CHAPTER 9

CONCLUSIONS AND SCOPE FOR FUTURE WORK

<table>
<thead>
<tr>
<th>Contents</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1 Introduction</td>
<td>322</td>
</tr>
<tr>
<td>9.2 Conclusions</td>
<td>322</td>
</tr>
<tr>
<td>9.3 Scope for future work</td>
<td>325</td>
</tr>
</tbody>
</table>
9.1 INTRODUCTION

The group of materials possessing layered structures are an extensively investigated subject in current physics and chemistry. A vast number of promising technological applications deal with intercalation compounds of layered materials. Intercalation in transition metal dichalcogenides has been investigated by a number of research groups. The large volume of work carried out in this field is of importance, not only in basic science but also in industrial and energy applications.

Author has investigated into the feasibility of growing indium intercalated tungsten diselenide single crystals and to study their various physical properties along with their uses in the fabrication of photoelectrochemical solar cells. The entire work carried out in the above manner has been described in the present thesis. Attempts have been made here to arrive at some important conclusions on the basis of the present work and to find out the scope for future work.

9.2 CONCLUSIONS

Growth and characterisation of single crystals of indium intercalated tungsten diselenide report in particular was not up to date one. In the past, growth of WSe₂ crystals could be reported by direct vapour transport and chemical vapour transport techniques using several transporting agents.
The crystals grown by chemical vapour transport and their behaviour are influenced by the incorporation of the transporting agents in their lattice. To avoid contamination of the transporting agent, the WSe$_2$ and its intercalated single crystals have been grown by the direct vapour transport method leaving aside the use of any sort of transporting agent.

The lattice parameters 'a' and 'c' determined by X-ray studies for indium intercalated compounds of tungsten diselenide destined that 'a' parameter remains constant while 'c' parameter increases linearly with an increase in the indium content. An estimation of particle size ordains that the crystallite size of the particles goes on increasing with increasing concentration of indium in WSe$_2$ thereby suggesting an increase in defects with an increase in the amount of intercalation. This observation is in tune with the estimation of stacking fault probability which clearly indicates an increase in the probability of formation of stacking faults upon intercalation of WSe$_2$ by indium.

The electrical measurements made on the grown crystals indicate that the variation of conductivity and thermoelectric power with temperature confirm the semiconducting nature of the single the crystals of In$_x$WSe$_2$. The values of Seebeck coefficient and Hall coefficient were found to be positive and negative indicating that all the crystals of WSe$_2$ are p-type in nature and majority charge carriers in them are holes, whereas all indium
intercalated crystals of WSe$_2$ are n-type in nature and majority charge carriers in them are electrons. The values of $m_e^*$ (effective mass for electrons) and $m_h^*$ (effective mass of holes) have been determined from the room temperature values of thermoelectric power and the carrier concentration.

The presence of growth layers and hexagonal spirals on the as grown faces of the crystals suggest that both layer growth and spiral growth mechanism are responsible for the growth of these crystals.

The optical absorption study has clearly shown that WSe$_2$ and its indium intercalated compounds have direct as well as indirect band gap. The direct optical band gap linearly decreases with increase in indium content, whereas the indirect band gaps are not affected by intercalation. An accurate analysis of the absorption data has shown that the indirect transitions represented by the absorption curves are indirect allowed involving two different phonons. The energies of these phonons have been determined. It can be concluded from the study that two dimensional model cannot be used satisfactorily to describe the main optical properties of indium intercalated compounds of WSe$_2$.

The investigations on indium intercalated tungsten diselenide were carried out with a view to study the effects of intercalation on
the photoresponse of the photoelectro-chemical solar cells fabricated with $\text{In}_x\text{WSe}_2$ ($x = 0, 0.33, 0.50$) single crystals as photoelectrodes. After choosing $0.125 \text{ M} \text{KI} + 0.005 \text{ M} \text{I}_2$ and regarding it as the best electrolyte, its suitability was adjudged. For all the photoelectrodes, the locations of valence and conduction band edges using the Mott-Schottky plots were decided. The nature of these plots absolutely confirm the p-type behaviour of WSe$_2$ and n-type behaviour of indium intercalated WSe$_2$ single crystals.

It was realised after a detailed photoelectro-chemical study that intercalation of WSe$_2$ by indium does not yield any surprising improvement in its photoelectrochemical behaviour. As a first step towards the improvement in efficiency, experiments on selection of proper back ohmic contacts for the photoelectrodes of WSe$_2$ single crystals has been undertaken. It is indeed seen that there is a dramatic increase in the $I_{sc}$ and $V_{oc}$ on the selection of the material for the ohmic contact.

9.3 SCOPE FOR FUTURE WORK

The author has the relief of satisfaction that undoubtedly efforts have been made by him in this direction and to a certain extent has achieved success, there are a considerable number of aspects remained untouched and deserve further investigations.

Among the various methods for synthesising the intercalated compounds, author has used the direct method for their
preparation from the stoichiometric mixture using a direct vapour transport technique. It would have been a nice idea to compare the physical properties of some compounds intercalated by using different techniques. One can also study the effects of intercalation on polytypism of the layered WSe\textsubscript{2} single crystals. It is thrilling to know that strong bonds exist within the layer, while between the adjacent layers they are weak. As a consequence the crystals have facile basal cleavage. A detailed study of dislocations using transmission electron microscopy and weak beam technique should, therefore, be carried out. Since the intercalated crystals of WSe\textsubscript{2} possess a layered structure like MoS\textsubscript{2}, their lubricating properties can also be persuaded.

A remarkable observation in the present work is that unintercalated WSe\textsubscript{2} is p-type. Upon intercalation by indium it becomes n-type. Thus there is an evidence of charge compensation. It will be worthwhile to grow crystals of WSe\textsubscript{2} intercalated by different amounts of indium. One should start with very little amount of indium and go on increasing it gradually and make a complete study of charge compensation occurring as a result of indium intercalation.

Since the aims of the PEC studies described in this thesis was to know the effect of intercalation on the photoreponse of the PEC solar cells, efforts to increase the overall efficiencies of PEC solar cells were beyond the scope of the present thesis.
The overall efficiencies of the cells can be substantiated by adopting the following procedure

(a) selecting a proper material for the back ohmic contact provided to the photoelectrode.

(b) reducing the reflectivity of the semiconductor electrode surface.

(c) decreasing the surface and bulk recombination rate.

(d) lowering the bulk resistivity of the material.

(e) minimising the absorption losses in the electrolyte.

The effects of surface treatments such as chemical etching, photoelectrochemical etching and dye layer applications can also be undertaken to further increase the overall efficiencies. Author has remarkably shown that even the selection of a proper back ohmic contact material to the photoelectrode dramatically affects its photoresponse and so one can certainly expect that if all the above procedures are taken into account a drastic improvement in the photo-conversion efficiency can be certainly expected.