CHAPTER-1

EXISTING INFORMATION ON TRANSITION METAL DISELENIDE SINGLE CRYSTALS
1.1 INTRODUCTION

Solid materials can be classified according to a variety of criteria. Among the more 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 characteristics 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.

The transition metal represents the filling of the atomic d-electron shell. Because the transition metals and their alloys typically have high melting temperature and hardness, their economic importance is immense. There has been rather little experimental work on phase transitions in transition metals because these elements are relatively incompressible yielding phase changes only at very high pressures beyond the experimental range.

The elemental information about the transitional metals (Nb, Mo, Ta and W) and chalcogen element (Se) used in the present work for the synthesis of single crystals of NbSe₂, MoSe₂, TaSe₂ and WSe₂ are as shown in Table 1.1.
Table 1.1 The atomic number, atomic weight, group, period, density and melting point of Nb, Mo, Ta, W and Se elements.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Nb</th>
<th>Mo</th>
<th>Ta</th>
<th>W</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic No.</td>
<td>41</td>
<td>42</td>
<td>73</td>
<td>74</td>
<td>34</td>
</tr>
<tr>
<td>Atomic Weight (gm)</td>
<td>92.91</td>
<td>95.94</td>
<td>180.95</td>
<td>183.84</td>
<td>78.96</td>
</tr>
<tr>
<td>Group</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>Period</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Density (gm cm⁻³)</td>
<td>8.58</td>
<td>10.28</td>
<td>16.68</td>
<td>19.26</td>
<td>4.82</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2468</td>
<td>2617</td>
<td>2996</td>
<td>3410</td>
<td>221</td>
</tr>
</tbody>
</table>

Niobium (Nb): It is a member of vanadium group. At room temperature and pressure (RTP), Nb is bcc. Static compression to 25 GPa (Ming et al., 1978; Vereshchagin et al., 1961) and shock wave experiments (Marsh S. P., 1980) up to 170 GPa shows no phase transitions.

Niobium metal has a number of important uses. It is a component of some stainless steels and also alloys with nonferrous metals. These alloys have good strength and other properties and are used in pipeline construction. The metal has a low capture cross-section for thermal neutrons and so finds use in the nuclear industries. The metal is used in arc-welding rods for some grades of stainless steel. It is used in advanced engineering systems such as those used in the Gemini space program. Some magnets contain niobium and superconductive magnets are made with Nb-Zr alloy wire. Because of its bluish colour, niobium is apparently being used for "body art" products, such as navel rings. The solid-state structure of niobium is shown in Figure 1.1 (a) and (b).
Molybdenum (Mo): It is a member of chromium group. Mo is bcc at RTP. There is no evidence for phase changes up to 280 GPa in DAC experiments at RT (Ming et al., 1978; Mao et al., 1978; Vohra et al., 1990). LMTO calculations on the fcc, hcp and bcc phases of Mo show that the bcc phase is destabilized by pressure and transitions to hcp at 320 GPa and then to fcc at 470 GPa are expected (Hixson et al., 1989). It is possible that the solid-solid phase transition found in shocked Mo is the bcc-hcp transition.

Almost all ultra-high strength steels contain molybdenum in amounts from 0.25 to 8%. Molybdenum improves the strength of steel at high temperatures. It is used as electrodes for electrically heated glass furnaces and also for nuclear energy applications as well as for missile and aircraft parts. It is a valuable catalyst in petroleum refining and used as a filament material in electrical applications. Molybdenum is an essential trace element in plant nutrition. Some soils are barren for lack of this element in the soil. The solid-state structure of molybdenum is shown in Figure 1.2 (a) and (b).
Tantalum (Ta): It is a member of vanadium Group. At RTP, Ta is bcc. Static compression at RT upto 77 GPa shows no phase transition (Ming et al., 1978; Xu et al., 1984). There is no obvious anomaly corresponding to a solid-solid transition on the shock Hugoniot (Marsh S. P., 1980; Mitchell et al., 1981).

Tantalum metal has a number of important uses. It is used to make steel with desirable properties such as high melting point, high strength and good ductility. It finds use in aircraft and missile manufacturing. It is very much inert and hence it is useful in the chemical and nuclear industries to line reactors. Tantalum wires were those used first for light bulbs (now tungsten is preferred). The metal is immune to human body liquids and the body tolerates the metal well. Therefore, tantalum has widespread use for surgical equipment. For instance, it can be used in sutures and as cranial repair plates. The metal is used in the electronics industry for capacitors. Its oxide is used to make special glass with a high index of refraction for camera lenses. The solid-state structure of Tantalum is shown in Figure 1.3 (a) and (b).
Tungsten (W): It is a member of chromium group. At RTP, W is bcc. Static compression to 364 GPa shows no phase change (Ruoff et al., 1990). LMTO calculations on W predict a bcc-hcp transition at pressures well above the 320 GPa. It is possible that the predicted transition in W is seen in the optical-analyzer results.

Tungsten is useful for glass-to-metal seals since the thermal expansion is about the same as borosilicate glass. Tungsten and its alloys are used extensively for filaments for electric lamps, electron and television tubes, and for metal evaporation work. It is also used for electrical contact points for car distributors, as X-ray targets, as windings and heating elements for electrical furnaces and for missile and high-temperature applications. High-speed tool steels and many other alloys contain tungsten. Calcium and magnesium tungstates are widely used in fluorescent lighting. Tungsten salts are used in the chemical and tanning industries. Tungsten disulphide is a dry, high-temperature lubricant, stable to 500°C. Tungsten bronzes and other tungsten compounds are used in paints. It is used for making TV tubes (electron tubes) and also as X-ray targets. The solid-state structure of tungsten is shown in Figure 1.4 (a) and (b).
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 (Stephens et al., 1986). They are also metastable monoclinic forms of Se based on Se₈ rings, similar to S₈ (Donohue D., 1974).

Selenium exhibits both photovoltaic actions, 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 photographic toner and additive for stainless steel. The solid-state structure of selenium is shown in Figure 1.5 (a) and (b).
A formal oxidation number and an electronic configuration for each element are given in Table 1.2.

Table 1.2 The formal oxidation number and electronic configuration for different elements of MSe$_2$ (M= Nb, Mo, Ta and W) single crystals.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Element</th>
<th>%</th>
<th>Formal oxidation state</th>
<th>Formal electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbSe$_2$</td>
<td>Nb</td>
<td>37.04</td>
<td>4</td>
<td>[Kr].4d$^1$</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>62.96</td>
<td>-2</td>
<td>[Ar].3d$^{10}$.4s$^2$.4p$^6$</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>37.79</td>
<td>4</td>
<td>[Kr].4d$^2$</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>Se</td>
<td>62.21</td>
<td>-2</td>
<td>[Ar].3d$^{10}$.4s$^2$.4p$^6$</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>53.40</td>
<td>4</td>
<td>[Xe].4f$^{14}$.5d$^1$</td>
</tr>
<tr>
<td>TaSe$_2$</td>
<td>Se</td>
<td>46.60</td>
<td>-2</td>
<td>[Ar].3d$^{10}$.4s$^2$.4p$^6$</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>W</td>
<td>53.79</td>
<td>4</td>
<td>[Xe].4f$^{14}$.5d$^2$</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>46.21</td>
<td>-2</td>
<td>[Ar].3d$^{10}$.4s$^2$.4p$^6$</td>
</tr>
</tbody>
</table>

The physical and chemical parameters for the MSe$_2$ (M=Nb, Mo, Ta and W) single crystals are given in Table 1.3.
Table 1.3  The standard data of the atomic weight, colour, appearance, melting point and density for the MSe₂ (M=Nb, Mo, Ta and W) single crystals.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NbSe₂</th>
<th>MoSe₂</th>
<th>TaSe₂</th>
<th>WSe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>250.826</td>
<td>253.86</td>
<td>338.868</td>
<td>341.76</td>
</tr>
<tr>
<td>Colour</td>
<td>gray</td>
<td>gray</td>
<td>gray</td>
<td>gray</td>
</tr>
<tr>
<td>Appearance</td>
<td>crystalline solid</td>
<td>crystalline solid</td>
<td>crystalline solid</td>
<td>crystalline solid</td>
</tr>
<tr>
<td>Melting point</td>
<td>&gt;1300°C</td>
<td>&gt;1200°C</td>
<td>&gt;1300°C</td>
<td>&gt;1200°C</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>6300 kg m⁻³</td>
<td>6900 kg m⁻³</td>
<td>6700 kg m⁻³</td>
<td>9200 kg m⁻³</td>
</tr>
</tbody>
</table>

The polytypical structure of molybdenum selenide, tantalum selenide and tungsten selenide are shown in Figure 1.6.

Figure 1.6  The polytypical structure of selenide of Mo, Ta and W.
The data on compounds of Nb, Mo, Ta and W are adapted from the primary literature and several other sources (Greenwood et al., 1997; Cotton et al., 1999; West A. R., 1999; Lide D. R., 1996; Macintyre J. E., 1992).

There has been interest in the two-dimensional (2D) layer type solids for some time, not just for from a basic or theoretical point of view but also because of the diverse application of these materials. The layered transition metal dichalcogenides are typical pseudo-2D solids in bulk form with strong covalent bonding within the layers and weak van der Waals bonds between layers (Wilson and Yoffe, 1969). They can also be dispersed into single molecular form in water or organic suspension (Joensen et al., 1986). Transition metal dichalcogenides have been used for many years as a catalyst for hydrodesulfurization in the petroleum industry (Daage et al., 1994, Chianelli, 1984), as a solid lubricant (Clauss, 1972), and also as a host material in rechargeable lithium batteries (Rouxel et al., 1986).

Transition metal dichalcogenides are semiconductors which can act as efficient electrodes in the realization of photoelectrochemical solar cells. For economic reasons, obtaining these compounds in thin films is very interesting. The photoelectric device performances may be improved by growing thin films having vertical grain boundaries (Pouzet et al., 1994).

Nanometer-sized particles have received considerable attention in recent years because of their special properties. A variety of methods for preparing nanoparticles and evaluating their properties have been developed (Chahavorty et al., 1991; Gleiter, 1991; Papoutsi et al., 1994). Nanostructure fabrication is very important to advance high density packing of semiconductor devices and storage devices. The fabrication using a scanning probe microscope is expected to open new process technique for them. The possibility has been demonstrated by many researchers (Albrecht et al., 1989; Eigler et al., 1990; Mamin et al., 1990; Hosoki et al., 1992; Betzig et al., 1992).
A scanning tunneling microscope (STM) was used to fabricate T-phase tantalum diselenide (TaSe$_2$) nanocrystals with sizes ranging from 7 to more than 100 nm within the surface layer of 2H-TaSe$_2$ crystals at liquid helium temperature (Zhang et al., 1996). Scanning tunneling microscopy studies have shown that TMDCs also possess unique properties for nanometer structuring and atomic scale structuring (Fuchs et al., 1991). Single crystals of indium intercalated WSe$_2$ have been grown by DVT method and are characterized by X-ray diffraction also the effect of intercalation has been studied by measuring their optical and electrical properties (Deshpande et al. 1999).

Vibrating reed measurements of the flexural resonance of thin cantilevered Nb foils and NbSe$_2$ single crystals reveal extended regions of temperature $T$ and magnetic field $H$ for reversible flux line motion. NbSe$_2$ crystals have micaceous morphologies, with the hexagonal ab planes weakly bonded via van der Waals interactions, resulting in electronic effective mass anisotropy ratios $\approx 9$ and coherence length anisotropy $\approx 3$ (Prober et al., 1980).

The tilted vortex lattice on the surface of 2H-NbSe$_2$ is investigated with a scanning-tunneling microscope (Hess et al., 1992). The X-ray absorption fine structure (XAFS) of single crystals of NbS$_2$ NbSe$_2$ and their intercalated variants were investigated at the Nb and Se edges (Freund et al., 1992). A number of X-ray absorption fine structure (XAFS) experiments have been made with NbS$_2$, NbSe$_2$ and their intercalated variants (Sonntag et al., 1974; Bourdillon et al., 1980; Davies et al., 1982; Ohno et al., 1983; Thulke et al., 1983; Sarode, 1986). 2H-NbSe$_2$ belongs to the 2H-MX$_2$ (M=Nb, Ta; X= S, Se) of the transition metal dichalcogenides. These metallic quasi two-dimensional compounds are well known for undergoing a charge density wave (CDW) transition. Some are also superconductors with a marked anisotropy at low temperature. (Ayache et al., 1992). Muon spin relaxation measurements in the layered superconductor NbSe$_2$
have been performed to study the magnetic field penetration depth $\lambda$. (Le et al., 1991).

The 1T polytape of the transition metal dichalcogenides TaSe$_2$ has anomalous properties which have been attributed to a static modulation in the 5d conduction electron density, associated with the formation of charge density waves (CDWs). (Wilson et al., 1975; Williams et al., 1974). To determine the eventual influence of the T nature of the transport agent used for the crystal growth, and of the M metal impurity concentration on physical properties of TSe$_2$ (T= Mo, W) single crystals, doped or not, impedance measurements are made at 100 kHz in a three-probe electrochemical cell. (Legma et al., 1992). A comparative study of Nernst effect and resistivity in underdoped cuprites has been performed and detected a finite Nernst signal in the normal-state of the conventional superconductor NbSe$_2$ (Behnia et al., 2004). Single vortices have been observed as they penetrate the edge of a superconductor using a high-sensitivity magneto-optical microscope (Olsen et al., 2004). The thermal conductivity of the layered s-wave superconductor NbSe$_2$ was measured down to $T_c/100$ throughout the vortex state (Boaknin et al., 2004).

The electronic density of states of NbSe$_2$ from 0.3 K upto its critical temperature (7.2 K) has been investigated and evidence of the presence of multiband superconductivity also found (Rodrigo et al., 2004). The MBE growth of II-VI semiconductor CdTe on a layered material NbSe$_2$ was studied (Kuroda et al., 2004). Magnetization measurements on NbSe$_2$ samples revealed an enhancement in the critical density $J_c$ with radiation dosage (Galvan et al., 2003). 2H- NbSe$_2$ is a van der Waals bonded layered structure, which undergoes a charge density wave (CDW) transition. The CDW transition have been investigated in NbSe$_2$ using grazing incidence X-ray diffraction (Murphy et al., 2003).

The charge density wave state was investigated in the transition metal dichalcogenides 2H-NbSe$_2$ (Higemoto et al., 2003). The non-uniform magnetic character of the mixed state is known to
result in a magnetic quadrupolar response of a type-II superconductor (Pal et al., 2002). The Fermi Surface (FS) and superconducting gap of 2H- NbSe$_2$ have been studied using angle resolved photoemission spectroscopy (Kiss et al., 2002). A universal phase diagram for weakly pinned low $T_c$ type-II superconductors is revisited and extended with new proposals. This proposal provides an explanation for the anomalies observed in the peak effect regime of 2H- NbSe$_2$ and several other low-$T_c$ materials (Banerjee et al., 2001).

The low field magnetization hysteresis and relaxation process in pure 2H- NbSe$_2$ single crystals have been studied (Mishra et al., 2000). The observation of a negative dynamic creep rate i.e. increasing irreversibility in the magnetic hysteresis loop for the decreasing sweep rate of the magnetic field, in 2H- NbSe$_2$ single crystal have been reported (Zhukov et al., 2000). Different techniques to study the dynamics of the vortex lattice in NbSe$_2$ single crystal samples have been presented (Pardo et al., 2000). The angle-resolved photoemission data on the Fermi surface topology and conduction band dispersion in the layered metal 2H- NbSe$_2$ have been presented (Straub et al., 1999).

Friction force versus normal load have been studied on the nanometer scale on three layered materials which are expected to exhibit different mechanical properties (Klein et al., 1997). Micro and FT-Raman spectra of NbSe$_2$ have been carried out (Leblanc et al. 1997). The thermodynamic nature of reentrant characteristic of PE curve in very clean sampled of 2H-NbSe$_2$ has been confirmed (Banerjee et al., 1997). Simultaneous magnetic decoration of the two sides of a superconducting sample can provide information about dimensionality, longitudinal distortions and elasticity of the vortex lattice. Double sided decoration for a single crystal of NbSe$_2$ was done and also reported (Marchevsky et al. 1997). Effects of intercalation on the lattice instability and the superconductivity of NbSe$_2$ was studied in the framework of the rigid band approximation (Motizuki et al. 1996).
The Fermi surface of 2H-NbSe$_2$ has been investigated using the torque method in strong magnetic fields up to 27 T and at temperature down to 0.4 K (Rettenberger et al. 1995). A 2a$_0$ superlattice and a well-defined elliptical contour of diffuse intensity in between the 3a$_0$ CDW spots have been observed (Chen, 1984). The dHvA effect for 2H-NbSe$_2$ was calculated for different directions of the external field (Klose et al., 1974). The dependence of superconducting transition temperatures on changes in composition and structure was observed in the niobium-selenium system (Revolinsly et al., 1965).

The formation of transition metal selenide thin-films has been studied in ultra high vacuum (UHV) by means of photoemission spectroscopy with synchrotron radiation (Saltaas et al., 2001). Recent instrumentation developments in photoemission are providing new insights into the physics of complex materials. With increased energy and momentum resolution, it has become possible to examine in detail different contributions to the self energy or inverse lifetime of the photohole created in the photoexcitation process. In studies of a metallic system such as Mo it is possible to isolate and identify the different contributions to the quasi-particle lifetime including electron-electron, electron-phonon and electron-impurity scattering (Johnson et al., 2001). Cs was adsorbed at room temperature on to the (0 0 0 1) cleavage planes of 1T-TaSe$_2$. The change in the electronic structure could not be interpreted within the rigid band model, but is tentatively explained by a localization effect, caused by the charge density wave phase transition (Crawack et al., 2000). High resolution transmission electron microscopy (HRTEM) images of the "incommensurate" structures of 2H-TaSe$_2$ is taken from a vide specimen area with homogeneous thickness (Onozuka et al., 2000).

The formation of TaSe$_2$ layered compound thin films, grown on polycrystalline Ta substrates was studied. The experiment was performed in UHV by means of photoemission spectroscopy with synchrotron radiation measurements (Papageorgopoulos et al., 2000). Lattice vibrations in 2H-TaSe$_2$ and 2H-NbSe$_2$ are investigated by one
and two phonon Raman scattering in the normal and charge density wave (CDW) phases (Sugai Shunji, 1983). Infrared and Raman spectra of 1T polytype TaSe$_2$ is investigated with particular interest in the phonon modes observed in the commensurate superlattice states (Uchida et al., 1981). The polarized Raman spectra of 1T- TaSe$_2$ and 2H-TaSe$_2$ were investigated (Sugai et al., 1981). The stacking of layers in transition metal dichalcogenides in the temperature range of about 40 K to 600 K has been studied by convergent beam electron microscopy (Fung et al., 1980).

In this chapter author survey the experimental and theoretical work done on transition metal diselenides.

1.2 IMPORTANCE OF TMDCs

Transition metal dichalcogenides, because of their layered structure may undergo structural and electronic transitions under pressure. TMDCs have attracted many research workers on account of the interesting properties of the compounds of this family. They are used in optoelectronics, holographic recording systems, switching, infrared generation and detection system. They can be used as cathode in rechargeable secondary cells, as selective oxidation and reduction agents, as high temperature solid lubricants, in SQUID detectors (Wilson et al., 1969), as anode & cathode material in PEC for solar energy conversion (Aruchamy, 1992), for nanometer structuring, as a substrate in van der Waals epitaxial growth, in deposition of Langmuir-Blodgett films and in the field of catalyst. They have many other applications too. Layered transition metal dichalcogenides MX$_2$ (M= metal; X= chalcogen) may be considered as ideal model systems for the investigations of fundamental aspects of semiconductor metal interactions. They have also been used to catalyses reactions such as hydrogenation (Sakata et al., 1986), hydrodesulphurisation (Saiprasad et al., 1992), methanation (Miremadi et al., 1990). It has been realized that diselenides are more efficient in solar cell fabrication than
disulphides (Canfield et al., 1981). In addition, the most efficient liquid junction solar cell reported so far has been prepared with n-WSe$_2$ photoelectrodes (Campet et al., 1988). Layered chalcogenides WSe$_2$ van der Waals surfaces are used as semiconductor substrate as they provide ideal surface properties for fundamental studies (Jaegermann et al., 2004).

1.3 OCCURANCE AND SYNTHESIS

All the members of the MSe$_2$ (M = Nb, Mo, Ta and W) single crystals are not known to occur naturally, hence majority of them are required to be synthesized in the laboratory. For the growth of these crystals, various growth techniques are available at present. These include both, growth from the melt as well as growth from the vapour. The well-known methods over the years for the growth of binary II-VI compounds include Bridgeman, direct vapour transport (DVT) and chemical vapour transport (CVT) techniques.

The literature survey on these compounds shows that vertical Bridgman-Stockberger method and chemical as well as direct vapour transport techniques are the most frequently used for the growth of the single crystals of MSe$_2$ (M=Nb, Mo, Ta and W). In principle, the chemical vapor transport technique is a cyclic reaction driven and maintained by a temperature gradient. An evacuated sealed quartz ampoule containing a stoichiometric mixture of elements and a small amount of transporting agent (iodine), is placed in a two zone furnace keeping temperature at two zone as $T_1$ and $T_2$ respectively for reaction and growth zone. For an endothermic reaction $T_1 > T_2$, but if the reaction is exothermic then $T_2 > T_1$. Temperature $T_1$ and $T_2$ are maintained accurately steady by temperature controllers. Over a period of several hours a reaction takes place of the type:

$$2MX_2 + 2I_2 \Leftrightarrow 2MI_2 + 2X_2 \text{ (Reaction)}$$

$$2MI_2 + 2X_2 \Leftrightarrow MI_4 + MX_2 \downarrow + X_2 \text{ (Growth)}$$
and single crystals of the diselenide condense in the growth end of the ampoule.

Among the transition metal dichalcogenides, the poly type 4Hb-TaSe$_2$ show interesting atomic and electronic properties, which are believed to mainly originate from the alternating layers of the trigonal co-ordination (1H) and octahedral co-ordination (1T) (Wilson et al., 1975; Coleman et al., 1988). Theoretical calculation and experimental results (Coleman et al., 1988; Friend et al., 1977; Doran et al., 1978) show that each layer maintains its characteristic features found in the corresponding pure phase, although there has been a small electron transfer between the two different layers. Layer by layer etching of the surface of transition metal dichalcogenides has been used earlier using STM (Parkinson, 1990; Volodin et al., 1994) and atomic force microscope (Delawski et al., 1992). NbSe$_2$ single crystals have been grown by chemical vapour transport technique and characterized by EDAX, XRD analysis with transport property measurement (Vaidya et al., 2005).

The WSe$_x$ films were characterized in terms of their hardness, elastic modulus, surface topography and wear performance. The structure of WSe$_x$ films was shown to consist of various nanocrystalline mixtures of WSe$_2$ and W$_3$O phases in an amorphous WSe$_x$ matrix (Shtansky et al., 2004).

1.4 CHARACTERIZATION OF TMDCs

1.4.1 Structural analysis

The TMDC compounds are made up of a sheet of metal atoms M, sandwiched between two sheets of chalcogen atoms X. These X-M-X sandwiches are loosely coupled to one another by relatively weak van der Waals force resulting in anisotropic physical properties. There are two different types of the coordination in these layered
compounds as shown in Figure 1.7. One is called 1T type structure (space group $D^{3}_{d}$) where each M atom is octahedrally coordinated with six chalcogen atoms and the other is called 2H poly type (space group $D^{4}_{h}$) where the coordination of the M atoms is trigonal prismatic and the unit cell spans two sandwiches in the c-direction. Thus there are twice as many bands in 2H-MX$_2$ as those in 1T-MX$_2$.

A 2D crystal is defined as a structure, which has periodicity in two dimensions only. A single layer of layered materials such as graphite or layered transition metal dichalcogenides is an example of a 2D crystal. While the lattice of the system is strictly 2D, the material may have a thickness in the third dimension (Yang et al., 1996). The physical and structural properties of crystalline transition metal dichalcogenides are reviewed by Wilson and Yoffe; 1969. Electronic band structure calculations were performed for 2H-MX$_2$ (M=Mo, W; X=S, Se) and are reviewed (Doni and Girlanda, 1986).

![Coordination of the metal M and chalcogen X atoms in (a) 1T- and (b) 2H-transition metal dichalcogenide MX$_2$.](image)

Since the number of atoms in a layer increases with its radius, the layers cannot be fully commensurate. This perturbation of the crystal structure cannot be described by XRD measurements since it is not periodical. The polytypes differ in the way the layers are stacked.
1.4.2 Optical properties measurements

The pioneer work (Tributsch et al., 1977), the behaviour of covalent semiconducting layer type group VI transition metal dichalcogenides and in particular of WSe\textsubscript{2} (Kautek et al., 1982 and Chaparro et al., 1993) and MoSe\textsubscript{2} (Lewerenz et al., 1984 and Chaparro et al., 1995) as electrodes in Photoelectrochemical (PEC) solar cells for conversion of solar energy into electrical energy has been extensively studied. The optical and electrical properties of the transition metal dichalcogenides have been investigated by many authors (Frind et al., 1963; Evans et al., 1965, 1967).

Since Tributsch and his coworkers (in 1979, 1981) have shown that MoSe\textsubscript{2} can act as an efficient in photoelectrochemical cells, a great deal of attention has been paid to MoSe\textsubscript{2} thin films (Bischel et al., 1984, 1985; Mallouky et al., 1988; Bernede et al., 1988, 1990; Pouzet et al., 1990, Pawlikowski, 1990).

1.4.3 Electrical properties measurements

Transition metal dichalcogenides have become increasingly important in the last 30 years. Crystals of such materials can be cleaved down to less than 1000 Å and are then transparent in the region of direct band to band transitions (Wilson and Yoffe, 1969).

Renewed interest in thermoelectric devices is driving the search for materials with higher thermoelectric efficiencies (Rowe, 1995; Mahan, 1998). The development of such improved materials could lead to major advances in important technologies such as refrigeration, electric power generation, cooling of both superconducting and electronic components. Pressure tuning studies of the properties of thermoelectric materials may provide insight into where to search for improved thermoelectric materials at ambient pressure. To perform pressure tuning studies, it is necessary
to measure thermoelectric power and other transport properties as a function of pressure.

In recent years, a large amount of work about incommensurate systems, like ferroelectric liquid crystals, improper ferroelectrics and transition metal dichalcogenides (Ribeiro, 1986; Rocha et al., 1990, 1991) has discussed some important properties of these materials. Some calculations in order to study the normal-incommensurate and incommensurate-commensurate phase transitions in layered 2H-polytype transition metal dichalcogenides like 2H-TaSe$_2$ and 2H-NbSe$_2$ were summarized (Rocha et al., 1998), which are two dimensional and present charge density waves (CDW), which are periodic modulations of the electronic charge with a period which can or cannot have a commensurate relationship with the period of the original lattice (Tritt et al., 1988). Many authors (McMillan, 1975, 1976, 1977; Moncton et al., 1975, 1977; Rocha et al., 1989) have studied 2H-TaSe$_2$ because this compound presents a very rich diversity of phenomena of CDWs superlattice including transitions between commensurate phase, orthorhombic incommensurate stripe and hexagonal incommensurate phase and normal phase.

1.4.4 High pressure study

The roots of Modern high-pressure science and technology can be traced back over many centuries. The first scientific approaches to the field of high pressure has been developed in 1662, when Boyle propounded his law relating the pressure of a perfect gas to its volume at constant temperature, $PV = \text{Constant}$. In 1802, L. J. Gay-Lussac showed that volume varied linearly with temperature at constant pressure. A result anticipated by J. A. C. Charles in 1787 and when combined with Boyle's law, the equation of state of the perfect gas i.e. $PV = nRT$ is obtained. These early experiments with gases were
conducted at pressure not far from atmospheric and were closely related to the problems of defining a temperature scale.

In the years following, high pressure research was dominated by two Frenchmen, E. H. Amaget and L. Cailletet, who worked extensively on the properties of condensed fluids up to ~3,000 bars. At the present time, the large-scale applications have increased interest in research at high pressure also increased in industrial, government and university research laboratories. Since the latest advances have utilized the strongest material known to men, i.e. diamond, there is great current interest in the possible synthesis of super-materials using ultra-high pressure technology.

Different units of pressure:

1 torr = 1 mm of Hg = 1333 microbar = 1.333 milibar

1 torr = 760 bar = 1 standard atmosphere = 133 Pascal

1 bar = 10^6 dyne/cm^2 = 0.9869 atm = 1.0197 kg/cm^2 = 10^5 N/m^2

1 N/m^2 = 1 Pascal = 10^-5 bar ✓

1 GPa = 10 kbar = 10^4 bar ✓

100 GPa = 1 Mbar ✓

Bridgman anvil set-up

The study of high-pressure phenomena is deep rooted. In the beginning of the 1906, P. W. Bridgman made a systematic study of almost all aspects of high-pressure phenomena. Astronomical objects like white dwarfs and neutron stars have very high pressures. At such extreme pressures, matter is composed of bare neutrons and protons. The understanding of material behaviour under pressure is of importance in a wide variety of discipline.
Diamond anvil cell

Diamond Anvil Cell (DAC) has a pivotal role in the investigation of the materials under high static pressures and temperatures because of the compact size, the non-evasive access to the pressure-temperature region, the safe generation and convenient measurement of pressure and temperature. This has been as a result of number of advances in the shaping and aligning of diamond anvils (DAs), gasketing technique, pressure-temperature measurement and characterization. The DAC can be coupled to most of the condensed matter experiment techniques (Jayaraman, 1983). With recent advances in diamond-cell technology, static pressures of several hundred GPa can be reached routinely in the laboratory. Physical and chemical properties of materials can be determined accurately at ultrahigh pressure (Mao et al., 1996). The advances are intimately linked with the evolution of synchrotron facilities, which provide high-brilliance radiation sources for studying a wide range of properties of samples in diamond cells (Mao et al., 1996). In addition, with simulation of pressure effects by simple scaling of the volume of the materials in the ab-initio condensed matter theories, it has opened up the possibility of consistency test between theoretical and experimental data.

1.4.5 Nanostructures

Now a days, one of the most important challenges to extending the storage density of magnetic disk drives beyond 150 Gbit/in² is suppression of media noise. To achieve this, the grain size has to be reduced, but this approach is rapidly limited by superparamagnetic instabilities. One approach to overcome this limit is to compensate the decrease of grain size by increasing the magneto-crystalline anisotropy. An attractive method for preparing such nanostructured media is based on self assembling of adatoms when deposited on the
surface of the layered chalcogenides crystal. The WSe$_2$ structure is characterized by a stacking of two-dimensional sandwich units (Se-W-Se) along the c-axis separated from each other by the so-called van der Waals gap, the Se atoms forming the outer hexagonal dense planes (Maret et al., 2005).

Nanoparticles of compounds with layered structure are of special interest because some of them may form fullerenes, nested fullerene-like structure or tubes. The nested fullerene-like structures are also known as “onion crystal”. This phenomenon found originally in the case of carbon. In the mean time similar phenomena found in few other compounds. First nested fullerene like structure in non-carbon compounds were found in WS$_2$ (Tenne et al., 1992), MoS$_2$ (Margulis et al., 1993; Yacaman et al., 1996) films on quartz substrates. This knowledge leads to the question of whether this is a general phenomenon found in layered structures. In this context, the dependency of the formation of these particles on the particle size is also open. To find a first answer to these questions, nanoparticles of compounds crystallizing in three different types of layered structure were synthesized and analyzed by several researchers (Feldman et al., 1995; Tenne et al., 1992; Margulis et al., 1993; Parilla et al., 1999).

Many researchers have done work on TMDCs about their synthesis and characterization, but little work has been reported related to high pressure studies as well as nanocrystallites form. Looking to the importance and applications of these compounds, author tried in the present work to study the effect of pressure on electrical properties using diamond anvil cell and presence of nanocrystallites on the surface of as grown crystals.
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