PREFACE

In recent interactions with industrial companies it became quite obvious, that the search for new materials with strong anisotropic properties are of paramount importance for the development of new advanced electronic and magnetic devices.

Modern technique of controlled materials synthesis and advances in measurement and modeling have made clear that multiscale complexity is intrinsic to complex electronic materials, both organic and inorganic. A unified approach to classes of these materials is urgently needed, requiring interdisciplinary input from chemistry, materials science and solid state physics.

The transition metal dichalcogenides (TMDC's) are about 60 in number. Two-third of these assume layer structures. The MX_2 layer materials form a structurally and chemically well-defined family. It seems possible that this material may undergo a semiconductor to metal transition. The binary layer compounds are in fact ideal for investigating the course of d-band formation since the metal atoms lie in well-defined hexagonal sheets. The basic atomic structure of loosely coupled X-M-X atom sheet sandwiches makes such materials extremely anisotropic, both mechanically and electrically. The forces between the layers are of the weak van der Waals type, whereas the forces inside the layers are ionic-covalent. According to existing representations, a weak interlayer interaction should result in splitting of each electronic level and intralayer vibration into several components equal to the number of layers in a primitive unit cell. In layer structures, moreover, the charge carriers and phonons seem to couple in a unique fashion. The structure of the MX_2 dichalcogenides falls into two distinct classes- layered and otherwise. Several of the MX_2 materials occur with layer structures that are distorted. The extremely anisotropic character of the layer compounds, built in at the atomic level, dominates all the properties of such materials, both mechanical and electrical.
The group XVI elements, viz, sulfur, selenium and tellurium are commonly referred to as the chalcogens. The periodic properties of the chalcogens have been summarized elsewhere (Cotton, et al., 1999). Tellurium is slightly metallic whereas sulfur and selenium are considered non-metallic. All three chalcogens undergo a variety of reactions with more electropositive elements including alkali and alkaline earth metals, transition metals and rare-earth metal elements. The ability of chalcogens to bond to themselves and to other elements is one of the reasons that they have been extensively investigated. Chalcogens have been used in the solid-state synthesis of binary, ternary and quaternary compounds. Several reviews of chalcogenides chemistry within organic, inorganic, organometallic and solid-state synthesis show the wide co-ordination environments available for S, Se and Te (Roof et al., 1993; Drake et al., 1994; Kanatzidis et al., 1994). Due to Industrially important properties chalcogenide chemistry continues to be an active area of research. Novel chalcogenide compounds and materials contain a wide spectrum of semiconducting, optical, thermoelectric, catalytic, magnetic and superconducting properties.

Optical band gap of semiconducting materials plays an important role in deciding their behaviour, study of the possible phase transition and photoconversion efficiency of a solar cell, fabricated with them. The author has obtained absorption spectra for asgrown crystals in the spectral range 700 nm to 1450 nm using UV-VIS-NIR spectrophotometer. All the Nb and Ta materials, whether distorted or not, are superconducting and the truly metallic ones to show band antiferromagnetism below about 150 K. In order to illuminate the origin of these unusual properties more clearly, an investigation has been made of the optical properties.

The advantages of pressure for studying semiconductors have been understood since the early 1950's, when Bridgman performed the first measurements of the electrical properties of Ge and Si. High pressure research on the optical properties of semiconductors was
started at the end of the 1950's. Pressure applied to semiconductors strongly modifies the electronic and vibrational properties to control the reduction of interatomic dimensions and cause continuous changes in the chemical bonding. Pressure enhances the interlayer coupling as a strong influencer on the crystal structure with 'rigid-layer' modes and finally leads to pressure induced phase transitions. These transitions may be reversible or irreversible.

With recent advances in diamond anvil cell technology, static pressures of several hundred GPa can be achieved in the laboratory. Physical and chemical properties of materials can be determined accurately at ultrahigh pressure (Mao, H. K. et al., 1996). The development of the gasketed diamond anvil cell (DAC) for optical measurements at hydrostatic pressures well above 10 GPa noticeably reduced the experimental difficulties and opened new perspective for studying the physics of semiconductors under pressure. There are many articles devoted to the physical properties of semiconductor under pressure (Goni, et al., 1998; Besson et al., 1993).

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 anvil cell (Mao et al., 1996). The diamond anvil cell has been used routinely in studies up to 100 GPa. X-ray diffraction is the primary experimental method for determination of equation of state and crystal structures. The high spatial resolution capability of synchrotron X-ray diffraction is essential for probing such microscopic samples at maximum pressures and temperatures and for minimizing the effect of gradients in these variables.

In order to review the advances in this field of crystal growth & characterization and for the development of new exciting ideas, which may lead to new experimental and theoretical techniques resulting in a deeper understanding of the material properties, author has carried out this work, which is in the form of a thesis. The research efforts have focused recently on the synthesis of binary transition metal (Nb,
Ta, Mo and W) selenide (Se) compounds containing anionic Se chalcogen building blocks coordinated to transition metal (Nb, Ta, Mo and W) cations. Single crystals are characterized by a strong anisotropy of the crystal structure and the physical properties. The work has centered on the layered transitional metal dichalcogenides of groups VB and VIb for the purpose of comparison.

The work proposed in this thesis has been divided into 9 chapters.

Chapter 1 deals with the existing information about transition metal diselenides viz. NbSe₂, MoSe₂, TaSe₂ and WSe₂.

Chapter 2 describes the growth of layered single crystals NbSe₂, MoSe₂, TaSe₂ and WSe₂ by chemical vapour transport (CVT) method using iodine as a transporting agent. The salient features of CVT method have been thoroughly explained. Details of ampoule preparation, cleaning of ampoule, furnace construction, its calibration and method of crystal growth have also been narrated.

A brief information about the experimental techniques, employed along with data collected by the way of characterizing these grown crystals using EDAX, XRD for structural studies has been provided. The details about the study of growth patterns on their finished surfaces examined by optical microscope have been discussed in Chapter 3.

Chapter 4 includes a brief discussion on optical properties of as grown crystals. A measurement of optical parameters gives information about the semiconducting behaviour of these crystals.

Temperature dependence of resistivity of these crystals has been studied and describes fully in Chapter 5. Hall effect measurements, anisotropy measurements, thermoelectric power measurements were studied and results obtained have been systematically represented in this chapter.
Chapter 6 reviews the techniques of high pressure generation and measurement of resistance under pressure up to 10 GPa using Bridgman opposed anvils set up.

The present status of high-pressure research with the diamond-anvil cell (DAC) is reviewed in Chapter 7. The different types of DACs that are currently in use are discussed. Resistance measurement data taken up to 25 GPa using DAC for NbSe$_2$, MoSe$_2$, TaSe$_2$ and WSe$_2$ single crystals has been given. The results obtained are represented as graph and explained with proper discussion.

Chapter 8 contains the theory about the nanoparticles presented in the as grown crystals, which are obtained by transmission electron microscope (TEM) for these crystals.

The theme of this thesis has been the impressive advances in experimental and theoretical condensed matter physics in recent years. These advances have come from many different sources and have converged in a mass of new experimental data and theoretical calculations. The results of all these experiments as a conclusion are given in Chapter 9. The scope of the future work are also narrated precisely in this chapter.
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