Much effort has been directed towards developing new and better solar energy conversion devices, and the interest is to develop new energy sources to supplement and eventually replace fossil fuels. In 1975, Gerischer succeeded in the direct conversion of solar energy into electricity by photoelectrochemical (PEC) solar cells. Semiconductor electrolyte interface in PEC solar cells is of prime importance in deciding the conversion efficiency. A study of performance evaluation of this interface is therefore highly desirable. It is essential that semiconductor surface should be non-corroding and stable under conditions of illumination and environment of electrolyte. It is also important that chosen semi conducting materials should have band gap in the range of 1.1 eV to 2.1 eV to provide good optical matching for better solar energy conversion. Since Transition Metal Dichalcogenides (TMDCs) occupy very favourable position in this regard, author has decided to concentrate on these materials for PEC solar cell investigations.

TMDCs have the general formula ‘MX₂,’ where ‘M’ is a transition metal from IVB, VB, and VIB group of the periodic table and ‘X’ is one of the chalcogenides namely Sulphur, Selenium and Tellurium. Its basic structure of loosely coupled ‘X-M-X’ sheet, makes the material extremely interesting because within a layer the bonds are sharp while between the layers they are remarkably weak.

While going through the literature, it is noticed that the TMDCs have attracted many researchers from different fields due to their interesting
properties and various applications e.g. (1) anode and cathode materials in photoelectrochemical cells 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 TMDCs are found to be of considerable interest in the search for durable and efficient non-oxide semi conducting photo electrode systems which ultimately lead to the fabrication of PEC solar cells. Visible and near infra-red radiation absorbed by these compounds produce a ‘d-d’ excitation of electrons which does not involve the breaking up of essential crystal bonds. This leads to generation of holes which do not directly lead to a photoelectrochemical conversion 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.

WSe$_2$ and WS$_2$ are semiconductors that belong to the layered TMDC group. The attractive properties of these materials include the band gap in the region of optical solar energy conversion efficiency, anisotropy in their electrical behavior and stability against photo conversion reaction. Values up to 17 % and 22 % efficiency in energy conversion have been reported for single crystals of n-WSe$_2$ photo electrodes, but more common values vary between 8 and 10 %.

From the variation of solar conversion efficiency versus the band gap ($E_g$) from literature it is found that the most promising material is one which has a band gap of 1.6 eV. The direct energy gap for WSe$_2$ is 1.35 eV and for WS$_2$ it is 1.77 eV. Among the TMDCs it is seen that the band gap can
be altered by varying the amounts of S and Se in the series WSxSe2-x; with
different values of x one can prepare a material of optimum band gap for solar
energy conversion.

It is generally observed that photo conversion efficiency obtained from
PEC solar cells is very low since a high degree of surface perfection is
required to obtain higher values of solar conversion efficiency. One has to
evolve a method by which the detrimental effect of steps on the surfaces of
the electrodes are alleviated.

In order to develop a PEC solar cell with maximum photo conversion
efficiency one can study in detail the effect of sulphur or selenium content in
WSxSe2-x on photo response and thereby undertake the pursuit of selecting the
most appropriate material for PEC solar cells.

In absence of any studies on PEC behavior of WSxSe2-x, author
proposed to carry out complete photoelectrochemical characterization of
single crystals of Tungsten Sulphoselenides WSxSe2-x (0 ≤ x ≤ 2) grown by a
chemical vapour transport technique.

The entire work proposed in thesis has been divided into 8 chapters.
Chapter -1 emphasis the importance of tungsten sulphoselenides. Review
of the existing information and scope for the present work are thoroughly
described in this chapter.

Chapter -2 provides a description of the various experimental
techniques employed for characterization in the present investigation.

Chapter -3 describes methodically, the growth of TMDC single
crystals using vapour phase method. The salient features of chemical vapour
transport (CVT) 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, characterization and studies of various physical properties of WS$_x$Se$_{2-x}$ ($0 \leq x \leq 2$) single crystals. These crystals have been grown by CVT technique. It is found that all the crystals are grown in the form of platelets in the colder region of the ampoules. Their characterization is done by X-ray diffraction (XRD) and Energy Dispersive Analysis of X-rays (EDAX) methods.

Various physical properties such as room temperature resistivity, Hall effect measurement and thermo power measurements of various mixed crystals of tungsten sulphoselenide single crystals have also been studied and the results are systematically presented.

The thermoelectric power measurement has been carried out as a function of temperature. From the study of thermoelectric power and Hall effect, it is concluded that all the members of the mixed dichalcogenides WS$_x$Se$_{2-x}$ ($0 \leq x \leq 2$) are p-type. The temperature variation of TEP has been studied and explained. The values of Fermi energy, the effective mass of the charge carriers i.e. holes and the scattering constants have been obtained from the analysis of the data on TEP. The information thus obtained is helpful in understanding the scattering mechanism in these semi-conducting compounds.

Since the optical band gap of a semi conducting material plays a vital role in its selection as an electrode in a photo electrochemical solar cell, a
detailed study of this parameter is extremely desirable. A thorough study on the determination of optical band gaps in CVT grown WS$_x$Se$_{2-x}$ (0 ≤ x ≤ 2) has therefore been made by optical absorption. The results thus obtained are elegantly presented in Chapter -5.

A necessary introduction to photo electrochemical solar cell 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 discusses the experimental techniques developed and used in the photo electrochemical characterization of WS$_x$Se$_{2-x}$ (0 ≤ x ≤ 2) single crystals grown by CVT technique. Techniques for improvement of PEC behavior of liquid junction cells fabricated with these crystals as anode have been thoroughly studied. Semiconductor electrolyte interfaces have been characterized by locating valence and conduction band edges, for which flat band potential measurements were carried out by using Mott-Schottky plots. Selection of appropriate electrolyte, suitability of semiconductor electrode surfaces, effect of cleaving, effect of ohmic contact, etching of electrode surfaces and use of monochromatic source of light for illuminating the semiconductor electrolyte interface have been investigated in detail and are described in this chapter.

Conclusions drawn from the entire work and scope for future work are described in Chapter -8.