Preface

For decades, the metal chalcogenides have attracted considerable interest of researchers in different fields of physics and materials science. Metal chalcogenides form an important class of inorganic materials, as common oxides, sulfides, selenides and tellurides containing different metal in various oxidation states which include many technologically important semiconductors. Semiconducting layered metal dichalcogenides are emerging as promising materials for a wide range of applications in optoelectronics and transistor technology. A characteristic feature of these layered crystals is their polytypism, arising due to infinite number of possible layer alternations which differ in the sequence of the constituent atoms. The lattice dynamics and electronic properties of these materials are of attention due to their two dimensional nature and wide application such as solid solution in solid state batteries. Broad band gap leads to photoconductance, and makes it possible to be promising candidates in solar cells, optoelectronic devices and their other features attract investigators in an effort to acquire a better insight into the physics of these compounds. It can be used as cathodic materials in lithium intercalation batteries and as antireflective layers in solar cell and is also of interest in holographic recording systems and electrical switching. Therefore, metal chalcogenides are considered to be important material towards unique applications in next generation electronics. Thus, knowledge of their structural stability range under conditions of variable temperature or pressure is important for such applications. Considering these aspects, it is essential to understand the dynamics of phonons in this material, particularly the phonon-phonon and electron-phonon interaction, in order to achieve the best device performance. Electron-phonon interaction is a key parameter in the design of high-speed devices as it governs the energy loss rate from electrons to the lattice via optical-phonon emission. For sufficiently long optical–phonon lifetimes, a large non-equilibrium phonon population can be maintained, which leads to phonon reabsorption and a significant reduction in the electron energy loss rate. Such hot-phonon effects may severely degrade the performance of high–speed, high–field devices by causing a drift velocity saturation at high electric fields to values lower
than predicted by theory. In this regard, Raman scattering is a powerful and sensitive technique to study phonons in such semiconducting layered materials.

Raman spectroscopy provides the information about vibration of each atom and thus a crystal structure can be discussed on the basis of lattice dynamics such as interatomic strength and bonding energy. The spectroscopy is a complementary method to X-ray diffraction study that analyze the crystal structure. High–pressure Raman spectroscopy is one of the most useful techniques to investigate the changes that matter undergoes under external pressure. Valuable information about intermolecular interactions, structural changes, phase transitions, and molecular vibrations can be obtained from Raman spectroscopy e.g., insulator and semiconductor to metal conversions are observed for wide varieties of solids under high pressure. The recent development of micro-Raman spectroscopy with charge coupled device (CCD) detection system significantly extended its applications to even smaller and weaker Raman scatterers, making Raman scattering technique more powerful in high pressure studies.

Pressure, like temperature, is a basic thermodynamic variable which can be applied in experiment over an enormous range, leading to important contributions in such diverse areas of science and technology as astrophysics, geophysics, condensed matter physics, chemistry, biology, and food processing. In general, the temperature effect interpreted in terms of anharmonic processes would lead to a better understanding of the electronic properties and application of semiconductors at different temperatures. It is widely known that crystal anharmonicity plays an important role in determining thermal properties of solids, such as thermal expansion and thermal conductivity. Crystal anharmonicity also plays an important role in controlling the lifetime of hot phonons which are generated during energy relaxation of carriers in semiconductors. In semiconductor devices, electrons are excited into conduction band either optically or by applying electric field. This high energy carriers decay towards their ground state, largely by emission of (near) zone-centre optical phonons. As discussed above, all applied research are focused in studying the temperature and pressure dependence of materials physical properties with a view to prepare the material which exhibit the expected properties in specific conditions of thermal and mechanical stress environment.
High-pressure structural science is a particularly strong example of an area that relies upon the complementarity of various techniques to achieve the final aim of the structural characterisation of novel materials. Furthermore, the advances in this field are intertwined with the evolution of complex sample environments for experiments at elevated temperatures and/or pressures, as well as the development of techniques for the collection and analysis of spectroscopic and diffraction data under extreme conditions. One of the aims of this research work is to point out that the measurements of temperature or pressure induced Raman frequency shifts are measurements of the anharmonicity of the interactions that supply the restoring force constants. Let us point out that because pressure or temperature induces isotropic or anisotropic deformations of molecules and crystals, the pressure or stress-induced and the temperature induced frequency shifts $\Delta \nu/\nu$ are mainly determined by the associated deformation in volume $dV/V$. It is thus important to analyze the effects of temperature and pressure together. The origin of the deformation induced by these two external parameters is different. Pressure affects the equilibrium spacing between nuclei, distorts the electron clouds and through them the restoring forces. Temperature affects the population of the different levels ($\nu = 0, 1, \ldots$) for each normal mode and because of the non-equidistance in energy of these levels, the average position of the atoms is changed. However, in both cases, the change in the lattice parameters is attributed to the anharmonicity of the potential. At the same time, the variations of the half-width $\Gamma$ of Raman bands under the effect of temperature or pressure are attributed to the decay of a given phonon into two or three phonons. In both cases, the phonon density of states is a critical parameter as far as temperature affects its population and pressure changes its form. Apart from this, the resistivity measurements at different pressure to study the possible phase transition in metal chalcogenides single crystals have the great interest to study the physical behavior under extreme high pressure.

Looking to the above aspect, we have decided to work on Raman spectroscopy and resistivity studies of metal chalcogenides single crystals with pressure and temperature. Raman spectra measurements at high pressure were carried out using Merrill-Bassett type diamond anvil cell with 400 $\mu$m diameter culet and hardened steel gasket. For pressure transmitting media we have used 16:3:1 methanol-ethanol-water mixture. Raman spectra was obtained by excitation with He-Ne laser beam using 632.8 nm line at power of 10 mW. Pressure measurement was done by the ruby
fluorescence technique and was taken to the average value from the ruby chips kept at different places to determine hydrostatic conditions in the sample chamber. Scattered light was analyzed using a HR-800 Horiba Jobin Yvon, micro-Raman spectrometer having spectral resolution of the order of \( \sim 1 \text{ cm}^{-1} \) equipped with an edge filter for Rayleigh line rejection, an 1800 grooves mm\(^{-1}\) grating and a CCD detector. Prior to the measurement, the system was calibrated by using 520 cm\(^{-1}\) Raman peak of polycrystalline Silicon. The measurements were made in the backscattering geometry with the incident beam linearly polarized. For temperature dependent Raman measurements the sample was kept in Linkam THMS-600, a liquid N\(_2\) cryo–cooler where we can maintain the temperature stability during measurements up to \( \pm 1 \) K. The room temperature electrical resistivity measurements on these metal chalcogenides single crystals, as a function of pressure were carried out up to 8 GPa. Pressure was generated with a Bridgman-type tungsten carbide opposed anvil (face diameter of 11.3 mm) cell and pressure was calibrated with bismuth transitions at 2.5 GPa. So, this study becomes very vital when one makes technological devices as well as when one tries to understand the interactions of the molecules in various environment.

The whole thesis has been divided into 7 chapters and their brief descriptions are narrated below:

**Chapter 1** deals with complete literature survey on the existing information of metal chalcogenides. This chapter also describes the present status of the research work going on across the globe in the field of Raman spectroscopy and resistivity studies of metal chalcogenides single crystals under high pressure and low temperature.

**Chapter 2** includes brief description of the theory involved in Raman scattering followed by a short account of the experimental set up used for Raman measurements. It also describes the technical details of high pressure technique using Diamond anvil cell (DAC), method of generation of pressure in DAC, gasket preparation and calibration of pressure using ruby fluorescence.

**Chapter 3** provides the details of the Raman scattering of MX\(_2\) (M = Mo, W; X = S, Se), single crystals which has been analyzed in terms of both zone-centre first order Raman scattering and second order Raman scattering enhanced by the coupling of
phonon modes to the electronic transition associated with the excitation states. The first-order Raman spectrum of MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$ single crystal grown by vapour transport technique was studied as a function of hydrostatic pressure (0–20 GPa) and temperature (80–300 K). The present study indicates absence of any phase transition in low temperature and high pressure range which makes MX$_2$ a technologically important and useful compound. Isobaric and isothermal mode-G"{u}r"{u}neisen parameter have been determined from the temperature and pressure dependent Raman spectra. The pressure dependence of the chalcogen-chalcogen and metal-chalcogen force constant was obtained using a central force model. The ratio of chalcogen-chalcogen bonding constant to metal-chalcogen bonding constant $\beta/\gamma$ is continuously increasing with pressure and rate of pressure dependence is small even at 15 GPa in MX$_2$ crystals. Separation of the temperature dependence of Raman mode frequencies into quasi-harmonic and purely anharmonic contributions using measured high pressure Raman data is also studied. This analysis allows us to extract the changes in the phonon frequencies arising exclusively due to anharmonic interactions.

**Chapter 4** consists of study on Raman spectra at varying composition of a series of Tin mixed dichalcogenide (SnS$_{2-x}$Se$_x$) layered crystals with $0 \leq x \leq 2$ grown by the vapour transport method. The asymmetry in the Raman line shape and the effect of crystal disorder on the line width broadening of the Raman active A$_{1g}$ mode are discussed. In the case of A$_{1g}$ mode, only chalcogen (S and Se) atoms vibrate together, and the resulting mass difference between the vibrating S and Se anions consequences in the two-mode behavior. Raman spectra of SnS$_2$, SnSSe and SnSe$_2$ have been measured at high pressures up to 20 GPa and temperatures from room temperature to 80 K. We do not observe any evidence of phase transitions, such as discontinuities or change in the pressure slopes, in the studied pressure range. By investigating Raman spectra as a function of temperature and pressure separately, it is possible to decouple the “true anharmonic” (the explicit temperature effect at constant volume) and “quasiharmonic” (the implicit effect caused by volume change) contributions to the total anharmonicities. Here, we report a detailed temperature–dependent Raman spectroscopy study of A$_{1g}$ phonon mode of Tin mixed dichalcogenide and analyzed the data based on anharmonicity models which are useful in modeling of thermodynamic entities.
Chapter 5 provides the analysis of Raman spectra as a function of pressure (0–12 GPa) and temperature (80–300 K) on grown Bi$_2$Se$_3$ single crystal by vapour transport technique. Polarized Raman experiments in the back-scattering configuration was used to determine the position of the two dominant first-order Raman-active modes, $E^2_g$ and $A^2_{1g}$ at around 132 and 174 cm$^{-1}$ respectively. High pressure Raman measurements provides the evidence that Bi$_2$Se$_3$ single crystal undergoes first order phase transition above 10 GPa. Isobaric and isothermal mode Grüneisen parameter have been determined from the temperature and pressure dependent Raman spectra for both Raman active modes of Bi$_2$Se$_3$ single crystal. The analysis of the experimental data showed that the temperature dependencies of the phonon frequencies and linewidths are well described by considering the contributions from thermal expansion and lattice anharmonicity. In the same way, we have extended our work on Raman spectra for other metal chalcogenides of the group V$_2$-VI$_3$ viz. Sb$_2$Se$_3$, Sb$_2$S$_3$ and Bi$_2$S$_3$ single crystals.

Chapter 6 describes the experimental arrangement of Bridgman anvil set up for the generation of high pressure which is used for resistivity measurements. It includes the results obtained from the high pressure study on the electrical resistivity measurements of different metal chalcogenides single crystals. It also provides information on electrical transport property measurements carried out on Bi$_2$Se$_3$ single crystals i.e. low temperature resistivity measurement in the temperature range 5 K to 300 K and magnetoresistance measurement carried out in the temperature range 5 K to 300 K in a magnetic field of the order of 0–8 Tesla with the facilities available at UGC–DAE, Indore.

Chapter 7 deals with the conclusion drawn from the entire work and scope for the future work.