Chapter 7

Summary, conclusions and future scope

This thesis reports the growth, characterization and study of temperature as well as pressure dependent electrical properties of $2\text{H-MoSe}_2\text{Te}_x$ single crystals. This last chapter deals with the summary of the thesis and discussion on the future prospects of current work and its relevance from the application point of view of these materials. It also contains some suggestions for possible enhancements in the experimental methodology in order to make the results more comprehensive.
7.1 SUMMARY AND REVIEW OF WORK

The possible applications of Transition Metal Dichalcogenides (TMDC) are promising materials for energy conversion (in Photo-electrochemical (PEC) solar cell as well thin film solar cell), solid lubricants, anode materials in lithium battery, host materials for intercalation, thermoelectric materials, optical coatings, light detection etc [1-6]. These are the reasons for studying their electrical and optical properties thoroughly and also in finding new materials of this family. Most of these materials are widely studied in order to find their suitable applications. Literature surveys of these materials reveal that still some materials such as molybdenum dichalcogenides (MoX$_2$) (X = Se and Te) are least studied for their electrical and optical behaviours. Up to the date MoSe$_2$ and MoTe$_2$ have been attended for limited study in terms of polytypes and semiconducting nature, but there is no report of their behaviour at very higher temperature. Work done in the recent years found some properties of these materials to be superior to the conventional materials as discussed in section 1.5.

On the basis of literature studies related to MoX$_2$ we would like to state the following:

- In the MoX$_2$ family except MoSe$_2$ and MoTe$_2$ other intercalated compounds are rarely reported.
- MoSe$_2$ and MoTe$_2$ are studied only for their electrical and optical properties at high temperature but there is no report of the intermediate compounds behaviour at high temperature as well as high pressure.
- These compounds are known to exhibit different polytypes but the systematic study of their structural parameters is not reported. Lattice parameters of several compounds are yet to be investigated.
- Effects of high pressure on electrical and optical properties of these compounds are not reported so far.
In order to fill up the above mentioned gaps in the available information in the series of 2H-MoSe$_{2-x}$Te$_x$ compounds present investigations have put up a humble effort to study the growth, characterization and high pressure studies of 2H-MoSe$_{2-x}$Te$_x$ (x = 0.25, 0.5, 1, 1.5, 1.75) single crystals. Single crystals of 2H polytypes of 2H-MoSe$_{2-x}$Te$_x$ (x = 0.25, 0.5, 1, 1.5, 1.75) were grown by chemical vapour transport technique using iodine as a transporting agent. The surface micro features of as grown crystals were characterized using optical microscope to study the growth mechanism. EDAX and powder XRD measurements were carried out for the confirmation of stoichiometric proportion of constituent elements and determination of crystal lattice parameters. The growth conditions of all the compounds were optimized by trial and error method. In addition with this the grown single crystals were studied for the effect of temperature and pressure on their electrical transport properties. For the measurement of optical properties of grown compounds, experimental facility is developed at our laboratory.

7.2 CONCLUSIONS

2H-MoSe$_{2-x}$Te$_x$ compounds are members of group VIB-VIA transition metal dichalcogenides. Almost all the materials of this family are well-known for exhibiting semiconducting nature. Due to this, major studies about these compounds were focused around room temperature and at some extent of high temperature behaviour of limited compounds. Present work has optimized the growth temperatures of 2H-MoSe$_{2-x}$Te$_x$ compounds and also some uncovered several structural, electrical and optical parameters of them. Conclusions drawn on the basis of obtained results are discussed in the thesis and they are systematically summarized below.

- High quality large sized single crystals of 2H-MoSe$_{2-x}$Te$_x$ (x = 0.25, 0.5, 1, 1.5, 1.75) can be grown by chemical vapour transport technique using iodine as a transporting agent. Crystals of all
these compounds are found to grow in the form of platelets having micrometer sized thickness. Growth temperatures of all compounds were optimized to get the largest crystal size by trial and error method. Studies of optical-microtopographs of grown crystals revealed that 2H-MoSeTe and 2H-MoSe_{0.5}Te_{1.5} were grown by lateral spreading of layers. The microtopography studies of 2H-MoSeTe also prove that 2H-MoSeTe grow by plane sheets and that the incompletion of the sheets leaves the trigons. While 2H-MoSe_{0.25}Te_{1.75} and 2H-MoSe_{1.5}Te_{0.5} were found to be grown by screw dislocation mechanism. The inclusion is also observed on the surface 2H-MoSe_{1.5}Te_{0.5} of which is acts as the initial point of the growth.

- Results of EDAX and powder XRD analysis were used to confirm the Stoichiometry, absence of foreign elements and determination of crystal lattice parameters. Growth temperatures for all the compounds could be optimized on the basis of minimum growth and deformation fault probabilities, which were calculated from the results of powder XRD measurements. Electron diffraction patterns for all the compounds show the spot patterns confirming the single crystalline nature of them. TGA studies show that all the materials are thermally stable up to the temperature 800K and after that all compounds start to decompose and they lose their mass up to 25-75% from initial.

- Optical absorbance of all the grown crystals was measured in the wavelength range of 200 nm to 3000 nm at room temperature.

- Smooth and minute variation of absorbance is observed for all the compounds under investigations and no transition is observed, which revealed the stability of compounds.

- It is now evident that the fundamental absorption edge in single crystal of 2H-MoSe_{2.4}Te_{x} is most probably due to the allowed indirect transition. It is seen that the three dimensional indirect
optical band gap of these materials varies from 0.93 eV to 1.20 eV at room temperature.

- The materials are found to be transparent for wavelengths above the fundamental edge. Moreover, the response remains constant up to the upper limit (2400 nm) of the measurement. Therefore this material may used for optical coating.

- Pressure dependent electrical resistivity measurements were performed using Bridgman anvil apparatus. Obtained results showed that in all the compounds, initially the resistivity decreases rapidly with increase in pressure and the rate of decrement of resistivity reduces with increase in pressure. Analysis of the obtained result confirmed the anisotropic behaviour of all the compounds. The d.c. resistivity decrease in the low pressure region of 0.4-2.20 GPa is more and the behaviour is attributed to the presence of the layer structure in the crystals. In the high pressure region, the decrease of resistivity with pressure is less. This is due to decrease in the intra-layer bonds and shift from a two-dimensional material to a more three-dimensional material. Thus, the charge carriers of the valence band contribute to the conduction band carriers.

- A sample holder for the measurement of temperature dependent electrical resistivity could be successfully designed at our laboratory. This extends the range of temperature dependent resistivity measurement from 200 ºC to 600º C.

- Behaviour of temperature dependent electrical resistivity along ab-plane of these compounds reveals that all the compounds are semiconducting in nature. Values of their resistivity (10 Ω.cm at room temperature) lie in the range of semiconductors. Resistivity parallel to c-axis of these compounds is found to be ~10 times higher than the perpendicular to c-axis resistivity of them, which proved their highly anisotropic electrical nature. Resistivities along c-axis in all the materials are found to behave differently
than that perpendicular to c-axis. Resistivity both parallel and perpendicular to c-axis of all the materials is found to decrease with increase in temperature at higher temperatures.

- Obtained values of the carrier concentrations for all the materials ($10^{16}$ to $10^{17}$ cm$^{-3}$) confirmed the semiconducting nature of them. Seebeck coefficients of all the materials are found to be of the order of 0.8 mV/K. Fermi energy and effective mass of electrons could be calculated from the obtained values of carrier concentration and Seebeck coefficient.

7.3 FUTURE PROSPECTS

The main aim of the work presented in this thesis was the growth, characterization and study of temperature as well as pressure dependent properties of 2H-MoSe$_{2-x}$Te$_x$ single crystals. We have a deep sense of satisfaction for these sincere efforts, made in this direction and the corresponding success achieved. Still there are some aspects remained untouched, which deserve further investigations.

MoSe$_2$ and MoTe$_2$ compounds are known to exist in hexagonal polytypes crystal structures but no such work is reported for the compounds with intermediate Stoichiometry. Systematic study of the growth and characterization of other polytypes of MoSe$_{2-x}$Te$_x$ compounds may uncover their suitability for any application. Very recently some patents have been claimed for the use of MoSe$_2$ and MoTe$_2$ (monolayer group VI transition metal dichalcogenides) emerged as semiconducting alternatives to graphene in which the true two-dimensionality (2D) is expected to illuminate new semiconducting physics. [7-12]. Other compounds of this family may also be investigated for the possibility of their superiority over these compounds.

- In the present work, quality of the grown crystals were concluded to be good on the basis of obtained values of growth fault probability and deformation fault probability but single crystal
X-ray diffraction measurement can give the exact information about the quality of single crystal. Investigations in this direction may help to confirm this conclusion.

- All the electrical resistivity measurements reported in thesis were performed in ambient environment. In such measurements the oxidization of sample may easily happen. In order to prevent this, measurements must be performed under vacuum. Sample holder used in present work is designed in such a way that it is possible to evacuate the sample chamber under test using a flanged quartz tube along with vacuum pump. Such arrangement will also enable the resistivity measurements under different gas environment. Here, in this study it was predicted only that the structural change occurring at different temperatures forces the resistivity values to change suddenly but the structural parameters of the new phases are not presented. The solution of the crystal structure of these new phases is still in progress.

- Measurements of pressure dependent in-plane resistivity of grown crystals are performed in the present work. Measurements of electrical resistivity along c-axis are also possible (two probe resistivity measurements) if enough care is taken. These measurements can help in the calculation of anisotropy ratio and its dependence on pressure.

- Pressure dependent TEP measurements are also possible by using Bridgman anvil apparatus. Currently these measurements are in progress.

- In future work the pressure dependent optical absorption spectra of 2H-MoSe$_{2-x}$Te$_x$ in DAC (Diamond Anvil Cell) were measured by ruby fluorescence technique. Therefore, it is also possible to perform Photoluminescence measurements using the same facility.

- The past thesis from our department has reported the pressure dependent optical absorption measurements of tantalum
dichalcogenides up to ~15 GPa but the DAC used in the future work is capable of sustaining the pressure up to~50 GPa (It has been successfully achieved during other measurements). Hence the measurements up to 50 GPa are also possible. Pressure dependent electrical resistance measurements are also possible using the same DAC.

- The spectrophotometer system installed in our department was specifically designed and developed for the pressure dependent optical absorption studies of solid samples in the wavelength range 200-3000 nm. Moreover, this set up involve simple microscope objective to focus the incident light on the sample loaded in DAC. The dispersion of light and aberration are major sources of error in this type of arrangement. In order to remove these errors Reflective Microscope Objectives (RMO) can be used. In the present configuration the light beam is directed through air with the help of lenses and mirrors. Since the size of sample loaded in the DAC is only 50-100 µm the dust particles suspending in air may cause the error in results. Optical fiber guided light beam system can avoid this problem. Installation of such optical fiber guiding system will also remove the difficulty in diverting the transmitted beam on the detectors.
REFERENCES


