Transition metal dichalcogenides (TMDCs) have the general formula \(MX_2\), where 'M' is a transition metal from IVB, VB and VIB group of the periodic table and 'X' is one of the chalcogens namely sulphur, selenium and tellurium. Its basic structure of loosely coupled X-M-X sheets makes the material extremely interesting, because within a layer the bonds are strong while between the layer they are remarkably weak.

While going through the literature, it is noticed that the TMDC's have attracted many researchers from different fields due to their interesting properties and various applications e.g. (1) anode and cathode materials in photoelectrochemical (PEC) cells and for solar energy conversion, (2) high temperature lubricants, (3) battery cathode in rechargeable secondary cells and (4) selective oxidation and reduction reagents.

Some of the TMDC's are found to be of considerable interest in the search of durable and efficient non-oxide semiconducting photoelectrode systems which ultimately lead to the
fabrication of PEC solar cells. Visible and near infrared radiation absorbed by these compounds produce a d-d excitation of electrons which does not involve the breaking of essential crystal bonds. This leads to the generation of holes which do not directly lead to a photoelectrochemical decomposition of the substrate, therefore, both the n-type as well as p-type layered TMDC compounds can favourably be employed in the fabrication of regenerative electrochemical solar cells.

Tungsten diselenide (WSe$_2$) is a semiconductor that belongs to the layered TMDC group. The attractive properties of this material include the band gap in the region of optical solar energy conversion efficiency, anisotropy in its electrical behaviour and stability against photoconversion reaction. Values upto 17% and 22% efficiency in energy conversion have been reported for single crystals of n-WSe$_2$ photoelectrodes, but more common values vary between 8 and 10%. Therefore, research on WSe$_2$ photoelectrode material takes a step closer to a viable liquid junction (PEC) solar cell. With this thing in mind scientists all over the world (USA, South Africa, Japan, France, Germany, Spain, Israel, U.K., etc.) have concentrated their attention on the growth and characterisation of WSe$_2$ both in
the form of single crystals and thin films and photoelectrochemical characterisation of WSe$_2$ electrolyte interface. Thus a lot of research work is being done to study the effect of different parameters on the enhancement of photoresponse of the PEC solar cells fabricated with WSe$_2$. However, the work on intercalated crystals of tungsten diselenide, in this direction is almost negligible.

It was therefore, decided to grow Indium (In) intercalated compounds of WSe$_2$ in the form of single crystals. After their proper characterisation it is proposed to use them in the design and fabrication of liquid junction (PEC) solar cells. It is hoped that after enough research and development it will be possible to see the effect of intercalation on photoresponse of WSe$_2$ photoelectrodes.

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

Chapter 1 provides a general introduction of the layered TMDC compounds. The process of intercalation is also explained. The emphasis has been given on WSe$_2$ and Indium intercalated WSe$_2$ crystals. Their structure and various properties have been
A detailed information about the various experimental techniques employed for characterisation in the present work has been provided in chapter 2.

Chapter 3 describes methodically, the growth of TMDC single crystals using vapour phase method. 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 crystal growth have also been narrated.

Chapter 4 deals with growth, characterisation and studies of various physical properties of Indium intercalated WSe$_2$ single crystals. These crystals have been grown by DVT technique. It is found that all the crystals are grown in the form of platelets over the distributed charge inside the ampoule. Their characterisation is done by X-ray diffraction (XRD) and Energy Dispersive Analysis of X-rays (EDAX) methods. The crystallite size for each specimen, as measured perpendicular to the various planes of reflection have been
calculated using the Scherrer's formula. The effect of Indium concentration on particle size has been studied. The half widths of the X-ray diffraction lines with both even and odd values of 'l' have been used to make a realistic estimation of the growth fault probability 'α' and the deformation fault probability 'p'.

Various physical properties such as room temperature resistivity, low temperature resistivity (77 K to room temperature), Hall effect measurements and thermopower measurements of various unintercalated and indium intercalated WSe$_2$ single crystals have also been studied and the results are systematically presented.

The room temperature value of the thermoelectric power has been used to evaluate the effective mass of the charge carriers, holes in the case of WSe$_2$ and electrons in the case of indium intercalated WSe$_2$. From the values of thermopower at different temperatures the carrier concentrations for all the crystals have been determined at temperatures ranging from 40°C to 170°C.

A study of microstructures on the as-grown faces of the crystals reveals the presence of spirals on them thereby suggesting a screw dislocation mechanism for their growth.
Since the optical band gap of a semiconducting material plays a vital role in deciding the photoconversion efficiency of a solar cell fabricated with the semiconductor, a detailed study of this parameter is extremely desirable. A thorough study on its determination of optical band gap in WSe$_2$ and its indium intercalated compounds has therefore been made by optical absorption. The results thus obtained are elegantly presented in Chapter 5.

A necessary introduction to photoelectrochemical solar cells has been presented in Chapter 6. Different types of solar cells have been described and discussed by giving their classification. The advantages and disadvantages of PEC solar cells over the solid state photovoltaic cells have also been discussed.

Chapter 7 describes author's attempt to fabricate PEC solar cells with indium intercalated WSe$_2$ 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 e.g. the fill factor (f.f.),
efficiency (n.), open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) have been determined for all the cells fabricated with crystals intercalated by different amounts of indium. In order to see the effect of intercalation on photoresponse, 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 them with the help of adhesive tape.

From the studies on PEC characterisation of intercalated compounds of $\text{WSe}_2$, it is clear that in order to fabricate a PEC solar cell with high efficiency it is highly desirable to realise a good quality back ohmic contact. Electrical back ohmic contacts in PEC solar cells described in chapter 7 were made with Ag paint, because the aim was to study the effect of intercalation on photoresponse. However, in order to determine an appropriate ohmic contact which will provide improved photoresponse for $p$-$\text{WSe}_2$ layered single crystals, a comparative study of commonly used metal contacts like In, Ti-Ag, Au and Ag with usual Ag-paint has been conducted and is presented in Chapter 8.

It is observed that Ag-metal is found to be most suitable of these materials. Photoresponse from PEC solar cells fabricated
with p-WSe$_2$ using Ag-metal contacts has been compared with those prepared from Ag-paint. The implications have been discussed.

Conclusions drawn from the entire work and its scope in future work finds the place in chapter 9.