SUMMARY

For about last two decades or so a huge variety of compound semiconductors has emerged as useful components of application oriented devices. Among such binary compounds, the IV-VI chalcogenides have their own merits next to the III-V compounds. These are all semiconductors of either p or n-type. These compounds have been thought to be promising candidates for photovoltaic energy conversion. Their thin films also have great potentiality as memory switching devices. 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 and junction characteristics of thin films. The materials included in the study are SnSe, SnS, SnSe$_2$ and SnTe.

The thesis is divided into two parts. Part - A contains general information which provides the basic background for present work. Chapter - 1 of this part discusses various methods of crystal growth in general and of crystal growth from melt in particular. 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.
Hardness and indentation creep of crystals are the main focus of the present study. Chapter - 2 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.

Optical measurements are most important means of determining the band structure of semiconductors. The absorption spectra in particular are supposed to be quite precise as regards evaluation of band gap. Chapter - 3 deals with a brief review of such studies done by previous workers. It also includes the electrical properties of crystals and films.

Chapter - 4 gives the general information on SnSe, SnS, SnSe₂ and SnTe crystals with regard to the structural and various electrophysical properties, available in literature.

Part - B of the thesis consists of five chapters. Chapter - 5 deals with the experimental techniques used during the course of the present work. The techniques include crystal growth, chemical etching, optical microscopy, hardness indentation, deformation and thin film preparation.

Chapter - 6 presents study of growth of SnSe, SnS and SnSe₂ single crystals by Bridgman - Stockbarger method. The effect of growth velocity on perfection of crystals has been studied. The results indicate that the
speed 0.4 cm/hr and temperature gradients around 45 °C/cm to 55 °C/cm are best suited for growth of these crystals. In the case of SnSe crystal growth the screw dislocation mechanism is found effective at low growth speeds whereas the layer mechanism is dominant at higher speeds. On the other hand, in the cases of SnS and SnSe₂, the layer mechanism of growth dominates at all growth speeds. Interesting results of vapour condensation overgrowth on the cleavage surface of SnSe crystal have also been discussed.

Chapter - 7 deals with chemical etching as applied to revealing dislocations. Development of new etchants to reveal dislocations intersecting the cleavage planes (001) of SnSe and SnS crystals has been detailed. It has been found that the etchant consisting of I₂ in methanol, methanol and conc. HNO₃ is suitable for SnSe crystals. Whereas, the etchant consisting of HCl and CH₃COOH works well in the case of SnS. Dislocation etching tests carried out are reported.

Chapter - 8 deals with hardness studies on SnSe, SnS and SnSe₂ crystals. The variation of hardness with applied load has been studied in detail. The effects of quenching and cold working on the load dependence of hardness have been investigated. 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 (III)
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 creep activation energy has been found to be around 0.2 Kcal/mole for these crystals. The surface anisotropy of hardness has been studied using Knoop as well as Vickers indenters. 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 SnSe, SnS and SnSe₂ crystals. The Knoop indenter gives similar results but the anisotropic differences are larger compared to those yielded by the Vickers indenter.

Chapter - 9 discusses the results obtained in thin film study of SnSe, SnTe and SnSe₂. These include the effect of film thickness on optical bandgap, the resistivity variation with temperature and associated activation energy. The results are discussed invoking the size effect operative in the thickness ranges used. This chapter also includes the I-V and C-V characteristic studies of the junctions, p-SnTe/n-SnSe₂ and In/p-SnTe fabricated as thin film structures.