Synopsis

Designing a material for a particular application requires an atomistic understanding of its properties. Recent development in first principles methods and supercomputing speeds has enabled researchers to compute materials properties accurately. This has opened up a window for computational designing of materials for various applications such as optoelectronics, thermoelectrics, magnetic shape memory alloys etc. In this thesis, first principles methods have been utilized to understand the properties of various materials such as TiS_2, TiS_3, GeO_2, Co_3(MoTaAl) alloys, Ni_2MnGa and graphene. This thesis has been organized as follows:

- **Chapter 1** introduces various functional materials and their application in the thermoelectric, optoelectronic, high temperature and magnetic shape memory. The microscopic understanding of materials properties such as structure, energetics, electronic structure, electronic transport, and lattice dynamics etc. can lead to novel ways of designing materials properties for various applications.

- **Chapter 2** describes the theoretical methodology adopted in this work. It gives a brief understanding of first principles based density functional theory (DFT) and various approximations to obtain accurate electronic properties. Methods employed for calculation of electronic and thermal transport are also discussed briefly.

- In **Chapter 3** we explore the tuning of the electronic structure of the transition metal dichalogenide TiS_2. We show that by engineering its electronic structure, it transforms from a semimetal to a semiconductor under biaxial strain. The thermoelectrics study shows that a 3 fold enhancement in thermopower can be achieved by application of 5% biaxial strain. This enhancement is driven by a small bandgap opening of $\sim$0.15 eV, which increases its thermopower at the same time decreasing its lattice thermal conductivity indicating improvement in ZT.

- In **Chapter 4** we study the possibility of inherent stacking fault in bulk TiS_3 and its effect on the electronic properties. We find that TiS_3 can exist in AB$'$ and AB$''$ geometries. The

energy difference between two structures is about 0.011 eV/f.u. The electronic structure is independent of the stacking fault due to the weak vdW interaction between the layers. The calculated thermopower is 200 μV/K in the carrier concentration range of 1×10^{20} cm^{-3} - 5×10^{20} cm^{-3}, which is comparable with other state of the art thermoelectric materials. The high thermopower and electrical conductivity in the carrier concentration range of 1×10^{20} cm^{-3} - 5×10^{20} cm^{-3} leads to a high power factor for both *p*- and *n*-type. Moreover, the power factor for *p*-type is three times higher than that of *n*-type carriers indicating that the thermoelectric performance for *p*-type will be much better than that of *n*-type.

- **Chapter 5** reveals the origin behind the large variation in the band gap ($\sim$ 2 eV) of GeO_2 calculated by standard DFT within LDA/GGA, which had remained unresolved. Using the many-body perturbation theory (GW approximation), we find that this large variation observed in literature is independent of the method used and depends strongly on the lattice parameter (volume strain). This strong dependence originates from a change in hybridization among O-*p* and Ge-(*s* and *p*) orbitals.

- **Chapter 6** deals with the structural stability of order intermetallic Co-based superalloys. We have shown that W free Co_3Al order structure can be stabilized in $L1_2$ structure by addition of Mo and Ta atoms. The enthalpy of formation of $L1_2$ structure significantly becomes more negative compared to the DO_{19} structure by the addition of $\geq$ 4% of Ta atoms. This implies that the $L1_2$ structure of Co_3(Al,Mo,Ta) structure is more stable compared to DO_{19}. The lowering in the enthalpy of formation is found due to the formation of the pseudo gap and the decrease in the states at the pseudo gap with increasing Ta concentration. The stability of the $L1_2$ structure can be further improved by the addition of Ni and Ti atoms.

- In **Chapter 7**, the lattice dynamics and electronic structure of X_2YZ [where X = Ni, Fe, Co; Y = Mn; Z = Al, Ga, Ge, In, Sn, Sb] stoichiometry compounds are investigated. The lattice instability of X_2MnZ depends on the position of the Fermi energy (E_F) with respect to the pseudo gap. The phonon mode softening along the Γ-K symmetry direction is observed for Ni_2MnZ in the austenite phase since E_F is located above the pseudo gap. This mode softening is mainly responsible for the MSM effect. On the other hand, Fe_2MnZ and Co_2MnZ [Z = Al, Ga, Ge, In, Sn, Sb] in the cubic phase do not show any phonon mode softening because E_F lies in the vicinity of the pseudo gap or at the pseudo gap. Thus, alloying Fe or Co at the Ni site in Ni_2Mn (Z = groups-IV and V) can tune the lattice

modulation. In addition, the magnetic moments of Fe_2Mn (Z = groups-IV and V) and Co_2Mn (Z = groups-IV and V) are much higher than those of Ni_2Mn (Z = groups-IV and V), indicating that the magnetic moments of Ni_2MnZ can be enhanced. The calculated phonon dispersion with magnetic moment indicates that the phonon mode softening is sensitive to the change in the local magnetic moment of the atoms, thereby enabling tunability in the MSM effect.

- **In chapter 8**, we show that the mono vacancy defects in graphene can be used as precursors to form novel clipped structures without explicit use of functional groups. These clipped structures can be transformed into one-dimensional (1D) double wall nanotubes (DWCNT) or multi-layered three dimensional (3D) structures. The clipped structures show good mechanical strength due to covalent bonding between multi-layers. Clipping also provides a unique way to simultaneously harness the conductivity of both walls of a double wall nanotube through covalently bonded scattering junctions. With additional conducting channels and improved mechanical stability, these clipped structures can lead to a myriad of applications in novel devices.

- **Chapter 9** summarizes and concludes the work presented in this thesis.