Layered structures are adopted by elements, intermetallics, oxides, hydroxides, halides, chalcogenides and various complex systems. Many of them occur in nature and a large number of layered materials have been synthesised in the laboratory. They are characterised by strong bonding within the layer and weak (van der Waals) interactions between the layers. The strong anisotropy of the crystal structure influences many of their physical and chemical properties. The layered materials are in practical use in widely different areas such as tribology, catalysis and electrochemical energy storage.

Following the energy crisis in 1970s, considerable effort was expected in the investigation of new semiconductors for interfacial solar energy conversion devices. The semiconducting layered metal dichalcogenides form a major class of new materials that have been investigated for energy conversion in photoelectrochemical (PEC) cells and in solid state (p-n Schottky) solar cells. However, the layered compounds have not yet found large scale applications in electronic devices. This is due to the fact that only limited materials research has been done 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.

The layered transition metal dichalcogenides (TMDCs) are the most widely investigated of the layered materials with regard to their electronic
properties. The TMDCs are very interesting solids since they display the whole spectrum of electronic properties covering insulators, semiconductors, normal metals and super conductors. Such a variation in the electronic behaviour of the transition metal dichalcogenides is due to mainly d-electronic character of the valence and conduction band that are derived from the non-bonding d-states of the transition metal.

Further, among TMDCs, tungsten dichalcogenides (\(\text{WSe}_2\) and \(\text{WS}_2\)) have been extensively studied as photoelectrodes in liquid junction photovoltaic cells. Single crystals of \(n\)-\(\text{WSe}_2\) 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 \(n\)-\(\text{WSe}_2\) photoelectrodes. Therefore research on \(\text{WSe}_2\) photoelectrode material takes a step closer to a viable liquid junction (PEC) solar cell. With this thing in mind, scientists all over the world (U.S.A., South Africa, Japan, France, Germany, Isreal, U.K. and India etc.) have concentrated their attention on the growth and characterisation of \(\text{WSe}_2\) both in the form of single crystals and thin films and photoelectrochemical characterisation of \(\text{WSe}_2\) electrolyte interface. Thus a lot of research work is being done to study the effect of different parameters on the enhancement of photoresponse from PEC solar cells fabricated with \(\text{WSe}_2\).

A variation of stoichiometry of \(\text{WSe}_2\) affects its physical properties and thereby influences its quantum efficiency for energy conversion. Lower selenium content during the crystal growth increases the quantum efficiency of
WSe$_2$ diodes. Additionally, the open circuit voltage could essentially be increased up to 545 mV (under 70 mW/cm$^2$ illumination) by reducing selenium content down to 1%. In short, it is seen that power conversion efficiency may be enhanced by controlling the selenium content during the single crystal growth. Unfortunately, there is no systematic study on the effect of stoichiometry in WSe$_2$ or WS$_2$. It therefore led the author to carry out a systematic growth of off-stoichiometric compounds of tungsten dichalcogenides, characterise them and see the effect of stoichiometry variation on the photo response of photoelectrochemical solar cells fabricated with these single crystals materials as electrodes.

Dichalcogenides of interest as self lubricating solids include the disulfides, diselenides and ditellurides of the metals molybdenum, tungsten, niobium and tantalum. So far the entire concentration has been made on MoS$_2$ as the best lubricating substance. A comparison between the physical properties MoS$_2$ and WS$_2$ suggest that WS$_2$ can provide better high temperature and high pressure electrical conduction than MoS$_2$. This property together with a low coefficient of friction, makes WS$_2$ appear promising for use in sliding electrical contacts. At present, sliding electrical contacts are being made with MoS$_2$ which has a much higher resistivity as compared to WS$_2$. It was therefore thought worthwhile by the author to study the effect of pressure on the physical properties of off-stoichiometric tungsten dichalcogenides synthesized in the present investigation.

The entire work proposed in the thesis has been divided into 12 chapters.
Chapter - 1 emphasises the importance of tungsten dichalcogenides and their off-stoichiometric compounds. Review of the existing information and scope for the present work are described.

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

A description of the vapour transport technique is given in Chapter - 3. Details of experimental set up, temperature controlling system, construction of the furnace etc. have been thoroughly described.

Chapter -4 deals with characterisation of the as grown single crystals of WSe$_2$ and its off-stoichiometric compound. Synthesised WSe$_{2-x}$ ($x = 0, 01$) were characterised by XRD, EDAX and optical microscopic techniques. The various transport property measurements made on these crystals have been thoroughly described.

Studies on growth, characterisation and various physical properties of WS$_{2-x}$ ($x = 0, 01$) single crystals grown by the physical vapour transport technique find a place in Chapter - 5.

Since the optical band - gap of a semiconductor plays an important role in its selection as a solar cell base material, a detailed study of the absorption spectra taken from WX$_{2-x}$ ($x = 0, 01$) single crystals has been carried out and the effect of stoichiometry on band gaps of WX$_{2-x}$ ($X = S, Se$) has been thoroughly discussed in Chapter -6.

Chapter -7 introduces and reviews the techniques for high pressure generation and measurement. Whereas Chapter -8 describes the variation of
electrical transport properties with pressure for WX$_{2-x}$ ($X = S$, Se and $x = 0, 0.1$) single crystals.

A necessary introduction to photoelectrochemical solar cells has been presented in Chapter - 9. 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 - 10 deals with the fabrication of photoelectrochemical solar cells using WSe$_{2-x}$ ($x = 0, 0.1$) single crystal photoelectrodes. This chapter also includes the semiconductor electrolyte interface characterisation in terms of location of valence band, conduction band edges and Fermi levels. The effect of stoichiometry variation on photoresponse of WSe$_2$ single crystals has been thoroughly investigated and described in this chapter.

Work similar to above has also been carried out on WS$_{2-x}$ ($x = 0, 0.1$) single crystals and the same has been thoroughly described in Chapter 11.

The thesis ends with the general conclusion drawn from the present investigation and scope for future work in Chapter - 12.