Synopsis

This thesis presents experimental as well as theoretical studies of three dimensional topological insulators (TIs) and transition metal dichalcogenides (TMDs). Raman spectroscopic measurements of these systems have been carried out as a function of pressure. For structural characterization as a function of pressure, x-ray diffraction measurements using synchrotron source have been pursued. The field effect transistor devices fabricated from MoS_2 are used in experiments to probe Raman evidence of electrostrictive and piezoelectric effects in multilayer and monolayer, respectively. In-situ photoluminescence (PL) and Raman measurements are performed as a function of laser-irradiation time to show healing of defects in MoS_2. We provide an overview of our work on these systems chapter-wise.

In **Chapter-1**, the brief introduction of the systems studied in this thesis has been provided. For topological insulators, the $\mathbb{Z}_2$ topological index has been discussed for three dimensional strong TIs as well as weak TIs. Then, the various properties of MoS_2 and $MoTe_2$ such as electronic, vibrational, structural and photoluminescence are discussed in details.

Chapter-2 includes a short introduction to Raman spectroscopy and x-ray diffraction. The technical details of the high pressure experiments which include the alignment of the diamond anvil cell, gasket preparation, loading the pressure medium are discussed. This is followed by the discussions on the sample preparation as well as the electron beam lithography techniques.

In **Chapter-3**, we present Raman spectroscopic measurements on a band insulator Sb_2Se_3 under high pressure upto 24.6 GPa. Different experimental techniques are being pursued to capture the surface electronic properties due to Dirac electrons and hence, thereby characterizing $\mathbb{Z}_2$ topology

of the system. The topological characterization of $\mathbb{Z}_2$ TIs is solely based on the isolated quantum system of electrons, but in real materials they are coupled to other low energy excitations of the system. Depending upon the strength of the coupling with the environment, it can induce an electronic topological transition. In fact, it has been proposed [*Phys. Rev. B 89, 205103 (2014)*] that the increment of temperature gives rise to an increase in electron-phonon coupling and thereby driving a trivial insulator to a topological insulator. Here, we address the inverse situation, i.e., can we trace the topological signature due to electronic topological transition (ETT) from the environment or nonelectronic baths of the system rather than from the electronic system itself, experimentally as well as theoretically ?

High pressure Raman spectroscopic measurements show a ETT transition at ~ 2.5 GPa marked by a large softening of the low frequency Raman mode by $\sim 16\%$ together with an anomalous increase of its linewidth by $\sim 200\%$ within a narrow pressure range of 0 to 2.5 GPa. Our calculations based on model Hamiltonian determined by projecting the electron-phonon coupling term onto the identity representation of the double group corresponding to the phonons of different irreducible representations (thereby ensuring the symmetry invariant Hamiltonian) captures the phonon anomalies qualitatively. It is convincing that the linewidth of phonon carries the non-trivial topological signature but there are few subtle things need to be considered. It is obvious from the linewidth that there is a band inversion at Fermi level but, it is not obvious that it probes strong topological $\mathbb{Z}_2$ invariant unless the band gap closing and opening occur at odd number of time reversal invariant momentum (TRIM) points in the Brillouin zone and hence, the observed maximum in linewidth of an optical phonon mode is necessary but not sufficient to probe the $\mathbb{Z}_2$ invariant. To the best of our knowledge, this is the first report where vibrational properties through the linewidth of a Raman mode can capture the electronic topological transition of $\mathbb{Z}_2$-type.

In **Chapter-4**, we present Raman spectroscopic measurements on three **strong** topological insulators as a function of pressure. This chapter consists of two parts: In **Part(I)**, we discuss the following **(A)** Bi_2Te_3; **(B)** Bi_2Se_3; and **(C)** $Bi_1Sb_1Te_{1.25}Se_{1.75}$. The stoichiometric materials of A_2B_3 type (Bi_2Te_3 and Bi_2Se_3) belong to the family of strong $\mathbb{Z}_2$ TIs at ambient conditions. Previous high pressure Raman and x–ray diffraction studies showed that there is an iso–structural transition at low pressure regime in the range of 3 to 5 GPa where the parallel component of bulk modulus shows a kink. Earlier, this low pressure transition had been assigned to be an ETT based on the changes observed in structural parameters without a detailed exploration of electronic structure or direct evidence for change in electronic topology around the transition pressure. Here, we

address this particular low pressure transition regime to clarify whether it is associated with the ETT or not ?

We revisit this low pressure transition in the present work using high pressure Raman experiments along with first-principles calculations on Bi_2Se_3 taken as a prototype of the family of A_2B_3 type TIs. We do not find any change in electronic topology of the both types (ETT of $\mathbb{Z}_2$–type and ETT of Lifshitz–type) as a function of pressure (P $\leq$ 8 GPa) by examining the density of states at Fermi level and the smallest electronic band gap as well as the $\mathbb{Z}_2$ index and the surface Dirac conical electronic structure. The pressure derivatives of Raman modes show a clear change at 2.4 GPa, without the appearance of any new mode. Hence, the lowest pressure transition should be better termed as an isostructural transition, and not an ETT. Many authors assign this low pressure transition regime as an ETT for all the 3D-topological insulators just by observing the structural distortions and consequent changes in the phonon spectrum. The signature of ETT will reflect in the anomalies for the phonons, but the reverse is not true, i.e. it is not correct to assign an ETT *prior* to the detailed exploration of electronic band structure.

In **Part(II)**, we present Raman spectroscopic measurements on a **weak** topological insulator Bi_1Se_1 as a function of pressure. The essential thing in order to understand TIs is the concept of band inversion. What it means that band orderings of valence and conduction bands are changed in such a way that it cannot be connected adiabatically to the atomic limit of the system. When the bands are inverted, the phonons signatures will be useful in order to capture a transition to a band-inverted phase. If a weak topological insulator (WTI) can undergo a transition to a trivial insulator or to a strong topological insulator (STI) by inverting band structures at even or odd number of TRIMs respectively, the corresponding signatures will be reflected in the phonon spectrum. However, it is worthy to remind that WTIs have been identified as *strong/robust* against the changes in the topology of the even number of Dirac cones at its surface as long as time reversal, translational invariance and $\mathbb{U}(1)$ gauge symmetries are preserved on average. In our work, we have shown that with the application of hydrostatic pressure (as a tunable parameter) upto $\sim$ 7 GPa, there is no change in topological signature of Bi_1Se_1 by probing optical phonons using Raman spectroscopic measurements.

Chapter-5 : It is not only the monolayer TMDs possessing tunable and electrical properties, they (TMDs) also exist in different bulk forms (polytypes) having different structure like 2H, 1T, 3R with different electrical and optical properties. Essentially the electrical and physical properties are not only limited to the dimension reduction or sample thickness, but also different crystal structures (polytypes) can also induce different electrical properties and high pressure technique

is a powerful way to switch between different thermodynamically stable structural polytypes without introducing impurities unlike chemical doping. Recent high pressure Raman studies [*Phys. Rev. Lett. 113, 036802 (2014) and J. Phys. Chem. C 118, 3230 (2014)*] on 2H-MoS$_2$ (P6$_3$/mmc) reveal that there is a onset of lateral shift of the adjacent S—Mo—S layers around $\sim$ 20 GPa leading to a mixed phase of 2H$_c$ (2H) and 2H$_a$ structures with the 2H$_c$-phase being the dominant one [*J. Phys. Chem. C 118, 3230 (2014)*] and thereby changes the pressure coefficients of the Raman modes. Motivated by the results of high pressure research on MoS$_2$, we investigated the high pressure induced different phase transitions in MoTe$_2$ and MoSSe using Raman, XRD and first-principles studies.

In **Part(A)**, we discuss the high pressure Raman spectroscopic studies of MoTe$_2$ upto $\sim$ 29 GPa. We have observed a pressure induced semiconductor to semi-metal transition at $\sim$ 6 GPa and a Lifshitz transition at $\sim$ 18 GPa in 2H-MoTe$_2$ by combining Raman measurements and first-principles calculations. The frequencies of the first order A$_{1g}$ and E$_{2g}^1$ Raman modes carry the signatures of semiconductor to semimetal and the Lifshitz transitions. The occurrence of a maximum in the integrated area ratio of the A$_{1g}$ and E$_{2g}^1$ modes is mainly due to non-monotonous change in Raman tensor of E$_{2g}^1$ mode with pressure. DFT calculations of pressure effects on Raman active modes show that pressure influences the electron-phonon coupling of the A$_{1g}$ mode most strongly.

In **Part(B)**, we present high pressure Raman (upto $\sim$ 26 GPa) and XRD studies (upto $\sim$ 20 GPa) of MoSSe. All the three Mo-based TMDs (MoS$_2$, MoSe$_2$ and MoTe$_2$) undergo semimetal transition and only for MoS$_2$, iso-structural transition precedes the metallization phase. The reason possibly could be attributed to the d-electron propagation which favors the Mo-atoms on top of each other in metallic 2H$_a$-phase than semiconducting 2H$_c$ (2H)-phase where Mo-atoms sit on top of S-atoms. However, in case of MoTe$_2$ and MoSe$_2$ the larger radius of chalcogen atoms increases the interlayer distance and thereby hinders the d-electron propagation mechanism, and hence favors the 2H$_c$-structural polytypes. The question we will address is that if we substitute one S-atom with the Se-atom, i.e. for MoSSe compound, what happens to pressure-induced phase transitions. We have shown that the substitution of S by Se reduces its crystal symmetry to P6$_3$mc (# 186) and an isostructural transition to a 2H$_a$-phase with the same space group takes place around 10.8 GPa, similar to the case of MoS$_2$. We suggest that layer sliding transition completes around 18 GPa as reflected in our Raman data where few modes undergo a slope change in pressure-dependent frequency (ω) plot. We also observe a low pressure (P) transition around $\sim$ 2 GPa where Raman modes show a change in dω/dP, which is also reflected in c/a ratio variations

obtained by synchrotron based x-ray diffraction experiments as a function of pressure. This low pressure transition at $\sim$ 2 GPa has not been reported so far for any of three MoX_2 (X = S, Se and Te) compounds discussed before.

Chapter–6 : Piezoelectric and electrostrictive materials are of significant interest in electromechanical devices to harvest energy as well as in a wide range of applications of sensors and actuators. Here, we report in-situ Raman spectroscopic studies on multilayer MoS_2 device to show that the observed changes in frequencies ($\Delta\omega$) of the A_{1g} and E_{2g}^1 optical modes varies quadratically as a function of applied electric field ($\Delta\omega \propto E_{DS}^2$) due to the electrostrictive effects and to the best of our knowledge, this is the first evidence of the observed electrostriction in multilayer MoS_2. The observed $\Delta\omega$ are $\sim$ 1.6 cm^{-1} and 1.4 cm^{-1} for the A_{1g} and E_{2g}^1 modes, respectively for the applied maximum electric field of 45 kV/cm. The electrostrictive coefficient is $\sim$ 3.6 $\times$ 10^{-14} m^2/V^2, corresponding to $\sim$ 0.7 % in-plane uniaxial tensile strain. This value is $\sim$ 428 times higher than the most commonly used electrostrictive material PMN ($PbMg_{1/3}Nb_{2/3}O_3$). We also carried out similar experiments on monolayer MoS_2 device and the observed frequency of the A_{1g} mode varies linearly ($\Delta\omega \propto E_{DS}$) due to piezoelectric effect. The A_{1g} mode hardens by $\sim$ 1.2 cm^{-1} with the applied electric filed of 7.2 kV/cm.

In Chapter–7, we present PL and Raman spectroscopic studies of monolayer MoS_2 as a function of laser irradiation time. The two-dimensional monolayer MoS_2 has enhanced Coulomb interactions than its bulk-counterpart. The change in the carrier concentration in the channel will lead to the renormalized binding energy for the relatively loosely bound trions and this fact will facilitate to modulate the PL spectrum of monolayer MoS_2 as a function of channel doping. By depleting the excess electrons from the monolayer MoS_2, we can not only destabilize the trion formation but also enhance radiative recombinations and hence, an increase in PL efficiency. While extracting or adding electrons change the optical properties, it also renormalize phonons.

To the best of our knowledge, there is no quantitative reported data on Raman study and the dynamics of enhanced trion as well as B-exciton PL emission as a function of laser irradiation time. Here, we show that exposing the monolayer MoS_2 in air to a modest laser intensity for a brief period of time enhances simultaneously the PL intensity associated with both the trions and excitons, together with $\sim$ 3 to 5 times increase in the Raman intensity of first and second order modes. The simultaneous increase of PL from trions and excitons cannot be understood based only on known-scenario of depletion of electron concentration in MoS_2 by adsorption of O_2 and H_2O molecules. This is explained by laser induced healing of defect states resulting in reduction of non-radiative Auger processes. This laser healing is corroborated by an observed increase in

intensity of both the first order and second order 2LA(M) Raman modes by a factor of $\sim$ 3 to 5. The A_{1g} mode hardens by $\sim$ 1.4 cm^{-1} whereas the E_{2g}^1 mode softens by $\sim$ 1 cm^{-1}. The second order 2LA(M) Raman mode at $\sim$ 440 cm^{-1} shows an increase in wavenumber by $\sim$ 8 cm^{-1} with laser exposure. These changes are a combined effect of the change in electron concentrations and oxygen-induced lattice displacements.

In Chapter–8, we have summarized our findings and highlighted few possibilities which can be pursued in future in order to have a better understanding of these systems.