The main thrust of the research for this thesis is focused on Zinc Sulfide (ZnS) nanostructure and growth of Bismuth selenide (Bi$_2$Se$_3$) single crystals by vapour phase technique.

ZnS is a direct wide band gap compound semiconductor belonging to II-VI group with a high index of refraction and a high transmittance in the visible range and is one of the most important material in photonics research. Zinc sulfide has two types of crystal structures: hexagonal wurtzite ZnS (referred to as “hexagonal phase”) and cubic zinc blende ZnS (referred to as “cubic phase”). Typically, the stable structure at room temperature is zinc blende, there are few reports of stable wurtzite ZnS also. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. The transition from the cubic form to the wurtzite form occurs at around 1020 °C.

The explosion in both academic and industrial interest over the past 20 years arises from the remarkable variations in fundamental electrical, optical and magnetic properties that occur as one progresses from an “infinitely extended” solid to a particle of material consisting of a countable number of atoms.

As a one-dimensional nanostructure, ZnS has been synthesized as nanowires, nanobelts, and nanocombs. ZnS nanobelts have been doped with manganese, by post annealing, without changing the crystallography of the ZnS nanobelts. Also, optically pumped lasing has been shown in single ZnS nanobelts. Recently ZnS has also been synthesized as nanohelices.

ZnS doped with manganese without changing their crystallography exhibits attractive light-emitting properties with increased optically active sites for applications as efficient phosphors. All of these properties make ZnS one dimensional nanostructures attractive candidates for use in devices and other technological applications. ZnS is also an important phosphor host lattice material used in electro-luminescent devices (ELD), because of the band gap large enough to emit visible light without absorption.
and the efficient transport of high energy electrons. Bhargava et al. first reported luminescence properties of manganese doped ZnS nanocrystals prepared by a chemical process at room temperature, which initiated investigation on luminescent ZnS nanostructures. ZnS nanobelts doped with manganese were synthesized by hydrogen-assisted thermal evaporation and exhibited lasing action. ZnS nanostructures synthesized by chemical vapor deposition (CVD) have a large number of defects, perhaps due to oxygen incorporation. Nath et al. studied the green luminescence of ZnS and ZnS:Cu quantum dots embedded in zeolite matrix. This study demonstrates the technological importance of semiconductor quantum dots prepared by low cost chemical route. Manzoor et al. reported the growth of Cu⁺-Al³⁺ and Cu⁺-Al³⁺-Mn²⁺ doped ZnS nanoparticles by wet chemical method for electroluminescent applications. The high fluorescent efficiency and dispersion in water makes ZnS nanoparticles an ideal candidate for biological labeling.

Compare to other methods, the microwave irradiation method is very fast technique to produce uniform size particles with high purity owing to short reaction time. It is found that this method is non toxic route to produce ZnS nanoparticles. Looking towards the synthesis on nanoparticles by chemical route, molarity of the solution used makes great impact on the properties of prepared nanostructures. Keeping that point in mind the molarity variation of the precursors used for the synthesis of ZnS nanoparticles in the present work is carried out.

Apart from the above work, we did study on Bi₂Se₃ single crystals and characterized it by various techniques. Because the narrow-gap-semiconductor Bi₂Se₃ (E₉ = 0.3 eV) and its alloys are considered to be the prime candidate for the best room temperature bulk thermoelectric materials found to date. The bonding between Bi-Se is predominantly covalent in character, while between Se-Se is of weak Van der Waals type with figure of merit (ZT) about 1 at room temperature. Looking to this aspect, we have grown single crystals of Bi₂Se₃ by vapour phase technique. But if we look at the literature most researchers have grown this crystal by Bridgman technique. Henceforth, this study on transport properties will provide a unique literature not available until now on Bi₂Se₃ single crystals grown by vapour phase technique.
The whole thesis has been divided into 7 chapters and their brief descriptions are narrated below:

**Chapter 1** deals with the complete literature survey on the existing information of Zinc sulphide material, its structure, various properties of Zinc sulphide along with its applications. This chapter also describes the present status of the research work going on in the field of synthesis of Zinc sulphide nanostructures across the globe.

**Chapter 2** provides the basic principle and instrumental details of EDAX (Energy Dispersive Analysis of X-rays), XRD (X-ray powder diffraction), TEM (Transmission Electron Microscopy), Raman spectroscopy, UV-VIS spectrophotometer, Photoluminescence spectra and TGA (Thermogravimetric Analysis) techniques used for characterization of ZnS nanoparticles prepared in the present work. Besides this, the fundamental working principles of Atomic Force Microscope (AFM), resistivity, Seebeck coefficient, and Hall effect measurement setup is also included in this chapter which were used to investigate thermoelectric properties of as the grown Bi$_2$Se$_3$ single crystals.

**Chapter 3** provides the details of the methods used for synthesis of ZnS nanoparticles by microwave irradiation. Discussion on effect of different precursors of Zn and S for preparation of nanoparticles and effect of molarity on particles size is also included in this chapter.

**Chapter 4** consists results and discussion of structural characterization of various ZnS nanoparticles synthesized by microwave irradiation method. EDAX provides information about chemical composition and purity of the sample with no foreign elements presence. XRD and Selected Area Electron Diffraction (SAED) confirms single crystalline compound with cubic structure having lattice parameters of $a=5.38$ Å with its bulk counterpart having value of $5.40\text{Å}$. The statistical analysis by TEM reveals the average nanoparticles diameter to be 8 to 10 nm. The crystallite size calculation using different established methods was lying between the range of 5 Å to 152 Å. The size distribution is having large variation and can be considered as
interesting point for deeper investigation of ZnS particle prepared using different methods and precursors.

**Chapter 5** consists of results and discussion of optical and thermal characterization of various ZnS nanoparticles synthesized by microwave irradiation method. Absorption spectra of various ZnS nanoparticles prepared exhibits the band edge approximately lying near 310 nm in comparison to the bulk material (i.e. 340 nm). While PL spectra of ZnS particle indicates emission wavelengths at 558,512,511,512,600,511,511,558 nm at different excitation wavelengths (511, 511, 312, 312, 312, 512, 511, 312,330 nm respectively). Thermogravimetric analysis of various ZnS nanoparticles shows their thermal stability upto 300°C and indicates their decomposition after that. The values of calculated thermal activation energy using Broido equation are also included here. Raman studies of these particles reveals Zinc blende ZnS belong to the F\textsubscript{4}3m (T\textsubscript{d}\textsuperscript{3}) space group having two atoms per primitive unit cell. It is most easily visualized as two face-centered cubic lattices displaced from one another by one-quarter of a body diagonal. One lattice consists of zinc atoms and the other of sulphur atoms and thus has six degrees of freedom, three acoustic and three optical phonons.

In consideration with Brafman and Mitra [30] we also have observed doubly degenerate transverse optical (TO) and single longitudinal optical (LO) zone center phonons of cubic ZnS crystals at 276 and 351 cm\textsuperscript{-1}, respectively, and the E\textsubscript{2} modes of wurtzite type ZnS at 72 and 286 cm\textsuperscript{-1}. The absence of any peak around 72 and 286 cm\textsuperscript{-1} in the Raman spectra of the present nanostructured ZnS sample confirmed the phase of the sample to be cubic. Raman peak at 340 cm\textsuperscript{-1} which are consistent with the T\textsubscript{2}(LO) modes and matches with the previous Raman studies for zinc blende ZnS results[31-33]. The disappearance of the transverse optical (TO) mode is considered due to the strong fluorescence background and extremely weak intensity as compared with LO mode [27]. The first order LO phonon peak of ZnS samples in the present study are shifted to lower frequency and the peak is asymmetrically broadened towards lower frequency side. Such a phonon softening and line broadening of the peaks can be attributed to phonon confinement effect.
Chapter 6 includes information about properties and applications of thermoelectric material along with growth of Bi$_2$Se$_3$ single crystals by vapour phase technique. This chapter also incorporates characterization of this crystal by EDAX, XRD, AFM and Seebeck coefficient, resistivity, Hall effect measurements from low temperature to near ambient temperature.

Chapter 7 deals with the conclusion drawn from the entire research work and scope for the future work.