PREFACE

While going through the literature survey, it is noticed that the transition metal dichalcogenides have attracted many researchers from several fields. Probably this is due to the interesting properties and various applications of these layered compounds. The experimental development of successfully growing perfect single crystals in laboratories of most of these compounds open the doors to careful examination of their fascinating properties.

At the juncture of the rapid scientific and technical development of the modern trends, these compounds have gained unique importance for their potential applications in the areas of semiconductors, superconductors, solid lubricants, optical windows, switching devices, model substances for testing and exploring photoemission methods including photoelectro-chemical (PEC) solar cells. PEC solar cells are very much useful to get adequate supply of energy which is at present a burning problem and a number of scientists are frantically hunting for the new sources of energy.

Transition metal dichalcogenide crystals (TMDC) have the general formula MX_2, where M is a transition metal from IV B, V B and VI B group of the periodic table and X is one of the chalcogens namely sulphur, selenium or tellurium the basic structure of loosely coupled X-M-X sheets make such materials extremely interesting because within a layer the bonds are strong while between the layers they are remarkably weak. This makes them anisotropic, both mechanically and electrically.

Recently, some of the transition metal dichalcogenides are found to be of considerable interest in the search for durable and efficient non-oxide semiconducting photoelectrode systems which ultimately leads to the fabrication of PEC solar cell. Visible and near infrared radiation absorbed by these compounds produces a d-d excitation of electrons, which does not involve the breaking up of essential crystal bonds. This leads to the generation of holes which do not directly lead to a photoelectrochemical corrosion of the substrate. Therefore both, the n-type as well as p-type layer compounds can favourably be employed in the fabrication of regenerative electrochemical solar cells.

The crystals of transition metal dichalcogenides (TMDC) are generally grown by using the chemical vapour transport method in which iodine or bromine is invariably used as the transporting agent. It has been observed that when the TMDC crystals, are grown by iodine or bromine as a transporting agent, intercalation of iodine or bromine into van der Waals gap of these crystals reacts with the holes and traps them which affects the purity of crystals. Moreover, the presence of transporting agents in the crystals also plays an important role in influencing their optical and transport properties.

In order to avoid the contamination of the transporting agents a physical vapour transport method has been adopted in the present work to grow the crystals of tungsten sulfoselenide (WS_xSe_{2-x} , $0 \leq x \leq 2$).

The investigations whose results are compiled in the form of a thesis consists of the growth of WS_xSe_{2-x} single crystals by direct vapour transport method. The characterization of the crystals is carried out by using X-ray diffraction and Energy Dispersive Analysis of X-rays (EDAX). Transmission electron microscopy and photoelectrochemical studies are also presented in the thesis.

A brief survey of the existing information on WSe_2 and WS_2 single crystals and the scope of the present work is described in Chapter 1.

Chapter 2 provides a description of the vapour transport technique. The salient features of chemical vapour transport method are pointed out in the earlier part of this chapter whereas the details of the direct vapour transport method is given in the later part. Details of experimental set up, temperature controlling system, construction of the furnace etc. have also been thoroughly described.

Chapter 3 deals with the brief review on the characterization of the single crystals of WS_xSe_{2-x}. Lattice parameters, cell volumes, X-ray densities and absorption coefficients have been determined. Thermoelectric measurements have also been taken to judge the semiconducting nature of the material. A study of the optical micrographs and scanning electron micrographs of the grown faces of the crystals reveals the presence of hexagonal spirals upon them. The compositions of the as grown crystals are examined by EDAX.

The general theory of transmission electron microscopy (TEM) is given in Chapter 4. It is observed that the dark field electron micrographs taken in weak diffracted beams significantly improve the structural lattice defects. In this case the dislocations appear as very narrow bright lines against low intensity back ground. TEM study of the crystals using weak beam microscopy is reported in Chapter 5.

The transmission electron microscopic techniques of convergent beam diffraction has been known for many years but until recently instrumental deficiencies have severely limited its usefulness and applications. Now that a number of commercial instruments capable of covergent beam diffraction has become available, attempts have been made to study the crystal symmetry, lattice parameters and its changes with low temperature and polytypism of the grown crystals with the help of convergent beam diffraction method in Chapter 6.

Since WS_xSe_{2-x} single crystals can be employed in the fabrication of photoelectrochemical solar cells, special attention is paid in this direction. The necessary introduction to PEC solar cells is presented in Chapter 7. Here different types of solar cells are described and discussed by giving classification of the cells. The advantages and disadvantages of PEC solar cells over the solid state photovoltaic cells are also discussed. Basic electrode processes and the Schottky barrier model is presented in this chapter. The basic mechanism of charge transfer processes into the electrolyte is also discussed.

As molybdenum disulphide (MoS_2) single crystals are available abundantly in nature, it was decided to investigate them thoroughly as a test case study for photoelectrochemical properties. The fabrication of PEC solar cells with these single crystals is given in Chapter 8. The complete characterization of the cell is done by studying the different parameters such as intensity of illumination, temperature and concentration of electrolyte. Ideality factor for the semiconductor/electrolyte junction and flat band potential measurements have also been carried out and incorporated in this chapter.

Chapter 9 deals with the study of PEC solar cells with tungsten sulfoselenide (WS_xSe_{2-x}) single crystals. The dark I-V characteristics have been investigated to determine the junction ideality factor. Illuminated I-V characteristics with fill factor and efficiency of the cell is also given in the first part of this chapter. The second part of the Chapter 9. consists of the study of the different solar cells parameters (intensity of illumination, temperature and concentration of the electrolyte) affecting the solar to electrical power conversion efficiency.

Spectral sensitivity of the semiconducting crystals used in the PEC solar cells is investigated by taking spectral response of the grown crystals of WS_xSe_{2-x} . The direct band gaps are determined from the peak values and on set values of the photocurrent spectra recorded at different wavelengths. In order to locate the positions of conduction band, valence band and Fermi level, flat band potential is estimated from Mott-Schottky plots. These results are presented in chapter 10.

A brief inference and the scope for the future usefulness of the present study are pointed out in chapter 11.