# 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. The elements of the IV subgroup are characterised by Selenides of MeSe type where Me stands for metal. In addition to this, Silicon, Germanium and Tin are also known to form compounds of $MeSe_2$ type. On passage from Germanium to Tin and Lead Selenides, the crystal lattice changes from rhombohedral for Germanium Selenide to cubic for Lead Selenide. These are all semiconductors of either p or n type. Tin mono and di Selenides have band gaps of about 0.9eV and 1.01 eV, respectively. Both of these compounds have considerably high absorption coefficients, more than $10^4 cm^{-1}$ in the strong absorption region. Therefore these compounds have been thought to be promising candidates for photovoltaic energy conversion. Thin films of Tin Selenide have great potentiality because of their application as memory switching devices.

The present investigation, the results of which are compiled in the form of this thesis, deals with the

growth, characterization and electrooptical properties of Tin mono and di Selenides in the bulk as well as thin film forms. Although these compounds have been studied to some extent in the past in relation to their basic properties, reports on the study of these compounds with reference to fabrication of their hetrojunctions are very few. Crystals of SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic have been grown. Characterization and measurements of electrooptic properties of the bulk of these materials and their thin films have been done. Also, in the case of SnSe, a comparative study of the films obtained by direct evaporation of the compound and those obtained by solid state reaction has been carried out.

The crystals of SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic have been grown by Bridgman-Stockbarger technique. After a large no. of trials the temperature gradients of 55°C/cm, and 33 °C/cm were found to yeild fairly good crystals of SnSe and $SnSe_2$, respectively. Also the lowering speeds were varied but the most suitable speed for growth was found to be 4mm/hr. The size of the crystals grown ranged around 2.5 cm in length and 1 cm in diameter. While the SnSe crystal has an easy and planar cleavage along (001), the $SnSe_2$ crystals have very soft cleavage along (0001), the cleavage resulting into severe plastic deformation. In the case of the eutectic, it was observed difficult to grow the crystals. At the temperature gradient of 50° C/cm and ampoule lowering speed of 4mm/hr, crystals having grains of large size could be obtained.

The crystals were characterized using X-ray diffraction. From the comparison of observed and calculated d values, the crystals were confirmed to belong to the respective systems and to have the parameters reported in the literature. It is important to note that in the case of SnSe, there is no $SnSe_2$ peak observed, indicating the material to be single phased unlike as reported by Albers who observed the material to contain small precipitates of $SnSe_2$. This may be becuase of the compound preparation method of long duration alloy mixing and synthesis effected by rocking of the molten alloy used in the present investigations. Also during the crystal growth, the growth rate was much lower than that used by Albers.

Thin films prepared from SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic compounds were deposited using the thermal evaporation technique. SnSe films were also obtained by solid state reaction. The films of various thicknesses were deposited at various substrate temperatures. The $SnSe_2$ films were deposited on different substrates like mica, glass and NaCl crystal in order to improve its conductivity. Films were characterised using X-ray diffraction, particularly the films obtained on glass substrates.

Electrical properties of the bulk crystals as well as thin films have also been studied. The measurements were obtained under different varied parameters like nature of substrates, substrate temperature, film thickness, thermal cycling and heat treatment. Valdės method was used for resistivity measurement of the crystals and linear four probe method for thin films.

In the cases of $SnSe_2$ and $SnSe-SnSe_2$ crystals, the resistivity was observed to decrease with the increase in temperature. Whereas, SnSe showed a different trend. From room temperature to 95°C, the resistivity increased and from 95°C onwards the resistivity decreased. This may be due to the change of the conductivity from extrinsic to intrinsic type . In the case of the thin films, the electrical resistivity decreased with increasing temperature, thickness and substrate temperature. The films deposited on NaCl crystals were found to have lower resistivity as compared to the resistivity of the films on mica and glass substrates. The solid state reacted films showed a ten fold decrease in resistivity as compared to that of SnSe films obtained by directly evaporating the SnSe compound. The carrier type has been determined by conventional hot probe technique. The films deposited from SnSe-$SnSe_2$ eutectic alloy were usually found to be p type. SnSe films were also found to be p type while $SnSe_2$ were of n type. Thermal cycling and annealing showed decrease in the electrical resistivity. In the case of $SnSe_2$, the films obtained at higher substrate temperatures, more than 150 °C, were found to be of poor quality, frequently exhibiting irregular variations of resistivity.

The study on optical measurements on the bulk crystals and the thin films were carried out using dual beam Spectrophotometer (UV-VIS-NIR). Using reflectance measurements, the band gap of the single crystals have been evaluated from the data. In the case of the thin films, the effects of film-thickness, substrate temperature and heat treatment on the band gap were studied by analysing the absorbance measurements. The band gap was found to decrease with the increasing thickness. In solid state reacted SnSe films, number of reacted layers has also been changed and band gap variations have been studied. The plot of band gap vs inverse square of thickness was obtained as a straight line which is explained in terms of quantum size effect or dislocation density.

Photoconductivity measurements were carried out on the SnSe solid state reacted films. Measurements were made in dark and under illumination. Photocurrent increased with illumination time and after certain time photocurrent showed saturation. As the intensity increased, the photocurrent increased. Photocurrent vs temperature variation has also been studied. $SnSe_2$ films do not exhibit photoconduction to any observable extent. This may be due to high resistivity of the films. It can be concluded that the method of solid state reaction to obtain SnSe thin films is successful and better compared to the method of evaporating the compound semiconductor directly ; particularly, the resistivity and photoconductivity have improved significantly.

The fabrication and characterization of heterojunction structures $SnSe/SnSe_2$, p-Si/$SnSe_2$, n-Si/SnSe were also done. Short circuit current, open circuit voltage, maximum power, I-V characteristic in dark and under illumination and C-V measurements were obtained. The short circuit current has increased in the case of junctions formed with solid state reacted SnSe and $SnSe_2$ as compared to the junctions obtained with directly evaporated films. However, the fill factor and efficiency have not been much affected. Metal semiconductor junctions have also been studied using metals like Cd, Zn, In and the intermetallic compound InBi. Their I - V and C - V characteristics have been studied. A comparison of the junctions has been discussed in light of the results obtained.