SUMMARY

Apart from the intensive research still going on on the primitive elemental semiconductors Ge and Si, at present much more attention is being paid to compound semiconductors, viz., binary, ternary and quaternary ones.. Among the binary compounds, the group II-IV, IV-VI, III-V and V_2-VI_3, semiconducting compounds have been receiving considerable attention due to their important photoconducting, photovoltaic, electrooptic and general electronic properties. Their pseudobinary and ternary compounds have also found their due significance. For the study of basic semiconducting properties, it is of primary importance that these properties be measured on bulk single crystals. The single crystals themselves are also most frequently required directly or indirectly for device fabrication. The performance of the devices principly depends on the bulk crystalline characteristics. Of the crucial importance among the characteristics are purity, perfection and homogeneity. Because of this, the field of crystal growth carries no less significance than the crystals themselves. In most of the applications the semiconductors are used in the form of single crystals or thin films or both at a time. These materials have been subject of study by quite a number of workers. Most of these studies are concerned with thin films and their opto-electronic characterization. The work reported in the present thesis includes crystal growth, dislocation etching and

hardness of crystals, as well as optical band gap electrical properties and photoconductivity of thin films. The materials included in the study are $Sb_{0.2}\,Bi_{1.8}Te_3$, $Sn_{0.2}\,Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$.

The thesis is presented in two parts. Part-1 of the thesis consists of two chapters. Chapter 1 gives a general introduction to the basic background for the present work. A brief survey of earlier work reported on growth, chemical etching and microhardness of the crystals (Bi_2Te_3 in particular) is given. It also includes reports on optical and electronic properties of these materials.

Chapter 2 deals with the experimental techniques used during the course of the present work. The techniques include the crystal growth, thin film preparation, optical microscopy, hardness indentation, electrical resistivity, Hall measurement, Thermoelectric power, optical band gap and photoconductivity measurments.

Part 2 of thethesis consists of five chapters. Chapter 3 deals with the results of growth of $Sb_{0.2}\,Bi_{1.8}Te_3$, $Sn_{0.2}\,Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ single crystals.The crystals were grown by Bridgman-Stockbarger method. Various methods of crystal growth in general and of crystal growth from melt in particular have been discussed. General aspects of chemical etching of a crystal surface and its use as a tool to reveal line imperfections, i.e., dislocations in crystals are briefly described. This chapter also presents study of growth of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ single crystals by Bridgman-Stockbarger method. Fairly large good quality crystals of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ could be obtained by the Bridgman-Stockbarger technique at the ampoule lowering rate of 3.5 mm / hr and temperature gradient around 45°C /cm. The $Sb_{0.2}Bi_{1.8}Te_3$ single crystals have also been grown by Zone melting method and the growth features on the free surface of the crystal have been studied. In the case of Bridgman growth, increase in growth velocity is observed to decrease the crystal perfection. The dislocation densities are found to be in the range of 10^5 cm^{-2} in the crystals grown under the above stated conditions. A new chemical etchant: 3 part conc. solution of iodine in methanol, 0.3 part HCl (70%) and 0.3 part HNO_3 (70%) was developed and found to be capable of revealing dislocations intersecting the cleavage plane. The XRD characterization of the grown crystals has been done.

Indentation hardness and creep of crystals are the main focus of the present study. Chapter 4 gives a qualitative survey of various techniques and empirical theories involved in this field. Particularly, a diversity of results reported in literature has been emphasized to indicate the complexities of these properties. Chapter 4 deals with hardness studies on $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$

and $Bi_2Te_{2.8}Se_{0.2}$ crystals. The variation of hardness with applied load has been studied in detail. The effects of quenching on the load dependence of hardness have been investigted. Particularly, the observed complex low load dependence of hardness has been explored in light of above investigations. The results indicate that the hardness peaks obtained in the low load range may be explained in terms deformation induced coherent regions. The dependence of hardness on loading time has been studied at various temperatures. The results obtained in these experiments have been used to study the creep characteristics of these crystals. The surface anisotropy of hardness has been studied using Vickers indenter. The results have been interpreted in terms of crystal plus indenter symmetry. Interestingly, the Vickers indenter is found to successfully reveal the surface anisotropy in $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals.

Chapter 5 presents study of electrical resistivity of bulk as well as thin films of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ and its variation with temperature. The study also includes the effect of film thickness. The chapter also discusses the results obtained of the thermoelectric power, carrier – concentration and mobility of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals.

Chapter 6 discusses the results on optical band gap of thin films and crystals of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$. These also include the effect of film thickness on optical band gap. The results are discussed invoking the size effect operative in the thickness range used.

Chapter 7 deals with photoconductivity measurements on the $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ thin films. The photoconductivity rise and decay observed in the present case show the presence of shallow traps. The photoconductivity variation with temperature up to 353 K has also been studied.