such as MMTeX (M’ = Fe, Co, Ni; M = Nb, Ta), stabilized by strong bonding interactions between early and late transition metals. Intercalation processes regard also 3D lattices, i.e., the Chevrel phases MₓMo₆X₈, Nb₃X₄ (X = S,
Se), A₅Ti₃S₄, Ti₅V₃S₄ (intercalation into tunnels), as well as 1D structures, i.e., MX₃ (M = Ti, Zr, Hf; X = S, Se), AFeS₂ (A = Na to Cs), AMo₃X₃ (A = alkali metal; X = S, Se) [43-45].

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 [46]. 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.

The early transition metals (Groups IV and V) form a wide variety of binary chalcogenides, which frequently differ in both stoichiometry and structure from the respective oxides. All the Group 4 dichalcogenides, MX₂, occur in layered CdI₂-type structures (1T stacking polytype). TiS₂, TiSe₂, TiTe₂, ZrTe₂, and HfTe₂ compounds may be roughly classified as metallic materials due to an overlap of the chalcogenide s and p states with the metal d states, whereas ZrS₂, ZrSe₂, HfS₂, and HfSe₂ are more ionic in nature [47].

Titanium monosulfide, TiS, assumes two forms, both of which are of the NiAs type. In Ti₅S₄, the packing of sulfur is of the ABAC type, with alternate layers of metal sites being fully occupied but the intermediate sites half filled. A series of intermediate phases Ti₃₃⁺ₓS₄ (0.2 < x < 1) also occurs. The trisulfide TiS₃ is best represented as TiS²⁻(S₂)²⁻. The trichalcogenides of Group IVA elements are typified by ZrSe₃, which exhibits a monoclinic structure consisting of chains of trigonal prismatic [ZrSe₆] units sharing opposite faces and has semiconducting properties.

Transition metal trichalcogenides MX₃ (M = Zr, Ti, Hf, Nb, Ta and X = S, Se & Te) that crystallize in the shape of parallel fiber constitute a diversified family ranging from superconductors to wide band gap semiconductor [48]. Different physical properties originate from small variation of the X-X and M-M legend lengths
resulting in structures possessing three different types of trigonal prismatic chains. Their basic structural units are formed as MX₆ trigonal prisms that share trigonal faces and consisting of chains parallel to the monoclinic b axis. Each chain shifted with respect to two neighboring ones by half the lattice parameter along the b direction. The chains are linked by metal-chalcogen bonds and form layers bound by much weaker van der Waals forces. Their structure makes them useful for battery cathode intercalation and photochemical cell applications [49].

The MX₃ layered compounds (ZrSe₃ and ZrS₃) crystallize monoclinically (space group P2₁/m) in fibrous strands or filamentary ribbon-shaped platelets. A linear chain of metal atoms is parallel to the b axis (the growth axis), and six chalcogen (X) atoms surround each metal atom forming distorted trigonal prisms as shown in figure 1.1. The layer-type lattice has the metal ions in the center of the distorted trigonal prisms which share trigonal faces thus forming isolated columns shown in figure 1.1.

![Three dimensional crystal structure of ZrSe₃](image)

**Figure 1.1** Three dimensional crystal structure of ZrSe₃

In the titanium–selenium system, various stoichiometries such as Ti₂Se, Ti₃Se, TiSe₀.₉₅, TiSe₁.₀₅, Ti₀.₇Se, Ti₃Se₄, Ti₅Se₈, TiSe₂ and TiSe₃ have been identified. A variety of phases are known also for the titanium–tellurium system, including the compounds Ti₅Te₄, Ti₃Te₄, Ti₂Te₃, Ti₃Te₆ and TiTe₂ [50].
The elements Zr and Hf are generally more similar in their chemistry than any other pair of congeneric elements as having nearly identical atomic or ionic radii, electronegativities, and elemental structures (actually, the similarities of Nb and Ta are nearly as close); however, their metal-rich chemistry is often surprising in its structural and physical aspects with fairly sharp distinctions emerging between the two elements [51].

1.4 PROPERTIES OF SOME TRANSITION METAL CHALCOGENIDES

Guest-host interactions of low-dimensional transition metal chalcogenides have been extensively studied because of such compounds exhibit unusual physical properties, interesting structural chemistry, and many applications [52-56].

Recently, much attention has been focused on the chemistry of ternary transition metal tellurides and, in particular, investigation of ternary layered group V M’-Te (M’=3d transition metals) systems have lately produced many interesting materials. [57]. A large number of layered transition metal chalcogenide compounds exhibiting a very large spectrum of electrical and optical properties are known today.

1.4.1 Electrical properties

Most of the technological, electronic and optoelectronic applications utilize semiconductor material in crystalline forms [58]. Transition metal dichalcogenides (TMDCs) form a class of compounds known for their layered structure, where the term “layered” refers to the existence of parallel planes where bonds are much weaker than inside the region that the limit. Such feature makes these materials highly anisotropic and in extreme cases two dimensional.

A large variety of properties arise from this peculiarity, rendering TMDCs interesting not only from the theoretical point of view (e.g. charge density waves [59-62], superconductivity [63-65]), but also for various practical applications. Due to their low shear resistance TMDCs are used as solid state lubricants [66-71]. Titanium Sulfides are nonstoichiometric compounds that have commercial applications in dry lubrication, semiconductors, and energy batteries [72].
Solid material that reveals some physical properties nearly invariant over a substantial temperature range can be very useful for the applications [73]. Electrical resistivity is a physical property of enormous importance, both for the understanding of the solids and their actual applications. The electrical resistivity of solids, apart from the possibility of superconductivity, can vary in the order of $10^{32}$ which may be the widest of any common physical properties of solids [74]. Moreover, the temperature dependence of the electrical resistivity behaves quite irregular, since various different mechanisms, including the phonon scattering, impurity and defect scattering, mutual scattering of electrons, and so forth, are involved in the electrical transport in different temperature ranges [74-75].

1.4.2 Optical properties

Optical properties of any semiconducting material play an important role for their device applications. The optical band gap $E_g$ of materials is one of the crucial optical parameters for this purpose. It has been found [76] that for maximum solar energy conversion, $E_g$ of any single crystal solar cells should be within 1.0 eV to 1.4 eV. The semiconducting materials having band gap value near to this optimum value are therefore considered to be a most suitable for photovoltaic applications. So, the study of optical band gap determination is desirable for all the semiconducting materials. The optical properties of the IVA trichalcogenides [77-79] are in contrast to the VB compounds. Preliminary optical absorption measurements on ZrS$_3$ were taken by Schairer and Schafer [80].

The class of compounds known as transition metal dichalcogenides (TMDCs) consists of about 60 compounds of the general formula MX$_2$, where X is a chalcogen (S, Se, Te), and M is Re, Pt, Sn, Pb, or a transition metal of the groups IVb, Vb, VIb. Some comprehensive reviews describe their structural, electronic, and optical properties [81-83]. The optical properties of TMDCs were first explained in terms of their electronic bands by Wilson and Joffe [81] in a model, which has been improved by theoretical calculations and experimental data, but so far has not been contradicted [83].
1.5 USES

Information about the physical properties of compound semiconductor would enable us to use them in various applications like detector, photoelectrode in solar cell etc. The main physical properties may include electrical properties, magnetic properties, density, structural properties etc. TMTCs have attracted many research workers on account of the interesting properties of the compounds of this family.

Layered transition metal trichalcogenides $\text{MX}_3$ ($M =$ metal; $X =$ chalcogen) may be considered as an ideal model system for the investigation of fundamental aspects of semiconductor metal interaction. The $\text{ZrS}_3$ seems to be a suitable electrode for solar energy conversion due to its ability to obtain relatively large photocurrents in aqueous electrode [84]. Transition metal trichalcogenides have been used as cathode in the lithium electrochemical cell [85]. n type $\text{ZrS}_3$ can be used with p type $\text{WSe}_2$ to form a heterojunction rectifier device [86]. These properties [87-88] suggest its stable and efficient application in the fabrication of photoelectrochemical solar cell.

With reference to these existing information about the technological importance of zirconium and titanium based chalcogenides, author has put efforts for the growth of $\text{ZrSTe}$, $\text{TiSTe}$ and $\text{TiSeTe}$ which is discussed in the next chapter.
REFERENCES


2. JA Wilson and AD Yoffe. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. Advances in Physics, 18(73) (1969) 193.


