PREFACE

During the past few years there has been considerable interest in the study of properties of solids having layer type structures. Layer structures are exhibited by some elements, inter metallics, oxides, hydroxides, halides, chalcogenides and various complex systems. Many of these materials can be found in nature and a large number of them has been synthesised in the laboratory. Whatever the source, they are characterised by strong bonding within the layer and weak (van der Waals') interactions between the layers and thus show structural anisotropy. The layered materials are in practical use in widely different areas such as tribology (e.g. MoS_2), catalysis (e.g. MoS_2, WS_2) and electrochemical energy storage (TiS_2).

The layered compounds have a drawback that they have not yet found large-scale practical applications in electronic devices. This is due to the fact that only limited materials have been studied in relation to the device potential of the layered semiconductors. On the other hand, they are quite promising and the studies reported so far, though exploratory in nature, serve to bring out the potential of these materials for photoelectronic devices.

There are large number of layered compounds exhibiting semiconducting properties but those containing chalcogenide anions (S,Se,Te) have attracted much attention. The layered transition metal dichalcogenides (TMDCs) are the most widely investigated of the layered materials because of their interesting electronic properties. They are very interesting solids since they display the whole spectrum of transport properties covering insulators, semiconductors, normal metals and superconductors.

Among the TMDCs, the disulfides, diselenides and ditellurides of tin, titanium, zirconium and hafnium are isomorphous members of a group of compounds, which crystallise in space group P3m1 with the characteristics of cadmium iodide type structures. Their structure consists of stacked composite layers each comprising of two sheets of hexagonally close packed chalcogenide atoms sandwiching a sheet of metal atoms in such a way that half of the octahedral interstitials are filled. The atomic stacking sequence is : BAB : BAB :, where B is the chalcogenide and A the metal atom. Since the primary valency is satisfied within the sandwich : BAB :, adjacent layers are held together only by relatively weak van der Walls forces. The resulting structure is markedly anisotropic, characterised by extended growth and pronounced cleavage perpendicular to the c-axis.

Stimulated by the work of Lee et al. who have reported the observation of current controlled negative resistance and switching in single crystals of tin disulfide, zirconium disulfide and hafnium disulfide, when an electric field is applied parallel to the three fold c-axis, many authors such as Chun et al. established similar behaviour for tin diselenide. Both tin disulphide and tin diselenide are semiconductors, having energy gap of respectively 2.22 eV and 1.09 eV, respectively.

A complete range of solid solutions would provide a good theme of research, with all above mentioned binary systems, isomorphous with the end members and, all having the cadmium iodide structure. Indeed in order to obtain variable conduction properties, immediate to those of binary systems, ternary mixed crystals (solid solutions) must be grown in the form of single crystals. Although the end members of the series (SnS_2 and $SnSe_2$) have been studied extensively, very few experimental results are available at present for the other members of the series SnS_xSe_{2-x} i.e. crystals with $0 \leq x \leq 2$. A systematic study on the preparation and characterisation of mixed crystals having the composition SnS_xSe_{2-x} with x = 0.5, 1 and 1.5 has therefore been carried out by the author in the present work.

A comparison of liquid junction photoelectrochemical (PEC) solar cells with conventional photovoltaic devices indicates that in the fabrication of PEC devices many processing steps required for conventional solid state solar cells (e.g. p-n junction) are either simplified or completely eliminated. This leads to a significant reduction in cost for the fabrication of a PEC device relative to solid state solar cells. In addition, PEC devices can also be used to store energy locked up in conventional fuels.

Several layered materials possess favorable semiconducting properties and have attracted attention as a new class of solar cell materials. Significant optical to electrical/chemical conversion efficiencies have been obtained in solid state photovoltaic and PEC solar cells. An attempt to use tin dicholcogenides in the fabrication of PEC solar cells was made by Katty and his group but the conversion efficiencies reported by them are very low. Also, in view of a poor photoresponse observed with tin sulphoselenides in this laboratory, author concentrated to look for TMDC having maximum potential for PEC solar cells. For this purpose, a critical literature survey was made by him. It is seen that among the layered TMDCs, tungsten dichalcogenides (WSe_2 and WS_2) have been extensively studied and used as photoelectrodes in PEC solar cells. Single crystals of n-WSe_2 have shown reasonable conversion efficiency in liquid junction cells - 14% for red light and greater than 13% for solar illumination. Recently values upto 17% and 22% efficiency in energy conversion have been reported for single crystals of n-WSe_2 photoelectrodes. Therefore research on WSe_2 photoelectrode material takes a step closer to a viable liquid junction (PEC) solar cell. Thus a lot of research work is being done to study the effect of different parameters for the enhancement of efficiency of PEC solar cells fabricated with WSe_2. In this context, the author has studied the effect of partial replacement of selenium by sulphur in the lattice of WSe_2 in the photoconversion behaviour of WSe_2 PEC solar cells.

The work presented in the thesis has been divided into ten chapters. The first chapter provides a general introduction of layered TMDC compounds. The emphasis has been given on tin dichalcogenide crystals with their structure and various properties. In chapter two, a detailed information about the various experimental techniques employed for the work on crystal characterisation has been provided.

In chapter three, a methodical description of the growth of TMDC single crystals using vapour phase method has been given. The salient features of chemical vapour transport (CVT) and direct vapour transport (DVT) techniques have been thoroughly explained. Details of experimental set up, furnace construction, temperature regulating circuit and method of growth have also been narrated.

Chapter four thoroughly describes the effect of growth parameters on the growth of single crystals of SnSSe using a direct vapour transport technique. It has been realised that the rate at which the ampoule is cooled after the required period of growth in the high temperature growth zone has a significant effect on the quality and size of the grown crystals.

Chapter five describes in detail the growth and characterisation of SnS_xSe_{2-x} single crystals by a DVT technique. The growth conditions optimised in chapter 4 have been used for growing crystals of suitable dimensions required in number for characterisation work. DVT technique has therefore been rigorously used to grow mixed crystals of SnS_xSe_{2-x}

with x = 0.5, 1.0 and 1.5 individually in different ampoules. The grown crystals have been characterised by XRD and EDAX methods. Their various physical properties such as room temperature resistivity, high temperature resistivity, anisotropy, low temperature resistivity (77K to room temperature), Hall effect measurements, thermoelectricpower measurements were studied and the results have been systematically presented. A study of microstructures on the grown surfaces has been carried out systematically to unfold the mechanism of growth of these crystals.

Since the optical band gap of a semiconducting material plays a vital role in deciding its effectiveness in electronic devices, a detailed study of this parameter is extremely desirable. A complete study on its determination in SnS_xSe_{2-x} mixed crystals has therefore been made by optical absorption. The results thus obtained are described elegantly in chapter six.

The nature and quantity of the transporting agent alters the dimensions and the morphology of the obtained single crystals. Therefore, in addition to DVT technique, author has used iodine and NH_4Cl (which are in the solid form at the ambient temperature and so are quite easy to handle) as the transporting agents to grow single crystals of SnSSe of maximum possible size. Studies on growth, characterisation and various physical properties of these crystals have been described in chapter seven.

Chapter eight accounts for the necessary introduction to PEC solar cells. Different types of solar cells have been explained and discussed under their classified heads. The advantages of PEC solar cells over the solid state photovoltaic cells have also been thoroughly discussed.

Chapter nine describes author's attempts to fabricate PEC solar cells using WSe_2 and WSSe single crystals. Semiconductor electrolyte interfaces have been characterised by locating valence and conduction band edges, for which flat band potential measurements were carried out by using Mott Schottky plots. These studies justify the selection of appropriate electrolyte for PEC work. Various solar cell parameters have been determined for cells fabricated with WSe_2 and WSSe (i.e. sulphur substituted for selenium in equal proportion in the lattice of WSe_2) crystals. In order to see the effect of substitution of selenium by sulphur on photoelectrochemical response, the electrolyte and the intensity of illumination were kept constant and all the electrodes were prepared from crystals, showing absolutely plane faces obtained through cleaving with the help of adhesive tape.

Conclusions drawn from the entire work and its scope for future work finds place in chapter ten.