SUMMARY

Tetrahedral semiconductors: Si, Ge, SiC, and the III-V and II-VI compounds have dominated both research and applications to such an extent that it is hardly realised that non-tetrahedral semiconductors even exist, let alone that they are extremely numerous and can show interesting and unusual combination of properties. Also there could be many kinds of application for semiconductor compounds that are rather different from the conventional tetrahedral materials: in lighting, in thermoelectric cooling and power generation and in sensors. In fact many other structure types can give rise to semiconductivity, which is not a rare phenomenon found, but have received less attention. These compounds can be categorised in terms of energy gap and even, perhaps, via a new concept: 'aniso-electronic substitution' (i.e. of donors or acceptors compensated for by ordered point defects), to optimise the choice of band structure and density of states (the latter being particularly important for improving thermoelectric devices and not without interest for signal handling and control devices since carrier mobility could be increased).

Antimony telluride belongs to the family of V_2VI_3 compounds. Among the V_2VI_3 compounds, Sb_2Te_3, Bi_2Te_3 and Bi_2Se_3 are isomorphous having hexagonal layered structures with the space group $R\bar{3}m$. These materials have widescope applications as strain gauges, precise temperature control of laser diodes, electromechanical devices, optical recording system, thermoelectric devices etc. Specifically, they find most important thermoelectric applications like thermoelectric cooler, thermoelectric generator, thermal sensors and IR thermopile detector. The device efficiency depends on material property and the performance of the material in this case is measured by the thermoelectric figure of merit. Even though Sb_2Te_3 and Bi_2Te_3 are both narrow band-gap materials with p-type conductivity, it has been found that the thermoelectric figure of merit of Sb_2Te_3 is

less than that of Bi_2Te_3. Also it is known that the solid solution alloying increases the thermoelectric figure of merit by reducing the lattice thermal conductivity. So it has been our subject of interest to enhance the figure of merit of Sb_2Te_3 by incorporating III, IV or V group elements in Sb_2Te_3 system. Moreover, since the melting points of these materials are low compared to other important thermoelectric materials like $CoSb_3$, $IrSb_3$ etc., they can be conveniently prepared in a laboratory having moderate facilities.

In the thesis "Experimental Investigation of pseudobinary antimony telluride systems", the results of the work carried out on crystal growth, etching, optical and thermoelectric properties of In and Bi incorporated Antimony telluride systems have been reported. A thorough investigation of $Bi_xSb_{2-x}Te_3$ (x=0,0.2,0.5 and 1) solid solution crystals has been carried out. Extensive work on the thermoelectric properties of the solid solutions of Bi_2Te_3-Sb_2Te_3 has been reported in literature but not much is reported on the thin films of $BiSbTe_3$. Hence it has been chosen as a representative system by the candidate and thin film preparation and electrical and optical study have been carried out on this system.

The thesis is presented in thirteen chapters.

Chapter 1 gives a general introduction to the subject under study, the importance of the thermoelectric materials and their applications. A brief survey of earlier work reported on Sb_2Te_3 crystals and thin films is given.

Chapter 2 describes different techniques used for the melt growth. Chapter 3 includes the techniques that can be used for the compositional and structural characterization of the crystals. Chapter 4 discusses the defects in crystals, their practical significance and techniques to detect them. Particularly, the techniques of revealing/ detecting dislocations in crystals have been discussed. Chapter 5 deals with a discussion of thermoelectricity and thermoelectric materials and their properties in general. Applications of optical measurements on these materials are the subject of Chapter 6. Specifically, the phenomena of optical absorption and absorption mechanisms in semiconductors are described. General optical spectrometric equipments used for obtaining the band gap are also discussed in this chapter. Chapter 7 includes the growth of single crystals of $Bi_xSb_{2-x}Te_3$ (x = 0, 0.2, 0.5, 1) and $In_{0.2}Sb_{1.8}Te_3$ by the Bridgman and Zone melting techniques. The crystals were prepared using 5N purity elements in stoichiometric proportion under a temperature gradient of ~30^0C and at a rate of 0.35cm/h. The growth features observed on the surface of the as-grown crystals have been studied using optical and electron microscopy. Chapter 8 includes dislocation study of the crystals under study. A nitric acid based reagent capable of revealing dislocations intersecting the cleavage planes of these crystals has been developed and tested by various ways like successive etching, scratch test and etching and matching of opposite cleavage planes. The dislocation density was measured for all the systems under study. The results of these studies have been detailed.

The X-ray powder diffraction analysis was carried out for the grown crystals using ASTM charts and computer program. The stoichiometric analysis of elements in the samples were made by EDAX technique. The structual and compositional characterizations of the crystals under study are given in Chapter 9. Chapter 10 deals with the experiments and results of the thermoelectric measurements carried out on the pseudobinary antimony telluride systems. The techniques employed for these measurements have been described. The electrical conductivity (σ) measurements of the samples were carried out using the four probe technique on the cleaved samples in the temperature range from 20K to 420K. The scattering mechanism prevalent in them was determined. Thermopower (α) measurements were carried out using the differential technique in the temperature range from room temperature to 390K. The room temperature thermal conductivity (κ) measurements of the samples were carried out using the dynamic method. The samples used were cut, lapped and polished prior to measurements. The room temperature figure of merit (Z) was hence evaluated using the observed values of σ, α and κ. Significantly it has been observed that the $Bi_{0.5}Sb_{1.5}Te_3$

crystal has the highest thermoelectric figure of merit amongst the systems unde study

Chapter 11 is devoted to the optical band gap determination of the system under consideration. The optical absorbance spectra of $Bi_xSb_{2-x}Te_3$ (x = 0, 0.2 0.5, 1) and $In_{0.2}Sb_{1.8}Te_3$ were obtained using FTIR spectrometry. The data have been used to evaluate optical band gap and its dependence on composition.

Chapter 12 deals with the various techniques and importance of thin film preparation. Chapter 13 deals with the thin film preparation and characterization of $BiSbTe_3$. The films of various thicknesses were prepared using PVD technique. The X-ray diffractograms of the films were obtained. The effect of annealing on the diffraction pattern has been studied for the films of different thicknesses and the defect density was evaluated from the FWHM of the diffraction peaks. Optical as well as electrical conductivity measurements were carried out on films of different thicknesses. The electrical conductivity was also measured through heating and cooling cycles of the films in the temperature range from room temperature to 150^0C. The activation energy of the films was evaluated. The optical band gap were evaluated as functions of thickness and heat treatment using the absorbance spectra.