CHAPTER 10

CONCLUSIONS AND SCOPE FOR FUTURE WORK

10.1 INTRODUCTION :

Materials with 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 have been carried out by a number of researchers. 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 tin sulphoselenides in the form of single crystals and to study their various physical properties. He has also seen the effect of using different transporting agents on the growth of tin sulphoselenide single crystals. Author has made an attempt to study the effect of partial replacement of selenium by sulphur on the photoresponse of PEC solar cells fabricated with the best reported TMDC i.e. WSe_2. The entire work carried out in the above manner has been described in the present thesis. Attempts have been made here to come to some important conclusions on the basis of the present work and to find out scope for future work.

10.2 CONCLUSIONS :

Since the growth conditions have a marked influence in the synthesis of crystals, attempts have been made by the author to optimise growth conditions which lead to the formation of well developed single crystals of tin sulphoselenide (SnSSe). The optimum conditions arrived at have been

then used for the growth of sulphur rich and sulphur deficient single crystals of tin sulphoselenides.

The results on unit cell volume, X-ray density, estimation of particle size, growth and deformation fault probabilities in crystals of SnSSe have clearly indicated that crystals obtained by slow cooling method are relatively more perfect. This slow cooling method has been successfully used to grow single crystals of SnS_xSe_{2-x} with (x = 0.5 and 1.5).

The lattice parameters 'a' and 'c' and the 'd' values for SnS_xSe_{2-x} are in agreement with those obtained by previous investigators. The microscopic examination of the crystal surfaces has revealed that growth of $SnS_{0.5}Se_{1.5}$, SnSSe and $SnS_{1.5}Se_{0.5}$ is free from spirals thereby suggesting a layered growth mechanism for their growth. The presence of growth layers initiating from edges and corners and spreading across the face clearly support this conjecture.

The variation of conductivity and thermoelectric power with temperature confirms the semiconducting nature of the single crystals of SnS_xSe_{2-x}. Moreover the negative values of Seebeck coefficient and Hall coefficient indicate that all of them are n-type and majority charge carriers in them are electrons. It has been observed that tin 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 proportions makes them proportionately more resistive.

The optical absorption study has clearly shown that SnS_xSe_{2-x}

compounds have direct as well as indirect band gaps. Both direct as well as indirect band gaps increase with increase of sulphur content in SnS_xSe_{2-x} single crystals. An accurate analysis of the absorption data has shown that the indirect transitions represented by the absorption curves are indirect allowed involving two different phonons. The energies of these phonons have been determined. It can be concluded from the study that two dimensional model cannot be used satisfactorily to describe the main optical properties of tin sulphoselenide crystals.

During growth of SnSSe single crystals using different transporting agents it has been realised that crystals grown using NH_4Cl as the transporting agent are largest in size and are relatively more perfect. The EDAX analysis of crystals grown using I_2 as the transporting agent not only suggests the presence of iodine in the host lattice of SnSSe but also brings out the fact that these crystals are slightly off-stoichiometric. The presence of defects due to incorporation of iodine is reflected in the microstructural investigations of the as grown faces of SnSSe.

The variation of different transport properties in iodine transported crystals as compared to SnSSe (DVT) and SnSSe (NH_4Cl) has been attributed to the presence of iodine in the lattice of SnSSe. The decrease in mobility in SnSSe (I_2) has been explained from the microstructural studies as due to the presence of inhomogeneities in them. These inhomogeneities tend to reduce the mobility of charge carriers and to give low values of Seebeck coefficient and so also the power factor.

The investigations on tungsten sulphoselenide (WSSe) were carried out with a view to see the effect of partial replacement of selenium by

sulphur in WSe_2 on the photoresponse of the photoelectrochemical solar cells fabricated with WSe_2 single crystals as photoelectrodes. After choosing 0.025M I_2 + 1M NaI + 2M Na_2SO_4 + 0.5M H_2SO_4 and regarding it as the best electrolyte, its suitability was adjudged. For the photoelectrodes of WSe_2 and WSSe, the locations of valence and conduction band edges using the Mott - Schottky plots were decided. The nature of these plots absolutely confirm the p-type behaviour of WSe_2 and WSSe single crystals.

It was realised after a detailed photoelectrochemical study that partial replacement of selenium by sulphur in WSe_2 does not yield any improvement in its photoelectrochemical behaviour.

10.3 SCOPE FOR FUTURE WORK :

The author has the relief of satisfaction that undoubtedly efforts have been made by him in this direction and to a certain extent has achieved success, there are a considerable number of aspects remained untouched and deserve further investigations.

Failure to account for the data on absorption spectrum from SnS_xSe_{2-x} single crystals on two dimensional model strictly suggests that although tin sulphoselenide 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 presence of stacking faults in tin sulphoselenides has been shown by the estimation of stacking fault probabilities, a more conclusive evidence will be to show the presence of such stacking faults by electron microscopy. Since strong bonds exist within

the layer, while between the adjacent 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 author feels that a detailed work on Hall effect can be carried out. The dependence of carrier concentration and mobility upon temperature as well as composition can still be determined in a wider range of temperatures and magnetic fields. This will enable one to understand the nature of charge carriers, their behaviour and conduction mechanism in different temperature ranges.

The similarity in physical properties of SnS_xSe_{2-x} with one of the useful thermoelectric material i.e. Zn_4Sb_3 prompted the author to look into the thermoelectric properties of SnS_xSe_{2-x} single crystals. The values of thermoelectric power factors obtained for these crystals are much lower than that for Zn_4Sb_3. One of the reasons for these low values is the approximate nature of the resistivity measurements used in their evaluation. Hence, for accurate determination of power factors, all the resistivity measurements in the different temperature ranges must be carried out by van der Pauw technique. Further, the value of the power factor goes on increasing as the content of sulphur in tin sulphoselenide is suppressed. Therefore, to increase the utility of tin sulphoselenide as a thermoelectric material one should totally suppress sulphur in SnS_xSe_{2-x}, which means that one should work with $SnSe_2$ and then make all attempts to decrease its resistivity without seriously affecting its Seebeck coefficient. This could be done either by altering the growth procedure for synthesis of $SnSe_2$ or by the incorporation of impurities in $SnSe_2$ during its growth.

Since the aim of the photoelectrochemical studies described in this thesis was to know the effect of partial substitution of selenium by sulphur on the photoresponse of the 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 the following procedures.

1. reducing the reflectivity of the semiconductor electrode surface,
2. decreasing the surface and bulk recombination rate.
3. lowering the bulk resistivity of the material.
4. minimising the absorption losses in the electrolyte.

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