PREFACE

Laminar compounds are characterised by their anisotropic properties along different crystallographic directions. With the advent of the close-vapour transport technique, a large number of these compounds can easily be obtained. An interesting feature of these compounds is that they crystallise as thin plates, a form very suitable for the investigation of the optical and electrical properties and the examination of crystal structure defects. Each crystal is composed of thin layers stacked upon each other, the atoms are bound together by predominantly covalent forces as in the chalcogenides or strongly ionic as in the iodides. The bonds between the layers are extremely weak (due to weak van der Wall's forces). Each layer may be formed of three atomic planes X-M-X (CdI₂-type structure), four planes X-M-X (e.g. Ga-chalcogenides) or the five planes X-M-X-M-X as for Bi₂Te₃.

Due to extremely weak interaction between the layers these compounds can be perfectly cleaved along the basal plane, to obtain very thin wafers. Thus, a favourable surface to bulk ratio can be obtained. Recently laminar semiconductors are attracting considerable interest because of the important opportunities they open, particularly in optoelectronics and photovoltaics. Despite the unusual interesting properties of these laminar crystals, their semiconducting properties have been studied only superficially. In particular this comment applies to layer like orthorhombic chalcogenides.
(GeS, GeSe, SnS and SnSe) which have recently attracted considerable interest. Never-the less, relatively little is known about these materials as compared with their cubic IV-VI counterparts (PbS, PbSe and PbTe).

Author has therefore chosen to work on the synthesis and characterisation of lesser studied Germanium monochalcogenides (particularly on the end members of the series GeS<sub>x</sub>Se<sub>1-x</sub>) and examine the possibility of their use in the fabrication of photoelectrochemical solar cells.

Further, the importance of understanding pressure induced structural and electronic effects in laminar semiconductors and conflicting accounts of pressure induced effects in GeS and GeSe prompted the author to undertake systematic measurements of ac resistivity and thermoelectric power at different pressures on single crystals of GeS and GeSe grown by different techniques.

The work proposed in the thesis has been divided into 13 chapters.

Chapter 1 deals with the survey of the literature and the existing information on germanium monochalcogenides.
A brief information about the various experimental techniques employed for characterisation in the present work has been provided in Chapter 2.

Chapter 3 describes methodically, the growth of laminar semiconductors in the form of single crystals using vapour phase method. The salient features of chemical vapour transport (CVT) and physical vapour transport (PVT) techniques have been thoroughly explained. Details of experimental set-up, furnace construction, temperature regulating circuit and method of crystal growth have also been narrated.

The nature and quantity of the transporting agent alters the dimensions and the morphology of the obtained single crystals. Therefore author has used PVT and CVT technique using iodine and NH₄Cl as the transporting agents to synthesize single crystals of the end members of the series GeSₓSe₁₋ₓ (x=0,1) of maximum possible size. Studies on growth, characterisation using EDAX, X-ray diffraction, Electron diffraction and transport properties on GeS crystals have been described in Chapter 4 while those on GeSe find a place in Chapter 5.

Since the optical band gap of a semiconducting material plays a vital role in deciding the photoconversion efficiency of a solar cell fabricated with the semiconductor, a study of this parameter is extremely desirable. A complete
study on its determination in GeS single crystals grown using different techniques has therefore been made by optical absorption. The results thus obtained are described elegantly in Chapter 6.

Chapter 7 describes an indepth study of the absorption spectra obtained from single crystals of GeSe grown using different transporting agents.

Chapter 8 reviews the techniques of high pressure research and describes in detail the production and measurement of high pressures upto 10 GPa.

The results of simultaneous thermoelectric power and resistivity measurements upto 8 GPa on single crystals of GeS grown using different techniques are reported in Chapter 9. The measurements show a decrease in ac resistivity with increase in frequency upto 66.6 kHz. This behaviour has been attributed to the presence of defects and impurity atoms in the semiconductor which can contribute to conduction by the hopping process.

It appears from the literature that there are conflicting accounts of pressure effects in GeSe and there is no record on ac resistivity measurements at different pressures in GeSe. Hence in view of the importance of understanding pressure induced electronic effects in materials, author has undertaken formal measurements of ac conductivity and thermoelectric power at different pressures.
on single crystals of GeSe grown by different techniques. The results obtained from this study are described elegantly in Chapter 10.

Chapter 11 accounts for the necessary introduction to PEC solar cells. Different types of solar cells have been explained and discussed under their classified heads. The advantages and disadvantages of PEC solar cells over the solid state photovoltaic cells have also been discussed.

Chapter 12 describes author's attempt to fabricate PEC solar cells using GeSe single crystals. Semiconductor electrolyte interface has been characterised by locating valence and conduction band edges, for which flat band potential measurements were carried out by using Mott Schottky plots. These studies justify the selection of appropriate electrolyte for PEC work. Various solar cell parameters have been determined for cells fabricated with GeSe crystals grown using different techniques. In order to see the effect of growth technique on photoelectrochemical response, the electrolyte and the intensity of illumination were kept constant and all the electrodes were prepared from crystals, showing absolutely plane faces obtained through cleaving with the help of adhesive tape.

Conclusions drawn from the entire work and scope for future work find place in Chapter 13.