

Synopsis

Thermoelectric materials offer applications in conversion of waste heat to useful electrical energy and are promising sources of renewable energy. To use a material efficiently in thermoelectric application it is necessary to have high figure of merit (ZT). The task of increasing ZT is challenging because of the competing relation between electrical conductivity, thermopower, and thermal conductivity. For enhancing ZT of a thermoelectric material, it is necessary to have a good understanding of its electronic structure as well as transport properties. The goal of the present work is to develop an understanding of the thermoelectric properties of selected materials and address some of the fundamental challenges for achieving enhanced performance in these materials. In this thesis, I have employed density functional theory based calculations combined with Boltzmann transport theory, to study electronic structures, and electronic and thermal transport properties of several promising class of thermoelectric materials, including the transition metal silicides (FeSi_2 , CrSi_2), Zintl compounds, sulphide (Bi_2S_3), intermetallics and transition metal dichalcogenides (MX_2 ($\text{M} = \text{Zr}, \text{Hf}$ and $\text{X} = \text{S}, \text{Se}$), and MoS_2). Based on the comprehensive study of electronic and thermoelectric properties we conclude that different strategies are required to improve the ZT of different class of materials. Our findings provide a better understanding of materials properties and can be generalized to other materials as well. This thesis has been organized as follows:

Chapter 1 introduces the thermoelectric materials, materials selection, and path ways to achieve optimized thermoelectric performance. An overview of the materials studied here is also given along with the traditional methods followed in the literature to optimized their thermoelectric properties. The motivation of the current research work has also been highlighted in this chapter.

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 exchange and correlation energy functional used here to obtain structural and electronic properties. Methods employed for calculation of electronic and thermal transport are also discussed briefly.

Chapter 3 investigates the thermoelectric properties of $\beta\text{-FeSi}_2$. We report a high ther-

mopower for both p - and n -type β -FeSi₂ over a wide range of carrier concentration and, the performance for n -type is higher than that of p -type. Our results indicate that depending upon temperature doping level of 0.09-0.605 electron/unit-cell can optimize the thermoelectric performance and lead to high ZT value.

Chapter 4 unravels excellent thermoelectric properties of Zintl phase compounds CdSb and ACd₂Sb₂ (A = Ca, Ba, Sr). The calculated electronic structures of these compounds show charge carrier pockets and heavy light bands near the band edge, which lead to large power factor. Furthermore, their large Grüneisen parameters and low phonon group velocity results into low lattice thermal conductivity. The combination of low thermal conductivity and the excellent transport properties give a high ZT value of ~ 1.4 - 1.9 in CaCd₂Sb₂ and BaCd₂Sb₂ at moderate p - and n -type doping. Our results indicate that well optimized Cd based Zintl phase compounds have a potential to match the performance of conventional thermoelectric materials.

Chapter 5 proposes that the thermoelectric performance of Bi₂S₃ can be improved significantly by applying hydrostatic pressure via carrier effective mass engineering. With application of hydrostatic pressure, the conductivity effective mass decreases and density of states effective mass increases leading to simultaneous enhancement in electrical conductivity and thermopower under n -type doping. Also lattice thermal conductivity exhibits very weak pressure dependence at low pressure range. The large power factor together with low lattice thermal conductivity results in a high ZT value of 1.1 under n -type doping, which is nearly two times higher than the previously reported value. Hence, this pressure-tuned behaviour can enable the development of efficient thermoelectric devices at moderate to high temperature range. Because of the similar electronic and crystal structure, our finding can be extended to other A₂S₃ (A = Sb, Bi, and As) type compounds.

Chapter 6 presents the electronic and thermal transport properties of bulk MX₂ compounds (M = Zr, Hf and X = S, Se). The band structure shows the confinement of heavy and light bands along the out of plane and in-plane directions, respectively. This results in high electrical conductivity (σ) and large thermopower (S), leading to a high power factor ($S^2\sigma$) for moderate n -type doping. The phonon dispersion demonstrates low frequency flat acoustical modes, which results in low group velocities (v_g). Consequently, lowering the lattice thermal conductivity (κ_l) below 2 W/m-K. Low κ_l combined with high power factor results in $ZT > 0.8$ for all the bulk MX₂ compounds at high temperatures of 1200 K. In particular, the ZT_{\max} of HfSe₂ exceeds 1 at 1400 K. Our results show that Hf/Zr based dichalcogenides are very promising for high temperature thermoelectric application.

Chapter 7 presents the effect of strain and number of layers on the transport properties of mul-

tilayered MoS₂. We optimize the transport properties as a function of layer thickness (number of layers) and applied strain. 3L- and 2L-MoS₂ emerge as the most efficient thermoelectric material under normal compressive and biaxial strain, respectively. The calculated thermopower is large and comparable to some of the best thermoelectric materials. Owing to the similar crystal structure and electronic properties, the proposed S-M transition mechanism and enhancement in thermoelectric properties for few layers of MoS₂ can be extended to all other semiconducting TMDs under various type of strains.

Chapter 8 investigates the electronic structure and thermoelectric properties of pseudo gap semiconducting intermetallic compounds. The presence of the narrow band gap and mixed band dispersion leads to a very high power factor under *n*-type doping. Due to the smaller phonon group velocities and higher anharmonicity Ga₂Ru exhibits 58% lower lattice thermal conductivity than Al₂Ru. Our results, indicate that a maximum *ZT* of 1.0 and 0.7 can be achieved by electron doping for Ga₂Ru and Al₂Ru, respectively.

Chapter 9 develops a method to tune operational temperature of a thermoelectric device by tuning the defect transition level. We show for doped CrSi₂ that the peak of thermopower occurs at the temperature, which corresponds to the position of defect transition level. Therefore, by modifying the defect transition level, a thermoelectric material with a given operational temperature can be designed.

Chapter 10 summarizes and concludes the work presented in this thesis.