Chapter 7

Summary and Future Prospects
Same as knowledge, scope of understanding never ends… Every experimental work leaves some curiosity with it ….. In this chapter, the overall summary along with the future possibilities of this work are discussed.

7.1 Summary

In modern material science and material technology the accurately defined structuring of known solid down to microscopically controlled dimensions is now becoming more important than the continual search for new chemical compound. This trend is most obvious in the domain of semiconductor research and development. The characterization of new structures and materials requires analytical techniques having high sensitivity and accuracy. Raman scattering spectroscopy is a powerful, non-destructive procedure, sensitivity to local environment, idea for in-suit probing during growth, and during device fabrication and operation. A variety of fundamental and practical questions have been answered through Raman scattering like; phases, material quality, collective excitation, defects, carrier characteristics, composition strains, effects of external perturbations (temperature, pressure, stress, field etc.) and their gradient. Like X–ray techniques, Raman scattering has becoming nowadays an indispensable characterization procedure, readily applicable to any bulk material system, in numerous disciplines of pure and applied science. The frequencies of vibrational modes in solids are sensitive to changes in applied pressure as a result of the volume and structural dependence of interatomic or intermolecular forces in the material. Vibrational spectroscopy can thus be used to probe structural properties of solids at high pressures and to identify pressure-induced phase transitions. In particular, the combination of vibrational Raman scattering spectroscopy with the diamond-anvil cell has proven to be an important technique for characterizing materials at very high pressures. Raman spectroscopy is ideally suited for studying the evolution of the bond character in diatomic molecules under compression because measurements of their vibrational properties provide a powerful diagnostic of this process. The electronic density function changes with compression to minimize the total energy of the system. For the molecular materials, pressure tends to destabilize the intramolecular bonds as the kinetic energy of the participating electrons increases steeply with compression. Raman spectroscopy at ultrahigh pressures complements direct structural methods that probe long-range order in materials, such as high-
pressure X-ray diffraction. The Raman technique provides additional structural information because lattice vibrations can be very sensitive to structural changes.

A metal chalcogenide is a compound made from a metallic element and a member of the chalcogenide family, namely the elements under oxygen–sulfur, selenium, and tellurium. Metal chalcogenides form an important class of inorganic materials, which include several technologically important applications. The design of metal chalcogenides is of technological interest and has encouraged recent research. Looking to the above aspect, in the present work pressure and temperature dependent Raman spectroscopy was used to study the vibrational properties of metal chalcogenides single crystals.

The experimental set up for efficient Raman scattering experiment was described in chapter 2, with focus on high-pressure diamond anvil (DAC) technique. In chapter 3, Raman scattering is used to investigate structural stability at high pressure up to 20 GPa and temperature up to 80 K, for transition-metal dichalcogenides single crystal viz. MoS\(_2\), MoSe\(_2\), WS\(_2\) and WSe\(_2\). By analyzing the Raman peaks by means of centre position and width, additional information is accessible. For this purpose, the peaks were fitted with a Lorentzian curve. A study of resonant Raman spectroscopy at different laser sources (488 nm and 633 nm) have been used to excite these single crystals, in order to obtain the dependence of the Raman features (intensities, frequencies and line widths) on the laser energy. The metal-chalcogen bonding (\(\gamma\)) was found to be much stronger than the chalcogen-chalcogen bonding (\(\beta\)) as determined using a central force model. This result coincides with the fact that the covalent bond is caused by the s-p mixed orbital from the ‘s’ electron in metal and the ‘p’ electron in chalcogen. The isothermal and isobaric mode Grüneisen parameters have been calculated and explicit anharmonic contributions and the implicit contributions of the quasiharmonic approximation are discussed in detail. Similarly high pressure and low temperature Raman spectroscopy investigation on tin mixed chalcogenide single crystal SnS\(_2\)–XSe\(_X\) (0 ≤ X ≤ 2) is presented in chapter 4 which indicates absence of any phase transition in a low temperature and high pressure range. The temperature dependence of phonon frequencies and their line widths are analyzed based on known anharmonicity model. Combining the temperature-dependent Raman data and pressure-dependent Raman
data on these crystals with reported thermal expansion coefficient and compressibility data, it has been possible to separate and evaluate quantitatively the volume and the pure temperature (anharmonic) contributions to the total shift of phonons with temperature. Apart from this, the shift of Raman-active phonon frequencies versus mixed crystals composition $x$ is described. The effect of crystal disorder on the line width broadening of three high-frequency Raman-active modes is reported.

By examining the polarization dependence of the Raman intensities in chapter 5, one is able to distinguish the symmetry of the vibration modes of the Bi$_2$Se$_3$ single crystals. Raman spectroscopic studies have been carried out on Bi$_2$Se$_3$ at high pressures up to 12 GPa beyond which we could observe structural transition. Using anharmonic approximation, it is then possible to distinguish the implicit from the explicit temperature contribution in the isobaric phonon wavenumber shifts by taking into account the knowledge of the volume thermal expansion and of the isothermal volume compressibility. High pressure Raman spectra of Bi$_2$S$_3$ reveals notable second-order isostructural transition beyond 4–6 GPa pressure, originating probably from a topological modification of the Bi$_2$S$_3$ electronic structure near that pressure. In analyzing the pressure dependence of the Raman data of Sb$_2$S$_3$, i.e. change in the wavenumber discontinuities; we were able to observe a phase transition undergone at 6 GPa, while low temperature Raman spectra of same crystal indicates discontinuous change in Raman mode frequencies near 150 K to 180 K temperature range. The behavior of Sb$_2$Se$_3$ single crystal under high pressure show an ETT transition at $\sim$3GPa and structural transition at pressure $\sim$12 GPa which can be associated with the rhombohedral to monoclinic phase transition.

In conjunction with this, high pressure resistivity of some of metal chalcogenide single crystals is measured up to 8 GPa by using Bridgman anvil set up. The electrical resistance decreases by an order of magnitude when pressure increases from atmospheric pressure to 8 GPa pressure. The variations in values of band gap with pressure are explained in chapter 6. Moreover, resistivity measurement under low temperature and applied magnetic field on Bi$_2$Se$_3$ crystal shows positive, non-saturating, and dominantly linear magnetoresistance.
7.2 Future Scope

- In future prospects one can try to investigate structural stability and phase transition study in metal chalcogenides single crystal by high pressure X–ray analysis using DAC cell.

- It is also possible to investigate pressure and temperature dependent Raman spectroscopy studies on metal chalcogenide in some other forms like nanoparticles, polycrystalline, pellets etc. and then their comparative study can be done.

- Helium gas can be used as a pressure-transmitting medium to ensure hydrostatic conditions at room temperature which can be utilize to generate higher pressure above 20 GPa.

- High pressure resistivity studies of these semiconducting single crystals can be done using diamond anvil cell where we can go above 8 GPa pressure.
PUBLICATIONS

Research papers published in National and International Journals

List of published research papers related to thesis:

1. Pressure and temperature dependence of Raman spectra and their anharmonic effects in Bi$_2$Se$_3$ single crystal.
   M. P. Deshpande, **Sandip V. Bhatt**, Vasant Sathe, Rekha Rao, S. H. Chaki
   Physica B, **433** (2014) 72–78.

2. Raman scattering in 2H–MoS$_2$ single crystal.
   M. P. Deshpande, **Sandip V. Bhatt**, Vasant Sathe, Bindiya H. Soni, Nitya Garg, S. H. Chaki

3. Study on transport properties of Bi$_2$Se$_3$ single crystals grown by vapour phase technique.
   M. P. Deshpande, Sunil H. Chaki, Nilesh N. Pandya, Pallavi Sakariya, **Sandip V. Bhatt**

4. Studies on transport properties of copper doped tungsten diselenide single crystals.
   M.P. Deshpande, M.N. Parmar, Nilesh N. Pandya, Sunil Chaki, **Sandip V. Bhatt**

   M. P. Deshpande, M. N. Parmar, Nilesh N. Pandya, **Sandip V. Bhatt**, Sunil Chaki

6. Raman spectroscopic investigations on transition-metal dichalcogenides MX$_2$ (M = Mo, W; X = S, Se) at high pressures and low temperature
   Sandip V. Bhatt, M. P. Deshpande, Vasant Sathe, Rekha Rao, S. H. Chaki
   Journal of Raman Spectroscopy (Communicated).
List of other research papers published:

   
   Sandip V. Bhatt, M. P. Deshpande, Bindiya H. Soni, Nitya Garg, Sunil Chaki

2. Structural, thermal and antimicrobial property of CdSe nanoparticles synthesized by chemical route.
   

3. Spectroscopy and structural study on CdSe thin films deposited by chemical bath deposition.
   
   M. P. Deshpande, Nitya Garg, Sandip V. Bhatt, Pallavi Sakariya, S. H. Chaki

4. Influence of Mn doping on optical properties of ZnO nanoparticles synthesized by microwave irradiation.
   

5. Characterization of CdSe thin films deposited by chemical bath solutions containing triethanolamine.
   
   M. P. Deshpande, Nitya Garg, Sandip V. Bhatt, Pallavi Sakariya, S. H. Chaki

   
   M. P. Deshpande, Nitya Garg, Sandip V. Bhatt, Bindiya Soni, S. H. Cha

7. X-ray diffraction, X-ray Photoelectron Spectroscopy and Raman spectroscopy of undoped and Mn doped ZnO nanoparticles prepared by Microwave irradiation.
   
   Bindiya H. Soni, M. P. Deshpande, Sandip V. Bhatt, Sunil H. Chaki, Vasant Sathe
8. Study on antimicrobial activity of undoped and Mn doped ZnO nanoparticles synthesized by microwave irradiation.
Bindiya H. Soni, M. P. Deshpande, Sandip V. Bhatt, Sunil H. Chaki and Haresh Kaheria

PAPERS PRESENTED AT CONFERENCES /SYMPOSIUMS/ SEMINARS / WORKSHOPS

1. Attended technical Seminar on Semiconducting Devices and Nanomaterials Characterization, organized at Department of Physics, Sardar Patel University, Vallabh Vidyanagar, in association with Agilent Technologies – (USA) on 7th July, 2011.


3. Attended and presented (oral) research paper entitled “Chemical Synthesis and Characterization of Lead Sulphide (PbS) Thin Films”
   **Sandip V. Bhatt, M. P. Deshpande, Bindiya H. Soni, Nitya Garg, S. H. Chaki**
   in the National Symposium on Advances in Materials Science and Technology, Gujarat University, Ahmedabad on 3rd to 4th February 2012


6. Attended and presented a poster on “Raman Scattering in 2H–MoS$_2$ Single Crystal”
   **M. P. Deshpande, Sandip V. Bhatt, Vasant Sath, Bindiya H. Soni, Nitya Garg, S. H. Chaki**

7. Attended and presented a poster on “Raman Scattering in 2H-WS$_2$ Single crystal”
   **M. P. Deshpande, Sandip V. Bhatt, Nilesh N. Pandya, S. H. Chaki,** in the Current Trends in Research and Application of Physical Sciences in Gujarat
8. Attended and presented a poster on “High Pressure and Low temperature Studies on Raman Spectra and Resistivity along with Magneto Transport Properties on Bi$_2$Se$_3$ Single Crystals”
M. P. Deshpande, **Sandip V. Bhatt** and S.H. Chaki in the XXVII Gujarat Science Congress 2013 at Charotar University of Science & Technology, Changa, 24$^{th}$ February 2013.


10. Attended and presented a poster on “Pressure and temperature dependence of Raman spectra and their anharmonic effects in Bi$_2$Se$_3$ single crystal”

11. Attended and presented a poster on “Effect of Composition, Pressure and temperature on the Raman A$_{1g}$ mode in Tin mixed chalcogenide single crystals”

12. Attended and presented a poster on “Raman spectroscopy of Tin mixed chalcogenide single crystals at high pressure and low temperature”