CHAPTER : 13

CONCLUSIONS

AND

SCOPE FOR FUTURE WORK
13.1 INTRODUCTION:

Materials with layered structures remain an extensively investigated subject in current Physics and Chemistry. Most of the promising technological applications deal with compounds having layered structure. The binary IV-VI compounds form a significant group of layered semiconductors, besides IV group elements and III-V compounds, but the attention paid to them has not been by far so great as in the case of latter two group of materials. Among these IV-VI compounds there are two important families of materials, especially those with cubic rock salt structure (PbS, PbSe, PbTe, SnTe) and those with distorted rock salt structure of the orthorhombic space group namely GeS, GeSe, SnS and SnSe. The materials of the first group, particularly PbS, have been studied intensively, whereas little attention – though increasing during several last years – has hitherto been paid to the materials of the second group.

Two serious problems mentioned in the introductory chapter, namely the problem of a dimensionality of these layer compounds and the problem of the existence of a novel phase transition in these materials, have not been solved satisfactorily till present. It has also been realised that properties of crystals strongly depend on growth conditions used for their synthesis. Author has investigated into the feasibility of growing GeS and GeSe belonging to the group IV-VI compounds 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 these crystals. He has
made a positive contribution towards the understanding of the problem of dimensionality and phase transitions in these compounds. An attempt has also been made by him to study the effect of using different transporting agents on the PEC solar cells fabricated with GeSe single crystals. 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.

13.2 CONCLUSIONS:

Single crystals of GeS and GeSe have been grown successfully by using different transporting agents. Single crystal nature of both the crystals has been confirmed from electron diffraction methods. The results on unit cell volume, X-ray density, estimation of particle size and EDAX analysis of the grown crystals have clearly indicated that GeS single crystals grown by CVT technique using iodine as transporting agent are stoichiometrically perfect while those grown by PVT technique are off-stoichiometric. In contrast to this, GeSe crystals grown by PVT technique are stoichiometrically perfect while those grown by CVT technique are off-stoichiometric.

The lattice parameters 'a' and 'c' and the 'd' values for GeS and GeSe are in agreement with those obtained by previous investigators. The microstructural examination of the crystal surfaces has revealed that
GeS (I₂) and GeSe (PVT) are free from spirals and exhibit perfectly flat surfaces thereby suggesting a layer growth mechanism for their growth. While GeS (NH₄Cl), GeS (PVT) and GeSe (CVT) grown crystals do exhibit spirals as well as growth layers implying thereby that both screw dislocation and layer growth mechanism are responsible for their formation.

The variation of conductivity with temperature confirms the semiconducting nature of both GeS and GeSe crystals. Moreover, the positive values of Hall coefficient indicates that both of them are p-type and majority charge carriers in them are holes. The resistivity variation with temperature in the case of GeSe single crystals grown using different agents show discontinuities at a temperature of ~ 150-160 K in the lower temperature range (10-300 K) and at ~ 413 K in the higher temperature range (300-560 K). Both these temperatures closely resemble the suggested novel phase transition temperatures in the literature. In the absence of any concrete proof about structural changes taking place at these temperatures from X-ray diffraction and TEM observations, the resistivity anomalies have been attributed to the presence of two different kinds of localised levels which correspond to the values of activation energies obtained from the linear portions below and above the temperatures at which the discontinuities are noticed.

The variation of TEP with temperature also confirms the semiconducting nature of GeSe. Also the positive values of Seebeck coefficient suggest that all of them are p-type.
An accurate analysis of the absorption spectra from GeS and GeSe single crystals grown using different transporting agents has shown for the first time the simultaneous presence of both direct and indirect transitions in them. It has been shown that the indirect transitions in both of them are phonon assisted. The energies of the phonons have been estimated. The values of band gaps for both compounds nearly match with the values reported in the literature. Both two and three dimensional models can be used satisfactorily to describe the indirect optical transitions in GeS and GeSe single crystals. It is not possible to obtain the values of direct band gaps on the basis of a 2 D model. Analysis based on 3 D model alone gives the values which are in agreement with the reported values in the literature. The fact that it is possible to account for the indirect transitions on the basis of 2D and 3D models and for direct transitions on the basis of a 3D model clearly support the view that it is perhaps not appropriate to classify GeS and GeSe as truly layer like (two dimensional) compounds but they should be regarded as intermediate cases between 2 D and 3 D structures or more appropriately as pseudo two dimensional systems.

In order to study the effect of high pressure on the transport properties of GeS and GeSe, simultaneous measurements of TEP and ac resistivity were carried out upto 8GPa on single crystals of these compounds grown using different transporting agents. The measurements showed a decrease in ac resistivity with increase in frequency upto 66.6 kHz. This behaviour was attributed to the presence of defects and impurity atoms in the semiconductor which could contribute to conduction by the hopping
process. The shift in resistance peaks at higher frequencies observed in both GeS and GeSe crystals has also been adequately explained. The sharp drop in resistivity and TEP beyond 4GPa suggested setting up of metallisation with increasing pressure.

In order to see the utility of GeSe in device fabrication and to observe the effect of using different transporting agents on the photoresponse of the photoelectrochemical solar cells fabricated with GeSe single crystals as photoelectrodes, PEC solar cells were prepared with GeSe (PVT), GeSe (NH₄Cl) and GeSe (I₂) crystals. After choosing 0.025M I₂ +0.5M NaI + 0.5M Na₂SO₄ and regarding it as the best electrolyte, its suitability was adjudged. For the photoelectrodes of GeSe (PVT), GeSe (NH₄Cl) and GeSe (I₂), 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 GeSe single crystals grown using different transporting agents. It was realised after a detailed photoelectrochemical study that GeSe (I₂) gave better photoresponse as compared to GeSe (PVT) and GeSe (NH₄Cl). The better performance was attributed to reduction in bulk resistivity and increase in carrier concentration of GeSe crystals grown by CVT technique using iodine as the transporting agent.
13.3 SCOPE FOR FUTURE WORK:

The author has the relief of satisfaction that undoubtedly efforts have been made by him in contributing to two major problems namely dimensionality and novel phase transitions in the layered GeS and GeSe semiconductors, there are still a considerable number of aspects remained untouched and deserve further investigation.

In order to confirm the existence of phase transitions in the low and high temperature range, crystals must be examined by X-ray diffraction and electron diffraction in these temperature ranges.

The effect of high pressure on transport properties of GeS and GeSe has only been studied upto 8 GPa. It will be highly desirable to extend this range of pressure to higher pressures to look for the possibility of phase transitions and to see the effect of using different transporting agents on the physical properties under extremely high pressures.

It appears from the literature that stoichiometric amount of germanium in GeS and GeSe has a considerable effect on its physical properties, one may therefore take up the growth of Ge$_{1-x}$S$_x$ and Ge$_{1-x}$Se$_x$ in the single crystal form using the vapour transport methods developed during the work carried out by the author for the present thesis and compare the results with polycrystalline and amorphous samples of the same materials.
It has been recently realised that a material can exhibit different properties when the size of its particles reach nanometer level. For instance, (Mo, W) dichalcogenides 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 GeSe and GeS in the nanocrystalline form and characterise them fully with all the available techniques of X-ray diffraction, electron diffraction and electron microscopy for their optimum usefulness in device fabrication.

The Seebeck coefficient measurements have clearly shown the superiority of GeSe ($I_2$) as a thermoelectric material and PEC measurements have shown its superiority as an efficient solar cell material. Efforts should therefore be made to synthesise GeSe single crystals using iodine as the transporting agent and concentration of iodine and temperature gradients during growth should be so adjusted to give GeSe crystals with lower values of resistivity and higher values of carrier concentration.

Moreover, since the aim of the photoelectrochemical studies described in Chapter 12 was to know the effect of using different transporting agents on the photoresponse of GeSe based PEC solar cells, efforts to
increase the overall efficiency of PEC solar cells were beyond scope for the present thesis.

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

(a) reducing the reflectivity of the semiconductor electrode surface,
(b) decreasing the surface and bulk recombination rate,
(c) lowering the bulk resistivity of the material and
(d) minimizing the absorption losses in the electrolyte.

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.
PUBLICATIONS:


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5. Electrical Transport Measurements in Semiconducting Mo_{0.5}W_{0.5}Se_2 Single Crystals
   Proceedings of the National Seminar on Characterisation of Semiconductor Materials for Device Applications
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   M.P. Deshpande, G.K. Solanki and M.K. Agarwal

7. Two and three-dimensional models for analysis of optical absorption in tungsten disulphide single crystals
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G.K.Solanki, P.D.Patel, M.K.Agarwal and S.N.Vaidya


LIST OF PAPERS SENT FOR PUBLICATION

1. Photoelectrochemical Studies of Indium Intercalated WSe₂ Single Crystals.
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2. Optical Band gap Studies of Tungsten Sulphoselenide Single Crystals Grown by a DVT Technique.
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Scientia Iranica (2001). (Accepted)

3. Thermoelectric power of mixed tungsten dichalcogenide single crystals grown by direct vapour transport technique
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2. Effect of Pressure on Electrical Properties of Some Chalcogenide Semiconductors.

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G.K.Solanki, P.D.Patel, M.P.Deshpande and M.K.Aggarwal
National Seminar on Characterisation of Semiconductor Materials for Device Applications, 4-6, March, 1998, Guru Nanak Dev University, AMRITSAR.

G.K.Solanki, S.G.Patel, Sunil Chaki and M.K.Aggarwal
Seminar Cum Workshop on Materials and Characterisation, 13-17, July, 1998, Central Electrochemical Research Institute, KARAIKUDI.

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DAE-SSPS'99, 20-24, December, 1999, Department of Material Science, IGCAR, KALPAKKAM.

6. Growth and characterisation of copper intercalated tungsten diselenide single crystals.
Bhavesh Desai, Rajeev Vaidya, G.K.Solanki and M.P.Deshpande
One Day Seminar on Condensed Matter Physics, March 25, 2001, Faculty of Science, M.S. University of Baroda, Baroda.

7. Optical and electrical characterisation of copper intercalated tungsten dichalcogenide single crystals.
J.B.Patel, M.H.Parmar, G.K.Solanki and M.P.Deshpande
March, 23, One Day Seminar, Department of Physics, V.V.Nagar, (Gujarat).
PROJECTS

1. A UGC SPONSORED MINOR RESEARCH PROJECT

TITLE OF THE PROJECT: High Pressure Studies on NbSe₂ Single Crystals grown by CVT Technique.
DATE OF STARTING: 12 - 12 - 1995
COMPLETE THE PROJECT: 31 - 03 - 1995
AMOUNT: Rs. 11,000
FINANCING AGENCY: U.G.C.

2. A UGC SPONSORED MAJOR RESEARCH PROJECT

TITLE OF THE PROJECT: Growth and characterization of mixed crystals of tungsten sulphoselenide and their application to PEC solar cells.
DATE OF STARTING: 13 - 12 - 1997
COMPLETE THE PROJECT: 12 - 07 - 2000
AMOUNT: Rs. 3.165 Lacka
FINANCING AGENCY: U.G.C.

I was working as co-investigator

3. A UGC SPONSORED MAJOR RESEARCH PROJECT (SUBMITTED)

AMOUNT: Rs. 3,184,600
FINANCING AGENCY: U.G.C.