12.1 INTRODUCTION:

Materials possessing layered structures remain an extensively investigated subject in current physics and chemistry. Most of the promising technological applications deal with the mixed compounds of layered materials. Investigations on mixed transition metal dichalcogenides (TMDCs) have been carried out by a large number of investigators. The large volume of work carried out in this field is of importance, not only in basic science but also in industrial and energy applications.

Author has investigated into the feasibility of growing sulphur rich and sulphur deficient mixed compounds of Zirconium Sulphoselenides in the form of single crystals and to study their various physical properties. Further, he has noticed that renewal of research on tin sulphide has occurred within the last 10 years following Engelken's work regarding chemical deposition, electrodeposition and characterisation of Sn\textsubscript{x}S films. The recent studies have focussed on deposition of polycrystalline films or growth and characterisation of single crystal Sn\textsubscript{x}S. Only within last 5 years there has been world wide attention to optoelectronic applications such as photovoltaic cells. Moreover, SnS is a low toxicity photoconductor that has
been studied much less than other IV – VI and II – VI semiconductors with similar electronic properties (i.e. CdS, PbS). Author has therefore undertaken work on the preparation and characterisation of SnS single crystals grown using different transporting agents.

Author has made an attempt to study the effect of enhancement of selenium content in Zirconium sulphoselenide on the photoresponse of PEC solar cells fabricated with selenium rich and selenium deficient ZrS\textsubscript{x} \text{Se}_{2-x}. Also he has carried out studies on electrochemical and photoelectrochemical behaviour in SnS single crystals grown using CVT and PVT techniques.

The entire work carried out in the above manner has been described in the present thesis. Attempts have been made to come to some important conclusions on the basis of the present work and to find out scope for future work.

12.2 CONCLUSIONS:

Author has modified the commonly employed vapour transport technique for the growth of layered TMDC single crystals and used this modified technique to grow selenium / sulphur rich and selenium / sulphur deficient single crystals of Zirconium sulphoselenide.

The lattice parameters 'a' and 'c' and the 'd' values for Zr S\textsubscript{0.5} Se\textsubscript{1.5} and Zr S\textsubscript{1.5} Se\textsubscript{0.5} are in agreement with those obtained by previous
investigators. The microscopic examination of the crystal surfaces has revealed that growth of these crystals is free from spirals suggesting a layered growth mechanism for their formation. The presence of growth layers initiating from edges and corners and spreading across the face clearly support this conjecture. The EDAX analysis of the grown crystals has shown that they are off-stoichiometric in nature. This supports the off-stoichiometric nature of Zirconium sulphoselenide compounds described in detail in chapter 1.

The variation of conductivity and thermoelectric power with temperature confirms the semiconducting nature of the single crystals of Zr S\textsubscript{0.5} Se\textsubscript{1.5} and Zr S\textsubscript{1.5} Se\textsubscript{0.5}. Moreover, the negative values of Seebeck coefficient and Hall coefficient indicate that both of them are n-type and majority charge carriers in them are electrons. It has been observed that Zirconium sulphoselenides become more and more anisotropic and resistive with increase in the sulphur content. This is because sulphur being non-metal is less conducting and therefore when incorporated into the crystal lattice in larger proportion makes them proportionately more resistive.

The optical absorption study has clearly shown that Zr S\textsubscript{0.5} Se\textsubscript{1.5} and Zr S\textsubscript{1.5} Se\textsubscript{0.5} compounds have direct as well as indirect band gaps. The values of direct and indirect band gaps have been reported for the first time since such a detailed study of the absorption spectra for these compounds is not available in the literature. Both direct as well as indirect band gaps
increase with increase in the sulphur content in ZrS$_x$Se$_{2-x}$ single crystals. The accurate analysis of the absorption data has shown that the indirect transitions represented by the absorption curves are indirect involving two phonons. The energies of the phonons have been estimated.

During growth of SnS single crystals using different transporting agents it has been realised that crystals grown by CVT technique are larger in size. The EDAX analysis of crystals reveals that crystals grown by PVT technique are stoichiometrically perfect while those grown with iodine as the transporting agent are slightly off-stoichiometric and SnS (NH$_4$Cl) crystals contain a lot of impurities in varying amounts.

The positive values of Seebeck coefficient and Hall coefficient indicate that SnS (PVT) and SnS (I$_2$) are p-type and majority charge carriers in them are holes whereas negative values of these parameters for SnS (NH$_4$Cl) point out that it is n-type. The existences of SnS in n and p type forms resulting from the use of different transporting agents is in agreement with such results reported in the literature.

The difference in transport properties in NH$_4$Cl transported crystals as compared to SnS (PVT) and SnS (I$_2$) has been attributed to the presence of impurities in the lattice of SnS. The decrease in resistivity and mobility and increase in carrier concentration in SnS (NH$_4$Cl) and lower values of Seebeck coefficient as compared to SnS (PVT) and SnS (I$_2$) suggest a trend towards metallic side. Both these conclusions are in support of each other. The higher values of thermoelectric power factor for SnS
(NH₄Cl) single crystals point out that they should work as superior thermoelectric materials in TEP based devices. The studies of microstructures suggest a layer growth mechanism for the growth of SnS single crystals.

The accurate analysis of the absorption spectra from SnS single crystals grown using different transporting agents has shown for the first time a simultaneous presence of both direct and indirect transitions in them. It has been shown that the indirect transitions are phonons assisted. The energies of the phonons have been evaluated. The values of band gaps nearly match with the values reported in the literature. Both two and three dimensional models can be used satisfactorily to described the indirect optical transitions in SnS single crystals. It is not possible to obtain the values of direct band gaps on the basis of a 2D model. Analysis based on 3D model alone gives the values which closely match the literature values. The effect of using different transporting agents on the optical band gaps (both direct and indirect) in SnS has been adequately explained in the thesis.

Investigations have been made with a view to see the effect of enhancement of selenium content in ZrSₓSe₂₋ₓ and use of different transporting agents in synthesis of SnS on the photoresponse of the photoelectrochemical solar cells fabricated with ZrS₀.₅ Se₁.₅ , ZrS₁.₅Se₀.₅ , SnS (PVT), SnS (I₂) and SnS (NH₄Cl) single crystals as photoelectrodes. After choosing 0.05 I₂ + 1MKI + 1 M Na₂SO₄ as the best electrolyte for Zr
$S_{0.5}Se_{1.5}$ and $ZrS_{1.5}Se_{0.5}$ and $0.1\ M\ K_3[Fe(\text{CN})_6] + 0.1\ M\ K_4[Fe(\text{CN})_6]$
$+ 0.5\ M\ H_2SO_4$ as the best electrolyte for SnS (PVT), SnS ($I_2$) and SnS ($NH_4Cl$) single crystal electrodes, their suitability were adjudged. For the photoelectrodes of Zirconium sulphoselenide and SnS, the locations of valance and conduction band edges using the Mott – Schottky plots were decided. The nature of these plots absolutely confirm the $n$ - type behaviour of $ZrS_{0.5}Se_{1.5}$, $ZrS_{1.5}Se_{0.5}$ and SnS ($NH_4Cl$) and $p$ - type behaviour of SnS (PVT) and SnS ($I_2$) single crystals.

It was realised after a detailed photoelectrochemical study that enhancement of selenium content in $ZrS_xSe_{2-x}$ leads to an improvement in its PEC behaviour. Further SnS crystals grown using ($NH_4Cl$) as the transporting agent gave increased value of photoconversion efficiency as compared to SnS (PVT) and SnS ($I_2$)

**SCOPE FOR FUTURE WORK:**

Author has the feeling of satisfaction undoubtedly efforts have been made by him in the synthesis and characterization of certain useful layered semiconductors and to a certain extent he has achieved success, there are still a considerable number of aspects remained untouched and deserve further investigations.

Ability to account for the data on absorption spectrum from $ZrS_{0.5}Se_{1.5}$ and $ZrS_{1.5}Se_{0.5}$ and SnS single crystals on three dimensional model
strictly suggests that although Zirconium sulphoselenide and SnS compounds are reported to be highly anisotropic, they do possess some conductivity along the c-axis because of the presence of stacking faults in them. This makes these crystals to behave three dimensionally. Although the presences of stacking faults has been postulated a conclusive evidence to show their presence is lacking. Efforts should therefore be made to show their presence by electron microscopy. Since strong bonds exist within the layer, while between the layers they are weak, the crystals have facile basal cleavage. A detailed study of defects using transmission electron microscopy involving weak beams should therefore be possible in these crystals.

The Seebeck coefficient measurements have clearly shown the superiority of ZrS$_{0.5}$Se$_{1.5}$ and SnS (NH$_4$Cl) as efficient thermoelectric materials and PEC measurements have shown their superiority as efficient solar cell materials. Efforts should therefore be made to synthesis Zirconium sulphoselenides with increasing amount of selenium content and SnS single crystals by using NH$_4$Cl as the transporting agent with concentration of NH$_4$Cl and temperature gradients during growth of adjusted that one one gets ZrS$_x$Se$_{2-x}$ and SnS crystals with lower value of bulk resistivities and higher values of carrier concentration to work as optimum materials for devices based on TEP and PEC behaviours.

Moreover, since the aim of the photoelectrochemical studies in chapters 10 and 11 was to know the effect of enhancement of selenium in
ZrS$_{x}$Se$_{2-x}$ and of using different transporting agents for the growth of SnS single crystals on the photoresponse of Zr S$_{x}$ Se$_{2-x}$ and SnS based PEC solar cells, efforts to increase the overall efficiencies of PEC solar cells were beyond scope of the present thesis.

The overall efficiencies of the cells can be substantiated by adopting the following procedures:

[a] reducing the reflectivities of the semiconductor electrode surface.
[b] decreasing the surface and bulk recombination rates.
[c] lowering the bulk resistivities of the materials and
[d] minimizing the absorption losses in the electrolytes.

The effects of surface treatments such as chemical etching, photoelectrochemical etching and dye layer application can also be undertaken to further increase the overall efficiencies.

Recently it has been observed that copper diffusion into the SnS appears to significantly enhances its photoconductivity. Recent work by Engelken's group indicates the potential for further investigations of SnS for optoelectronic applications. Follow up – work could include optimisation steps such as studies of dopants, hydrogen incorporation and encapsulants and characterization steps to determine states within the band gap and carrier diffusion lengths.

It has been also recently realized that a material can exhibit different properties when the size of its particles reach nanometer level. For instance, (Mo, W) dichalcogenide nanoparticles outperform their bulk
counterparts as solid state lubricants in every respect (friction, wear and lifetime of the lubricant) under varied test conditions. Moreover, nanostructural materials have potential applications in solar energy conversion and nanoscale electronic and optical devices. Also, in the face of increasing miniaturization of electronic and mechanical devices it will be worthwhile to take up synthesis of SnS and mixed crystals of Zirconium sulphoselenide in the nanocrystalline forms and characterize them fully with all the available techniques of X-ray diffraction, electron diffraction and electron microscopy for their optimum utilization in device fabrication. Such efforts are indeed going on in different laboratories in the world but such attempts in our country need more attention.

Further, currently it has been realized that SnS can be used to form an interesting class of materials called as 'misfit layer compounds', some details of these compounds have been provided in the introductory chapter of the thesis. These multilayer compounds in the form of single crystals are potential materials for use in microelectronics, since their electrical and transport properties strongly depends on the crystallographic direction. The CVT technique developed in the present work can be conveniently used for the preparation of these compounds in the form of single crystals; because of the paucity of time this work could not be carried out by the author. In future, efforts can be made to concentrate in this recent field of misfit layer compounds.