Science has helped the world in taking quantum leaps, built up a glittering civilization, opened up innumerable avenues for the growth of a vast and ever-widening ocean of knowledge and has added to the power of man to such an extent that for the first time it is possible to conceive that man can triumph over and shape his physical environment. The enthusiasm in the study of crystals, one of the magnificent branches of physics, has had a steady following even from the Middle Ages where people were always looking for what was called the ‘Philosopher’s Stone’ which was supposed to have the virtue of turning base metals into gold. Today the studies in electronics, in semiconductors form the backbone of human progress and, their applications demand a fine co-ordination among scientific communities.

Certainly science illumines the dark corners of life and makes us face reality.

Layered compounds, transition metal dichalcogenide are interesting materials in their own right. Within a layer, the bonds are strong, while between adjacent layers they are remarkably weak. As a consequence the crystals have facile basic cleavage, lubricity and marked anisotropy in many physical properties which account, for the great concentration in this family of materials. Imbued with this right sense, crystal growers have adopted consummate techniques to achieve their goals.

For the preparation of single crystals, the discovery of the chemical vapour transport (CVT) technique has been of great influence. It enabled to grow single crystals of substances hitherto known as ‘difficult materials’.

This thesis is a comprehensive account of the experimental and theoretical aspects of different stages of growth and properties of transition metal diselenides. Doped and undoped tungsten diselenide single crystals have been successfully grown by chemical vapour transport technique.

The thesis is divided into six chapters. Chapter one deals with the various methods of crystal growth. A special emphasis has been laid on the crystallization from the vapour for it plays a key role in semiconductor electronics. Keeping in mind the Kaldis’s rules, the importance of chemical and geometrical parameters on chemical vapour transport are discussed. Different temperature profiles for CVT are also explained. The aim of the present investigation in the light of merit and demerit of CVT are also discussed.

Chapter two focuses the thermodynamics of chemical vapour transport technique. While discussing various thermodynamical models; the importance of making thermodynamical analysis of CVT and, a particular model are described. Thermodynamical feasibility of some ternary chalcogenides [CuInS2, CuInSe2, CuAlS2, CuAlSe2, CuGaTe2, CuGaTe2, AgGaS2, AgGaSe2, AgGaTe2, AgInSe2, AgInTe2] using iodine or hydrogen iodide as
transporting agents is discussed with the help of the model. Prediction of source zone and growth zone temperatures has been done by applying the model to a new binary system tungsten diselenide \([\text{WSe}_2]\).

Chapter three gives an attention to the practical aspects of chemical vapour transport technique and growth of crystals employing both CVT and direct vapour transport [DVT]. The growth parameters of doped and undoped tungsten diselenide are found to corroborate the theoretical model. The temperature gradient's role on the growth of crystals during the CVT is experimentally studied. It has been observed that a particular temperature profile which is very close to the theoretical limits is found suitable for growing crystals of appreciable size.

Chapter four consists of electrical, structural and elemental characterization of the grown crystal. Hall coefficient, mobility and charge carrier concentration at the ambient conditions for the crystals were measured. Conductivity studies on crystals have been successfully performed, and a semiconductor to metallic transition is observed in titanium doped tungsten diselenide \([\text{W}_{0.97}\text{Ti}_{0.03}\text{Se}_2]\) crystals. The structural evolution and compositional analysis have been done by X-ray powder diffraction and Energy dispersive X-ray analysis techniques respectively.

Chapter five stands for the microhardness test performed on the grown crystal. Different microhardness tests, measurement corrections and precautions are discussed in the earlier portions. The hardness variation of the crystals and the stress flow patterns near the indentation marks are studied in detail. It is found that the variation in the hardness value of the doped crystal is due to the slip system caused by the substitutional impurity present in the matrix. The study of stress distribution near the indentation marks reveals that the stress distribution on the indenter-indentation interface is not a constant but rather a function of the indentation size. The idea of resistance pressure of the crystal specimen is also found applicable to pure and doped \text{WSe}_2.

Chapter six explores morphological survey of doped and undoped tungsten diselenide single crystals. Optical and Scanning electron microscopes are used to study the surface features of the grown crystals. It is observed that both doped and undoped \text{WSe}_2 crystal surfaces reveal an appearance of sideways growing plates overlapping each other. Successive etching has been performed on the crystals to study the nature of dislocation.

Finally the thesis ends in a conclusion which is a looking glass to the scope of future research on this work. The references have been listed at the end of each chapter.

Some part of the work has been presented at various seminars and published in scientific journals.
Research papers published / communicated for publication

1. The growth and thermodynamical feasibility of tungsten diselenide single crystals using chemical vapour transport technique

2. Design and application of two zone tubular furnace for the growth of semiconductor crystals.

3. Micro-indentation studies on single crystals of doped and undoped tungsten diselenide grown by physical vapour transport.
   Crystal Research Technology (communicated)

4. A crystal growth system with modified pulling arrangement and temperature controller.
   Measurement Science Technology 5 (1994) 1018

Papers presented

1. Growth of Tungsten diselenide by vapour transport technique.
   XI International Conference on crystal growth Hague, Netherland 1995

   VII Kerala Science Congress, Kochi, Kerala 1996

3. Electrical conductivity behavior of doped tungsten diselenide single crystals.
   National Conference on Fundamentals of Crystal Growth, Anna University, Madras, 1996

4. Thermodynamical feasibility study of some I-III-VI ternary compounds for chemical vapour transport (CVT) growth technique.
   International Conference on Chemical and Biological Thermodynamics, Amritsar, India, 1997